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**OAK
RIDGE
NATIONAL
LABORATORY**

MASTER

**CHEMISTRY DIVISION
ANNUAL PROGRESS REPORT
for Period Ending July 31, 1981**

ORNL--5817

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CHEMISTRY DIVISION ANNUAL PROGRESS REPORT
for Period Ending July 31, 1981

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1. INTRODUCTION AND DIVISIONAL OVERVIEW

Since our last Annual Report of a year and a half ago, the Division Staff has capitalized on some developments of that time and made some new developments for forging into the future. Some highlights are:

(1) Jointly with Exxon applied our newly developed high temperature-high pressure capability in electron spin resonance (ESR) to verify spectroscopically the mechanism of bibenzyl pyrolysis proposed by them as part of their coal liquefaction research.

(2) Resolved a question of how solvent might be lost in the Kerr-McGee Critical Solvent Deashing process used in SRC coal liquefaction pilot plants.

(3) Combined ^{13}C NMR and ^{14}C tracer techniques to find that only about 50% to 80% of the carbon in typical coals is detected in solid state NMR studies.

(4) Found by ^1H NMR and GC-MS analysis that $\text{SbCl}_3\text{-AlCl}_3$ is an extremely active hydrocracking catalyst for polynuclear aromatics, even at the low temperature of 130°C .

(5) Applied our newly developed atomic carbon beam to the analysis of the carbon-sulfur dioxide reaction by the crossed beams technique.

(6) Developed new processes scalable to industrial proportions for removing silver, cyanide and other contaminants from photographic waste solutions to the levels demanded by new EPA regulations.

(7) Used synchrotron radiation in collaboration with the University of Tennessee and the University of Wisconsin for exciting angle resolved electron spectra of gaseous polyatomic molecules whose wave functions were then characterized experimentally and theoretically in an immensely more critical and meaningful way than is possible by the usual methods based on energy alone.

(8) Discovered that backscattered K^+ ions as probes of metal surface structures achieve very high intensities, allowing much more information to be obtained than was previously possible.

(9) Analyzed the kinetics and thermodynamics of iodine hydrolysis reactions needed for understanding iodine non-volatility in nuclear accidents such as TMI (partly in collaboration with the University of Frankfurt).

(10) Developed molten magnesium-molten uranium alloy solvent extraction systems for recovering non-radioactive palladium and rhodium from high-level radioactive waste.

(11) In collaboration with the University of Liege and Los Alamos National Laboratory measured the heat of solution of berkelium metal and the heats of vaporization and the vapor pressures of berkelium and californium metals.

(12) Obtained atom pair distribution functions for hydrogen in liquid water to augment those previously obtained for oxygen.

(13) Measured thermodynamic properties of aqueous NaCl by a new calorimetric technique to 400°C for the first time.

(14) Determined unequivocally by x-ray and Raman techniques that cation-cation complexes involving neptunyl and uranyl ions exist in aqueous solutions.

(15) Showed that micellar formation is not needed to lower the surface tension using "micellar flood" approaches to enhanced oil recovery.

(16) Completed high pressure (414 MPa)-high temperature (1400°C) facility for study of deep crustal processes (15 km depth) responsible for crystallization of magmas.

(17) Completed isopiestic measurements of all soluble non-hydrolyzing chlorides and sulfates (except Rb) and some mixtures to 250°C demonstrating the reduced dependence on ion-size and charge at high temperatures.

(18) Measured the association behavior of MgCl_2 and CaCl_2 to 600°C to explain chemical migration and geochemical processes (joint with Carnegie Institution, Washington, D.C.).

(19) Determined solubilities of amorphous silica in aqueous salt solutions and mixtures up to 350°C and discovered additive relations of importance in geochemistry and in steam generator applications.

As these highlights illustrate, the Chemistry Division Staff continues to maintain the highest standards and a freshness of approach to building a scientific base for energy developments of the future. Although our research impinges on several areas, our special concentration is on the nuclear and fossil energies. The Table of Contents of the Annual is a handy guide to the Division's work. The Organization Chart included in this Annual gives a view of our staff, and the table on Divisional Person Power and Financial Summary gives a breakdown of our efforts by program.

Visiting scientists and students from universities, industry, and research institutes continue to enrich the work of the Division. In the last four years, the Division has had 20 Visiting Scientists from foreign institutions (23 publications), 38 Visiting Professors from American universities (49 publications), along with a number of graduate students (8 Ph.D. and 2 M.S. degrees awarded). Collaboration with students of the Great Lakes Colleges Association, Oak Ridge Associated Universities, various co-op programs, and the Southern Colleges and University Union resulted in 10 publications.

Legal and institutional barriers to industrially funded projects in the Laboratory are falling, and we are expecting several such projects to be funded soon. Such collaborative research is driven by international industrial competition. Another area we are just getting into, cooperation in weapons related research, is driven by the perceived need by the nation for defense preparedness. We are thus beginning to bring to bear the considerable powers of the Chemistry Division in industrial and weapons research areas of considerable importance to the United States.

2. CHEMISTRY OF COAL AND COAL LIQUEFACTION

2.1 Organic Chemistry and Spectroscopy of Coal and Model Compounds

2.1.1 Cleavage of Carbon-Carbon Bonds by Solvated Electrons

(C. J. Collins, B. E. Maxwell, B. M. Benjamin, D. R. McKamey)

In conjunction with our high-resolution, solid-state ^{13}C NMR studies of coals and of the changes in structure brought about by reducing the coals with alkali metals (Section 2.1.2), we are concurrently investigating the chemistry of the reductions using model compounds. The reaction of bibenzyl with Na-K in glyme-triglyme solution at 0°C was reported¹ to give toluene (85%) after a water quench. The mechanism proposed was cleavage of bibenzyl radical anion to produce a benzyl radical and a benzyl anion both of which eventually lead to toluene. Diphenylmethane under similar conditions also gave toluene (43%), but the absence of benzene and the presence of benzylbiphenyl (33%) in the reaction products led us to believe that diphenylmethane reacts through a bimolecular mechanism (there were also some products of Birch-Hückel reduction^{2,3,4}).

We have now definitely identified the benzylbiphenyl as the *meta*-isomer through independent synthesis. 3-Methylbiphenyl was converted to the bromide (with *N*-bromosuccinimide) and thence to 3-phenylbenzaldehyde (in DMSO and NaHCO_3), which was treated with phenylmagnesium bromide to give 3-phenylbenzhydrol. Conversion of the latter to the chloride with thionyl chloride followed by reduction with lithium aluminum hydride in THF afforded 3-benzylbiphenyl⁵ whose ^1H - and ^{13}C -NMR spectra were identical with those of the product isolated from the reaction of diphenylmethane with Na-K in glyme-triglyme solution. The reaction of diphenylmethane in the presence of Na-K is best formulated as a bimolecular reaction, eq. (1). The radical anion of diphenylmethane in eq. (1) (written for convenience as one of the several contributing resonance structures) attacks the *ipso*-position of another diphenylmethane molecule to give the

intermediate⁶ shown, which then fragments to produce a carbanion and a radical. The benzyl carbanion, on water quenching, goes to toluene, eq. (2), whereas the radical may either lose a

hydrogen atom directly, or take on another electron⁷ and then lose hydride as shown in eq. (3) to give *m*-benzylbiphenyl.

If we project the results of these model compound studies to coal, it seems that $\text{ArCH}_2\text{CH}_2\text{Ar}$ $\text{sp}^3\text{-sp}^3$ bonds should cleave much more readily than ArCH_2Ar $\text{sp}^2\text{-sp}^3$ bonds, since the reaction portrayed in eq. (1) is bimolecular in diphenylmethane. It seems doubtful, therefore, that a significant number of diarylmethane moieties in the rigid coal structure could engage in bimolecular reactions. This conflicts with Niemann's statement⁸ that methyl group formation during reduction of Westerholt coal arises through

fragmentation of diarylmethane structures. The sp^2 - sp^3 bonds in diphenylmethane have bond energies⁹ of ~ 375 kJ/mole, whereas the sp^3 - sp^3 bond energy in bibenzyl is only ~ 250 kJ/mol. The extra 125 kJ of energy required, therefore, to bring about cleavage in diphenylmethane is derived from bond-making during the bimolecular reaction portrayed in eq. (1). Because, however, of structure-reactivity relationships in model compound studies,¹⁰ it is not wise to generalize from the behavior of diphenylmethane and to assume that all diarylmethanes and all diarylmethane moieties in coal will act the same way when treated with Na-K in glyme-triglyme solution. As we have repeatedly emphasized,¹⁰ model compound studies must include ranges of compounds, each of which contains the structure under investigation, so that its behavior in different structural environments can be studied. For this reason we prepared α -benzyl-naphthalene and subjected it to Na-K reduction. Tetralin (13%) and toluene (31%) were produced along with other products. No benzene was formed, as demonstrated by using α -benzyl-(phenyl- ^{14}C)naphthalene as the reactant, and searching for labeled benzene among the products. There was evidence, however, for the $\alpha\text{-C}_{10}\text{H}_7\text{CH}_2^-$ anion, since 37% of a mixture of hydrogenated α -ethylnaphthalenes (GC-MS) were identified, which must have arisen through an S_N2 reaction between $\alpha\text{-C}_{10}\text{H}_7\text{CH}_2^-$ and the solvent. The presence of tetralin and the absence of naphthalene indicate Birch-Hückel reduction of the reactant to α -benzyltetralin, followed by cleavage, eq. (4), by a mechanism similar to that postulated for the cleavage of

bibenzyl. The tentative identification (GC-MS) of α -benzyltetralin among the products lends credence to the foregoing mechanism. The absence of benzene and the appearance of α -ethylnaphthalene are good evidence for a competing bimolecular reaction similar to that shown in eq. (1). Given the bimolecular mechanism, eq. (1), it might be possible to carry out the Na-K reduction of diphenylmethane in the presence of benzene and generate the benzene radical anion which then would react with diphenylmethane with the results shown in eq. (5). The products of

eq. (5), on reacting with water, should produce biphenyl and toluene. The products observed for a typical run of 3 h at 0°C were: toluene, 56%; biphenyl and hydrogenated biphenyls, 32%; *m*-benzylbiphenyl, 2%, and dihydro-*m*-benzylbiphenyl, 6%. Forty-eight percent of the diphenylmethane was recovered unchanged. That the biphenyl and hydrogenated biphenyls formed involved both reactants was demonstrated by labeling the diphenylmethane (in the phenyl group) with ^{14}C and showing that the C_{12} products were radioactive. The same result was obtained when benzene- ^{14}C was used as one of the starting materials.

In summary, sp^3 - sp^3 bonds in bibenzyl can cleave in the presence of Na-K at 0°C in glyme-triglyme by simple fragmentation of the substrate radical anion. In the case of diphenylmethane, the

sp^2 - sp^3 bond is too strong to be cleaved by simple fragmentation. In this event cleavage occurs through a bimolecular reaction between a diphenylmethane molecule and a diphenylmethane radical anion. When the reaction of diphenylmethane with Na-K is carried out in the presence of benzene, a bimolecular reaction between benzene radical anion and diphenylmethane occurs to give, among other products, toluene, biphenyl, and hydrogenated biphenyls. α -Benzyl-naphthalene, under the same conditions, appears to cleave both through the mechanism shown in eq. (4), as well as by *ipso*-nucleophilic attack of the radical anion on α -benzyl-naphthalene.

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2.1.2 Monitoring Chemical Reactions of Coal by Solid State ^{13}C -NMR Spectroscopy: Reductive Alkylation of Coal by Na-K Alloy in Mixed Glymes

(E. W. Hagaman, M. C. Woody)

Resonance bandshapes of high-resolution, solid-state ^{13}C -NMR (CP/MAS- ^{13}C -NMR) coal spectra are rarely symmetrical envelopes devoid of structure. We have been interested in the decomposition of these broad envelopes into components which reveal a more detailed structural description of the organic matter in coal. Using a combination of NMR and chemical resolution enhancement techniques, the sp^2 - and sp^3 -carbon resonance manifolds each can be partitioned into fractions representing protonated and non-protonated carbons, and these in turn can be divided again using chemical shift criteria into subgroups reflecting the presence or absence of directly bonded oxygen substituents. Thus, within the approximation that the organic matter of coal can be considered to be composed of carbon, hydrogen, and oxygen, the area under each hybridization resonance envelope may be divided into at least three fractions, reflecting the immediate bonding environment of carbon. The techniques which prove of value in this spectral decomposition, i.e., convolution difference methods, partial polarization spectroscopy, spectral subtraction and ^{13}C -chemical enrichment, are discussed in the following paragraphs and employed in the analysis of the products from a reductive alkylation of a typical bituminous coal.

Convolution Difference Spectroscopy. Figs. 2.1A and 2.1A' are typical CP/MAS- ^{13}C NMR spectra of a bituminous (Illinois No. 6 vitrain) and subbituminous (Wyodak) coal, respectively. Processing the free induction decay (FID) of the spectrum in Fig. 2.1A(A') by standard convolution difference (CD) techniques that discriminate against components of the FID with fast T_2^* results in the spectrum in Fig. 2.1B(B').¹⁻³ The CD spectrum reveals that the carbon magnetization of these coals possesses an inherent relaxation time dispersion. Attenuating the broad line components of the spectrum enhances the asymmetric lineshape in both the sp^2 - and sp^3 -carbon resonance

envelopes of the spectrum. The spectrum in Fig. 2.1B(B') is obtained from the FID of the spectrum in Fig. 2.1A(A') after multiplication of the latter by $e^{-\tau/T_A} - Ke^{-\tau/T_B}$. The CD variables T_A , T_B , and K are selected empirically to optimize the compromise between enhanced resolution and reduced signal-to-noise (see Fig. legend).

This mathematical operation is equivalent to the subtraction of a broad from a narrow Lorentzian line and effectively removes resonances from the spectrum for which $T_2^* \ll T_B$. Figure 2.1B(B') retains ca. 25% of the total resonance area measured in Fig. 2.1A(A'). Variation of the CD parameters to generate spectra which contain 25-

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Fig. 2.1. CP/MAS- ^{13}C nmr spectra of bituminous (A-D) and subbituminous coal (A'-D'). Spectrum A(A') was generated with $T_{cp} = 1.0$ ms and 2.0 s recycle delay; ca. 15,000 transients. Spectrum B(B') was obtained by multiplication of the FID of A(A') by $e^{-t/.0064} - 0.80 e^{-t/.0032}$. Spectrum C(C') was generated with $T_{cp} = 20$ μs and 2.0 s recycle delay; ca. 90,000 transients. The FID was processed as for B(B'). C(C') is shown with an arbitrary vertical scale expansion. Spectrum D(D') is the difference spectrum B - C (B' - C').

100% of the area of the spectrum in Fig. 2.1A(A') and subsequent integration reveal that f_a (the fraction of total carbon which is sp^2 -hybridized) is nearly independent of the extent of line narrowing ($\pm 5\%$). Structural features emerge from the asymmetric hybridization envelopes by gradual sharpening across the bandwidth, not by preferential signal attenuation of specific spectral regions. This behavior indicates that the relaxation time dispersion is largely independent of the statistical distribution of the carbon types within the sp^2 - and sp^3 -carbon resonance envelopes. The relaxation time dispersion may result from a random distribution of paramagnetic centers in the sample and/or to regions of the coal matrix which differ in mobility. In either case, the CD spectra appear to be an undistorted representation of the whole coal sample.

Resolution enhancement techniques that rely on selective removal of broad resonance components from coal spectra can not be expected to achieve dramatic increases in resolution within the hybridization bands. In the idealized case of coal spectra consisting only of sharp individual transitions, the myriad resonances will still coalesce into broad bands. Nevertheless differences in average distribution of resonances within the hybridization bands of different coals becomes quite apparent (cf. the aromatic bands in Figs. 2.1B and 2.1B'). The CD spectra do allow evaluation of the carbon resonance areas at the band extreme without interference from broad resonance contributions. The 60-90 ppm spectral region in the coal spectra of Fig. 2.1 is at baseline indicating that the concentration of sp^3 -carbons directly bound to oxygen in these coals is negligible. Aliphatic ether and carbonyl bands are prominent and well-resolved in the CD spectra of lignite and lower rank coals.

Partial Polarization Spectra. Carbon magnetization accrues in the CP experiment by spin polarization transfer from protons to carbon atoms. The 1H - ^{13}C cross-polarization rate (T_{CH}^{-1}), maximized at the Hartmann-Hahn condition, $\gamma_{CH}H_C = \gamma_H H_H$, is governed by, *inter alia*, the strength of local static 1H - ^{13}C dipolar interactions and follows an inverse sixth power

dependence on 1H - ^{13}C internuclear distance.⁴ Thus carbons with directly bonded protons ($r_{CH} \approx 1.1 \text{ \AA}$) cross polarize faster than carbons which must rely on nearest neighbor protons ($r_{CH} > 2.0 \text{ \AA}$). Schaefer *et al* have demonstrated that the dependence of T_{CH} on 1H - ^{13}C -internuclear distance can be used as an assignment criterion and as a resolution enhancement technique.⁵ The discrimination between protonated and non-protonated carbons as a function of cross-polarization contact time is valid if all carbons have similar correlation times. Molecular motion can reduce 1H - ^{13}C dipolar interactions. In solids, methyl groups undergoing fast internal rotation exhibit diminished dipolar coupling and have T_{CH} values more aligned with non-protonated carbons. This circumstance allows methyl carbon resonances to be differentiated from all remaining protonated carbons and, on chemical shift criteria, from non-protonated sp^3 -carbon resonances.

Quantitative relaxation times of the coals examined herein have not been measured but average T_{CH} of 50 and 300 μs for protonated and non-protonated carbons, respectively, have been estimated from partial polarization spectra. Assuming an exponential form for T_{CH} , these values predict a >80% suppression of resonance area of non-protonated carbons with respect to the normalized protonated carbon resonance area, in spectra recorded with a 20 μs cross-polarization contact time. Partial polarization spectra obtained with this CP contact time and processed with CD parameters used in Fig. 2.1B(B') are shown in Fig. 2.1C(C'). These spectra reveal a nearly complete elimination of the resonance area in the spectral region below 148 ppm and a strong attenuation of the resonance area in the central portion of the aromatic envelope. Hence, the resonance area below 148 ppm in Fig. 2.1B(B') arises from non-protonated carbons, which on chemical shift criteria must bear (predominantly) oxygen substituents. The absence of aliphatic oxygenated carbon moieties indicates that in these coals the organic oxygen is contained predominantly in phenolic and diaryl ether moieties.

The partial polarization spectra reveal a narrowing of the sp^3 -carbon manifold resulting

from preferential signal loss from the low and high field extrema of this band, particularly evident in the subbituminous coal (Fig. 2.1C').

The carbon resonances with long T_{CH} eliminated in Fig. 2.1C(C') are displayed in Fig. 2.1D(D'), the difference spectrum obtained by subtraction of the spectrum in Fig. 2.1C(C') from that in Fig. 2.1B(B'). The criterion used in this subtraction is baseline nulling of the area in the aromatic envelope in the spectral region above 115 ppm. Chemical shift considerations of a broad spectrum of aromatic model compounds indicate that this spectral region will contain only aromatic methine carbons. The low intensity bands centered at 47 and 20 ppm in Fig. 2.1D(D') are due to quaternary (and conceivable R_3C-X , $X=N, S$) and methyl carbon resonances, respectively. The prominent aromatic band centered at 127-129 ppm in Fig. 2.1B(B') is a composite of overlapping non-protonated and methine carbon resonances.

Reconstruction of the spectrum in Fig. 2.1B by summation of that in Figs. 2.1C and 2.1D indicates that ca. 70% of the sp^2 -carbon resonance area is due to non-protonated carbon resonances. Using chemical shift criteria [phenols, aromatic ethers; 160-142 ppm; alkyl/aryl substituted aromatic carbons (ring junction and sidechain attachment sites); 148-125 ppm] the resonance area in the spectrum of Fig. 2.1D may be roughly partitioned into components arising from oxygenated and non-oxygenated species in a 1:6 ratio. Hence the total sp^2 -carbon resonance area

may be partitioned into components due to carbon substituted by oxygen, carbon, and hydrogen in a 1:6:3 ratio, respectively. The ratio statistically corresponds to the distribution of these three aromatic carbon types in a tetra-alkyl-substituted naphthol or naphthyl ether.

In the sp^3 -carbon region of the spectrum, partial polarization spectra identify non-protonated and methyl carbon resonance contributions to the total resonance area. Utilizing the gross carbon chemical shift dependence on electronegative substituents, each of these carbon types may be further partitioned into subgroups, depending upon the presence or absence of direct oxygen substitution. The remaining and dominant fraction of the sp^3 -carbon resonance area in these coals arises from methine and methylene carbons whose resonances extend throughout the 20-50 ppm interval.

The decomposition of the sp^2 - and sp^3 -carbon resonance envelopes of solid-state coal spectra into fractions reflecting immediate carbon bonding environment is summarized schematically in Fig. 2.2. The neglect of organic nitrogen and sulfur moieties and the partially overlapping resonance zones of non-protonated C_{sp^2-C} and C_{sp^2-O} species limit the quantitative characterization of coals according to this scheme. The methods nonetheless provide a more detailed description of major carbon types within the hybridization envelopes which can be monitored to map out the principal structural changes of chemically modified coals.

Fig. 2.2. Decompositions of the C_{sp^2} - and C_{sp^3} -resonance envelopes of CP/MAS- ^{13}C nmr spectra of coals.

Spectral Analysis of the Coal Products from the Na-K Reduction of Illinois No. 6 Vitrain in Mixed Glymes. The repeated reduction of coal by the action of Na-K alloy in glyme-triglyme followed by quenching with a proton donor or with methyl iodide is an efficient low-temperature method for degrading coal by cleavage of aliphatic and aromatic-aliphatic carbon-carbon bonds.^{6,7} Birch-Hückel reduction products (di- and tetrahydro-aromatic moieties) are suppressed but not eliminated in this solvent system. We have examined the chemically altered products of Illinois No. 6 vitrain obtained by this reduction scheme, utilizing both natural abundance and 20% ^{13}C -enriched methyl iodide as quenching agent. Multiple reductions were performed by subjecting the total isolated solid product (>95% of the starting material) from one reduction pass to identical reaction conditions following spectral examination.

The CP/MAS- ^{13}C -NMR spectrum depicted in Fig. 2.3A is of the initial reduction product obtained with a natural abundance methyl iodide quench. The spectrum was acquired using a long cross-polarization time (1.0 ms) for which all carbon resonances show maximum intensity. The general character of the spectrum is similar to that of the chemically unaltered coal but with a broadened sp^3 -carbon resonance envelope. The changes in this region of the spectrum are apparent in Fig. 2.3B, the difference spectrum obtained by subtracting the spectrum of the starting material from the spectrum in Fig. 2.3A (arbitrary scale expansion). The criterion used for the subtraction is nulling of the aromatic resonance envelope. Birch-Hückel reduction products, not expected to result in a linear attenuation in the area across the full width of the sp^2 -carbon resonance envelope, are thus not formed in this reaction in detectable concentrations. Since the generation of 30 dihydroaromatic species per hundred individual aromatic rings will cause a 10% reduction in the total sp^2 -carbon resonance area, i.e., a change estimated to be the minimum significant detectable area difference, cancellation of the aromatic area in these spectra provides an upper limit estimate of the concentration of these products.

Fig. 2.3. CP/MAS- ^{13}C -nmr spectra of the Na-K reduction product of Illinois No. 6 vitrain obtained by quenching the reaction with 1.1% $^{13}\text{CH}_3\text{I}$. (A) Full spectrum, 1.0 ms CP contact time; (B) Difference spectrum obtained by subtraction of A from the spectrum of the unreacted coal; (C) Partial polarization difference spectrum.

The low and high field "bands" centered at 57 and 20 ppm in the difference spectrum can be assigned to O-CH_3 and C-CH_3 resonances, respectively, solely on chemical shift bases. These carbon types arise from capping phenolate and carbanionic centers generated in the reduction medium. The composition of the central band is revealed in Fig. 2.3C, the partial polarization difference spectrum analogous to the spectrum in Fig. 2.1D. The low field portion of the central band in this spectrum is retained, indicating the resonances are due to non-protonated, i.e., quaternary, carbon centers.

Spectra similar to those in Figs. 2.3A and 2.3B but of the vitrain derivative obtained following the second reduction-quench sequence with 20% $^{13}\text{CH}_3\text{I}$ are presented in Fig. 2.4. Only O-CH_3 and C-CH_3 bands appear in the difference spectrum of Fig. 2.4B, confirming that the methyl iodide con-

Fig. 2.4. CP/MAS- ^{13}C -nmr spectra of the Na-K reduction product of Illinois No. 6 vitrain obtained by quenching the reaction with 20% $^{13}\text{CH}_3\text{I}$. (A) Full spectrum, 1.0 ms CP contact time; (B) Difference spectrum obtained by subtraction of A from the spectrum of the chemically unaltered coal.

sumed in the reaction does not contribute to the resonances in the central band observed in the spectrum of Fig. 2.3B. Thus this band must arise from the generation of highly substituted aliphatic carbon centers in the course of the reaction.

The spectrum shown in Fig. 2.4A is one of a series of six corresponding to six sequential reductions of vitrain using 20% $^{13}\text{CH}_3\text{I}$ as quench reagent. The O-methyl resonance bands in this series all appear similar to that in Fig. 2.4A, i.e., partially resolved into two components centered at 55 and 60 ppm. These shift values are characteristic resonances of aromatic methyl ethers in unhindered (one or both *ortho*-positions unsubstituted) and hindered (*ortho-ortho'*-disubstituted) environments, respectively, and are largely independent of the nature of the *ortho* substituents. The 60 ppm value reflects the fact that the methoxyl group is prevented from adopting a conformer in which the methyl group lies in the plane of the aromatic ring. The resolution of the O-methyl band into these components yields unprecedented structural data on the environments of the phenolic residues in coals.

The relative concentration of O-methyl and C-methyl residues introduced into the coal can be obtained from difference spectra, e.g., Fig. 2.4B, of coal derivatives quenched with 20% $^{13}\text{CH}_3\text{I}$. The integrals contain an error from the neglect of the reorganized carbon resonances which account for the central aliphatic band in spectrum 2.3B. The use of enriched methyl iodide minimizes this error, estimated to be <5%. Fig. 2.5 is a plot of the $\text{XCH}_3/\text{C}_{\text{sp}^2}$ area ratio vs. reduction step number for six sequential reductions of vitrain. The ratios for all the data are scaled under the assumption that the area of the sp^2 -carbon resonance envelope remains

Fig. 2.5. Plot of the $\text{OCH}_3/\text{aromatic carbon}$ and $\text{CCH}_3/\text{aromatic carbon}$ area ratios vs. reduction step number of Illinois No. 6 vitrain.

constant throughout the sequence (vide supra). The plot reveals that by the third reduction the $\text{O-CH}_3/\text{C}_{\text{sp}^2}$ area ratio has attained its maximum value and thereafter remains constant. The concentration of aromatic methyl ether moieties indicated is 9 per 100 aromatic carbon atoms. This value overestimates the number of methyl ether moieties introduced into the coal by a factor of two as determined by $^{13}\text{C}/^{14}\text{C}$ double labeling experiments (see Section 2.1.3). A corrected value of 4-5 aromatic methyl ether residues per 100 aromatic carbons is in good agreement with the number of free phenolic residues in Illinois No. 6 coal.⁸ Whether this value measures just the free phenolic content of

the coal or also contains a contribution from aromatic ethers that have been opened in the reduction milieu is under further investigation.

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2.1.3 Statistical Coal Structure Analysis by Solid State ^{13}C -NMR Spectroscopy: Quantitative Evaluation of Aromaticity Parameters

(E. W. Hagaman, M. C. Woody)

The distributions of aromatic and aliphatic hydrogen and carbon in the organic matter of coals are important parameters in the characterization of these materials and in evaluations of their chemically modified derivatives. In addition to the directly measurable carbon aromaticity of coals, f_a , by CP- ^{13}C NMR spectroscopy,¹⁻⁴ the decomposition of the aromatic and aliphatic resonance bands into components arising from protonated and non-protonated carbons has also been accomplished (Sect. 2.1.2).⁵ This separation may be effected utilizing the ^1H - ^{13}C distance dependence of the cross polarization time or the ^1H - ^{13}C dipolar relaxation rate differential of carbon magnetization under the influence of the full ^1H - ^{13}C dipolar interaction.⁶ The decomposition does not involve unique relaxation times, but rather is complicated by the dispersive nature of the parameters characteristic of heterogeneous, amorphous materials. Fig. 2.6 compares the spectrum of a bituminous coal, Illinois #6 vitrain, (A), with its subspectra representing its non-protonated carbon, (B), and

CP/MAS- ^{13}C -NMR SPECTRA OF A COAL

Fig. 2.6. CP/MAS- ^{13}C -nmr spectra of Illinois #6 vitrain. (a) Full spectrum, 1.0 ms cross polarization time. (b) Non-protonated carbon subspectra of this coal, 1.0 ms cross polarization time and 80 μs decoupling gas following the cross polarization period and prior to data acquisition; (c) Protonated carbon subspectra of this coal obtained by subtraction of spectrum (b) from spectrum (a).

protonated carbon, (C), fractions (see Figure caption for details).

These spectra present the interesting possibility of measuring hydrogen aromaticity given by

$$f_{a_H} = \left(\frac{C}{H}\right) f_{a_{CH}} \quad (1)$$

where C and H represent the number of atoms of these elements determined from the empirical formula of the coal and $f_{a_{CH}}$ is the fraction of total carbon in the coal which arises from protonated aromatic centers, i.e., $\text{CH}_{\text{arom.}}/\text{C}_t$. Expression (1) utilizes the one-to-one carbon-

hydrogen atom constraint of aromatic methines to equate the number of protonated aromatic carbons with the number of aromatic hydrogens.

Though measurements of f_a of coals evaluated from the observable magnetization of CP/MAS- ^{13}C spectra are increasing, the fundamental prerequisite for quantitative applications using this and related parameters demands that the measurement of total carbon, C_t , does in fact reflect unit intensity response from all carbons in coal. The deviation from this requirement is a realistic measure of the quantitative capability of this technique. Early attempts to evaluate this response have provided inconclusive results with estimates ranging from 40-100% for the fraction of total carbon observed in the CP- ^{13}C NMR experiment.^{1,7}

We have evaluated the measurement of C_t using a double-labeling experiment consisting of chemically introducing methyl groups into coal via alkylation with ^{13}C , ^{14}C -methyl iodide (^{14}C , 11.86 mCi/mole; ^{13}C , 18.56%). Radioassay of a weighed amount of the coal derivative in conjunction with its elemental analysis provides the ratio of introduced carbon (gr-atom)/total carbon (gr-atom), C_{int}/C_t . This quantity is taken as the standard against which the CP/MAS- ^{13}C NMR integration, expressed as CH_3 resonance area/total carbon area, CH_3/C_t , is measured.

The methyl label was introduced using two chemical procedures. In one set of experiments Illinois #6 vitrain was subjected to Na-K alloy reduction in a mixed glyme solvent and the anionic sites generated were capped with the doubly labeled methyl iodide.⁸ This reductive alkylation was repeated sequentially six times with isolation and ^{13}C , ^{14}C analysis at each stage. The analytical results comprise the first six entries in Table 2.1. The spectra of these materials indicate that the reaction introduces both O- and C-methyl groups. In a separate experiment, Illinois #6 vitrain was alkylated in aqueous THF at room temperature using tetra-*n*-butylammonium hydroxide as base. This mild procedure introduces only O- CH_3 moieties into the coal.⁹ The analytical data from this experiment is entry 7 in Table 2.1.

Table 2.1. ^{14}C radioassay and ^{13}C -NMR analysis of coal derivatives

Item	^{13}C (CH_3/C_t)100,%	^{14}C (C_{int}/C_t)100,%	$^{14}\text{C}/^{13}\text{C}$
1	10.9	5.77	0.53
2	15.7	8.82	0.56
3	19.6	10.85	0.56
4	21.9	12.64	0.58
5	24.0	13.90	0.57
6	27.9	14.22	0.53
7	4.9	2.66	0.55

The ^{13}C NMR spectra were obtained using a single contact Hartmann-Hahn cross polarization experiment with r.f. field strengths of $(\gamma\text{C}/2\pi)H_{1\text{C}} = (\gamma\text{H}/2\pi)H_{1\text{H}} = 24\text{ KHz}$, 1.0 ms cross polarization time and 1.66 s delay for reestablishment of the proton magnetization. Since we measure average T_{CH} for non-protonated carbon (aromatic), protonated carbon (aromatic and aliphatic) and introduced OCH_3 of 140 μs , 20 μs , and 50 μs , respectively, and average proton $T_{1\rho}$ for aromatic, aliphatic and OCH_3 carbon of 4.4 ms, 5.5 ms, and 3.8 ms, respectively, the experimental parameters favor slightly the enhancement of magnetization from native carbon in coal over that of introduced methyl.

The constant $^{14}\text{C}/^{13}\text{C}$ ratio in Table 2.1 for the Na-K reduction products, 0.55 ± 0.03 , establishes that experimental parameters determined for untreated coal are valid in the analysis of highly modified coals. The coal derivative obtained following the sixth Na-K reduction- CH_3I quench reaction, for example, has fourteen methyl groups incorporated into the coal network for every hundred native coal carbons. The $^{14}\text{C}/^{13}\text{C}$ ratio from the O-methylation of coal (entry 7) is identical to that found in the Na-K reduction products. The NMR results consistently yield a ratio of CH_3/C_t that is almost a factor of two larger than the ^{14}C ratio. Under the assumption that the CP/MAS- ^{13}C NMR spectra registers unit

intensity response from all introduced methyl groups, the last column in Table 2.1, represents the fraction of native carbon in coal that is detected in these experiments. These results indicate that caution must be exercised in interpreting data from this simplest CP/MAS- ^{13}C NMR experiment. Correlations using hydrogen and carbon aromaticity parameters from such experiments apply only to the observable carbon magnetization and may not reflect accurately the structures of coal.

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2.1.4 Thermolysis of Model Coal Structures: 1,3-Diphenylpropane and 1,4-Diphenylbutane

(M. L. Poutsma, C. W. Dyer)

We are studying the thermolysis of α,ω -diphenylalkanes, $\text{Ph}(\text{CH}_2)_n\text{Ph}$, as models for the aliphatic connecting linkages between the aromatic clusters in coal. Thermochemical considerations¹ of bond dissociation energies (BDE) predict that the weakest C-C bond will occur for bibenzyl ($n=2$) because of the possibility of forming two resonance-stabilized benzyl radicals in step (1). Studies by ourselves² and others³

have now shown that bibenzyl decomposes in a first-order, nonchain fashion with an E_a value consistent with the predicted BDE. Hence C-C bond homolysis (step (1); $n=2$) is the rate-controlling step and is followed by hydrogen atom transfer step (2); product formation then occurs largely by radical-radical interactions.

If n is increased to 3, BDE considerations predict a considerably slower rate of thermal decomposition for 1,3-diphenylpropane (1). In fact, we find the initial rate of decomposition of liquid 1 at 350-425°C to be some 20 times more rapid than that of bibenzyl. At low conversion levels, the products are cleanly toluene and styrene; at longer reaction times, styrene is partially consumed by secondary reactions, one of which is readdition to 1 to produce 1,3,5-triphenylpentane.

This major discrepancy between prediction based on BDE values and observation indicates the occurrence of some reaction pathway for 1 which is not available to bibenzyl. We have considered two plausible hypotheses: a chain reaction⁴ consisting of a repetition of steps (3) and (4) for

which C-C homolysis (step (1); $n=3$) serves only as the initiating event; and (2) an orbital symmetry-allowed retroene reaction⁵ depicted in (5). Although these mechanisms are not directly distinguishable by product criteria, they will have different kinetic behavior.

Because of the occurrence of secondary reactions, kinetic measurements must be made in a differential rather than integral manner. We have determined initial rates of thermolysis (2-5% conversion) at 365°C as a function of initial concentration of 1 which was varied by a factor of 10^3 from neat liquid (~ 3 M) through a series of dilutions with biphenyl and finally into the gas phase (3.8×10^{-3} M at 20 kPa). The log-log plot (Fig. 2.7) indicates a kinetic order near 1.5 compared with 1.0 for bibenzyl. Such behavior is clearly inconsistent with the molecular process depicted in eq. (5) which must be first-order. However, steady-state analysis of the free-radical chain mechanism predicts an order of 1.5 if $k_\beta \gg k_H [\underline{1}]$. (This is equivalent to defining the simplified case where radical termination (steps not shown) is dominated by coupling of benzyl radicals.) Although these specific rate constants have not been measured, they can be estimated from those of similar ele-

mentary radical processes^{1,6} modified for expected structure-reactivity effects.^{3a,6} We

$$\text{estimate } k_\beta \approx 10^{14.5} \exp\left(\frac{-113000}{RT}\right) \text{ s}^{-1} \text{ and } k_H \approx 10^{8.6} \exp\left(\frac{-67000}{RT}\right) \text{ M}^{-1} \text{ s}^{-1} \text{ from which, at}$$

365°C and $[\underline{1}] \leq 3$ M, k_β indeed exceeds $k_H[\underline{1}]$ by ≥ 50 -fold. Hence we conclude that the "accelerated" rate of thermolysis of 1 results from a long chain reaction. We observed $E_a \approx 218$ kJ/mol over the range 340-425°C. For the chain process with benzyl radical termination, E_a^{exp} is identified with $1/2(\text{BDE}) + E_H \approx 1/2(297) + 67 \approx 216$ kJ/mol. Thus the observed temperature effect is fully consistent with our mechanistic conclusion.

The structural feature which differentiates 1 from bibenzyl is that β -scission step (4) to expel benzyl radical is estimated to be endothermic by only ~ 88 kJ/mol and hence is kinetically assessable at 350-400°C. In contrast, the homologous step (6) for bibenzyl is endothermic by

~ 209 kJ/mol because the much less stable phenyl radical must be expelled. This energy barrier cannot be surmounted rapidly enough to compete with radical coupling reactions.²

The thermolysis of the next homologue, 1,4-diphenylbutane (2), while somewhat slower than that of 1, is again much faster than anticipated from BDE considerations. Simple extrapolation from the homologues of steps 3-5 suggests that in this case the two mechanistic hypotheses could be distinguished on the basis of products because the radical chain should produce ethylbenzene and styrene while the retroene process must produce toluene and allylbenzene. In fact, both pairs of products are formed initially in a ratio which depends on the concentration of 2. We feel this result does not signify that both mechanisms are operative but rather that the chain process is now more complex. Two isomeric radicals can be produced by hydrogen atom transfer, and both must be considered as reactive intermediates. Whereas benzylic radical 3 will be more stable than secondary radical 4 by ~ 42 kJ/mol, the enthalpy of its β -scission will

Fig. 2.7. Rate of initial thermolysis of 1,3-diphenylpropane as a function of initial concentration.

be less favorable as shown in the following diagram of estimated energetics:

Hence a complete set of chain propagation steps must include equations (7)-(13). The key step

revealed by the concentration dependence of the product ratios is step (13). β -Scission of radical 3 (step (9)) is slow enough to allow some hydrogen transfer from 2; this effects an inter-conversion of radical 3 to radical 4 which then undergoes step (10) almost instantaneously because of its very favorable energetics.

Steady-state analysis of steps (7)-(13) predicts that:

$$\frac{(\text{PhCH}_3)}{(\text{PhCH}_2\text{CH}_3)} = \left(\frac{k_{H1} + k_{H2}}{k_{H1}} \right) \left\{ \frac{k'_{H2}}{(k'_{H1} + k'_{H2})} + \frac{k_{12}}{k_{\beta 1}} [\underline{2}] \right\}$$

Experimental correspondence to this prediction of linearity has indeed been demonstrated with $(\text{PhCH}_3)/(\text{PhCH}_2\text{CH}_3)$ decreasing from 1.0 in the neat liquid to 0.2 in the dilute gas. The significance of these results for modeling coal decomposition is that dimethylene linkages ($n=2$) are not the only likely locus of C-C bond instability. In fact, longer bridges ($n \geq 3$) should be just as labile once they are activated by hydrogen abstraction by radicals generated elsewhere in the coal structure. Secondly, one must consider all possible radicals because the least stable ones may be the most reactive and hence may participate in the chemistry to a significant extent.

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2.1.5 Thermolysis of Model Coal Structures: Naphthols

(M. L. Poutsma, C. W. Dyer)

Phenolic functionality is a common structural feature of coals and coal-derived products and process solvents. Several proposals, often conflicting, have been made for possible chemical involvement of phenolic groups during coal processing.¹ However, the chemical basis for these is weak because of the scarcity of knowledge

regarding the chemistry of phenols under high-temperature conditions. We have been carrying out basic studies of the thermal chemistry of naphthols to provide such background. In the previous Annual Report,² we described some phenomenology of the behavior of liquid 1-naphthol (1) at 400°C. To summarize briefly the initial stages of the chemistry, we found that two molecules of 1 condense at the *ortho* position to form binaphthol 2 which rapidly cyclizes to form dinaphthofuran 3; the equivalent of hydrogen made available by formation of 2 is transferred intermolecularly to another molecule of 1 to form ring-reduced products 4 and 5 in a ratio of ~5:1. The mechanistic puzzles posed by these observations were the nature of regiospecific C-C bond formation at C-2 and the mode of hydrogen transfer without formation of molecular hydrogen.

We have now explored the effects of certain diluents and potential catalysts. Dilution with "inert" hydrocarbons such as *m*-terphenyl led to a rapid falloff in rate; log-log plots of initial rate vs. initial concentration were linear with a slope of 2.5. This is indicative of a high, complex kinetic order, although some additional possible effects of polarity of the medium have not been dissected. In contrast, dilution with benzophenone led to rate acceleration and replacement of products 4 and 5 by diphenylmethane. Clearly there is some point in the mechanism where benzophenone can intervene as a more efficient hydrogen acceptor than 1 itself.

Addition of H_3PO_4 induced some formation of *bis*(1-naphthyl) ether, but had little effect on the rate of formation of (2+3). Similarly, addition of NaOH lead to an additional product, a naphthyl-naphthol, but had only minor effect on the parent reaction. Hence there is no strong evidence for acid-base catalysis.

We have also now carried out analogous product studies for 2-naphthol (6). The meager literature background³ was especially confusing in this case because of dispute concerning the structure of the furan product. We find that thermolysis of 6 at 400°C proceeds somewhat more slowly than that of 1; a typical product distribution at low conversion is shown below:

Two isomeric dinaphthofurans 7 and 8 are formed which can be distinguished by ^{13}C NMR. Symmetrical furan 7 is preceded by binaphthol 9 whose ring closure is much slower than that of 2, probably because of developing steric hindrance in 7. In fact, thermolysis of pure 9 give not only furan 7 but also some reversion to 6. The (unknown) binaphthol structurally related to the unsymmetrical furan 8 has not been detected as yet and hence must not accumulate in significant amounts. Reduction products 10 and 11 are analogous to 4 and 5. Finally, variable amounts of ether formation occur. It appears that the

ratio 8:(7+9) gradually increases with increasing conversion level, but this conclusion is subject to further verification because unfortunately results have been found recently to be somewhat dependent on the exact laboratory purification procedure used for 6.

Although we have thus obtained additional kinetic and product information, we have not yet solved the mechanistic puzzle of naphthol thermolysis. Space here does not allow elaboration of the subtleties of the various mechanistic hypotheses being considered. Suffice it to say that a critical unknown input is the coupling behavior of naphthoxy radicals at high temperature, in particular the possibility that the regioselectivity is determined by a competition between enolization and dissociation and/or sigmatropic rearrangements of initially formed benzocyclohexadienones.

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2.1.6 Preparation of a Dimethylbipiperidobenzene (F. M. Schell,¹ C. J. Collins)

The synthetic sequence worked out² and shown in Scheme 2.1 has been repeated for the purpose of

building up a stockpile (>1.0 g) of the compound represented by the penultimate structure. A little over 1 g of the N,N-dimethyl-9-bromobipiperidobenzene has been prepared, and approximately 100 mg of it has been photolyzed in cyclohexane in the presence of hexamethylditin to yield the compound shown in the last structure of Scheme 2.1, which is the sole product. It remains only to carry out the photolysis of N,N-dimethyl-9-bromobipiperidobenzene and also of the perdeuteriodimethyl compound in an esr cavity and thus calculate the extent of the H_k/D_k isotope effect in order to determine whether the reaction exhibits a large quantum-mechanical tunnelling factor.

1. Part-time employee from the University of Tennessee, Knoxville.

2. C. J. Collins, F. M. Schell, A. Egozy, and R. D'Costa, *Chem. Div. Annu. Prog. Rep. Feb. 29, 1980*, ORNL-5665 (July 1980), p. 13.

2.1.7 X-Ray Scattering Evidence for Extensive Graphite Monolayers in Wyodak Coal

(W. E. Thiessen, J. W. Larsen, A. H. Narten)

As part of a project to determine whether there are preferred distances between various functional groups (e.g., carboxyl, hydroxyl) in coal, we have measured the x-ray scattering from powdered undried Wyodak (Rawhide Seam) sub-bituminous coal over the range of 0.3 to 16 $\text{\AA}^{-1}$. The atom pair distribution derived from these scattering data is well fit with a model of single graphite layers similar to that used by Warren¹ to interpret the scattering from carbon black. In this model, any single carbon atom in the hexagonal array has three first neighbors, six second-, three third- and six fourth-, fifth-, sixth-, and seventh-nearest neighbors (Fig. 2.8). When the scattering from a model with these weights is fitted to the observed scattering and then subtracted from it, only one feature remains in the residual atom pair distribution out to 5.6 $\text{\AA}$ -- a small broad peak centered at 3.3 $\text{\AA}$, the interlayer spacing of crystalline graphite. Otherwise, the residual atom pair distribution rises monotonically from

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Fig. 2.8. Arrangement of carbon atom neighbors about a reference atom in a single graphite layer.

a value of zero below $2.4 \text{ \AA}$ to the expected value of one at long distances ($>5.8 \text{ \AA}$). We thus conclude that an important component of the structure of Wyodak coal consists of essentially planar hexagonal sheets, roughly $75\text{--}80 \text{ \AA}^2$ in area, which are only very roughly coplanar with any neighboring sheets. This structure is very different from the stacked $20 \text{ \AA}^2$ "clusters" ringed by amorphous material proposed by Cartz and Hirsch² for European brown coals.

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2.1.8 Small Angle Neutron Scattering from Coal Extracts

(R. Triolo, H. R. Child,^{1a} J. W. Larsen,^{1b} T. Green^{1b})

The wide variations reported for the average molecular weights of coal and coal derivatives² are a clear indication of the difficulties inherent in estimating such quantities for complex mixtures of compounds possessing different chemical properties. Recently SANS measurements have been proposed for the measurement of weight average molecular weights.³ We have started a critical analysis of the method for the purpose of assessing the reproducibility of the extraction and of the measurements as well as the stability of the samples once in the measurement cell. Finally, we have tried to find an empirical way to by-pass the most serious uncertainty

associated with the use of SANS experiments to measure weight average molecular weights in systems in which chemical changes become important upon dilution.

In a previous note⁴ we reported some results on an extract from a sample of Illinois #6 coal. We noticed that at high concentrations the extrapolated zero angle scattering intensity seemed to become constant; the same behavior was noticed for the correlation length, obtained by fitting the data to a Debye-type function. Here we present data on several samples of different extracts at concentrations much higher than those previously reported. The four pyridine extracts studied are:

1. Coal extract I6-1. This sample has been studied as a function of the concentration in the range 41.2 mg/ml to 20.0 mg/ml .
2. Coal extract I6-2. This sample was obtained with exactly the same procedure used to obtain the sample I6-1; the starting material (Illinois #6 coal) as well as the duration, the temperature and the conditions used during the extraction were the same. Samples I6-1 and I6-2 have been studied for the purpose of assessing the reproducibility of the extraction. This sample has also been studied as a function of the concentration.
3. Coal extract B-1. This was obtained by treatment of a sample of Bruceton coal and has been studied as a function of concentration.
4. Coal extract I6-3S. This was an Illinois #6 coal extract which has been silylated.

In the extraction procedure, $\sim 1.2\text{--}1.4 \text{ g}$ of 100-mesh coal was exhaustively extracted in a Soxhlet extractor under dry nitrogen for ~ 4 days using $\sim 10 \text{ g}$ of pyridine- d_5 . Samples of I6-1 and I6-2 were centrifuged at $80,000 \text{ rpm}$ for two hours. No colloidal material appeared to be present. The solutions were filtered through a 0.2μ Teflon filter. A small sample was analyzed while the rest was sealed in a quartz cell used for SANS measurements. Sample B-1 was also centrifuged at $80,000 \text{ rpm}$ for two hours. Colloidal material was evident, and this was removed from the extract by passing it through a 0.2μ Teflon filter. The colloidal material present was about 13% of the original extract. Sample I6-3S was silylated

using well-known procedures^{5,6} consisting of adding 5.0 ml of HMDS (hexamethyldisilazane) and a catalytic amount of TMCS (tetramethylchlorosilane) to 5.0 ml of an Illinois #6 coal extract (conc. 49 mg/ml). The solution was refluxed for three days under dry nitrogen and subsequently both the solvent and the reagents were removed by evaporation. The modified extract obtained was again extracted with pyridine-d₅ and then filtered through 0.2 μ Teflon filter. Some characteristics of the solutions used are presented in Table 2.2.

The experimental scattering results are shown in Fig. 2.9. As can be noted, samples I6-1 and I6-2 (which should be identical) behave very differently and so we can conclude that the extraction does not furnish reproducible samples.

Table 2.2. Characteristics of coal extract solutions

Sample	Extract Concentration (mg/ml)	% Extractable ^a
I6-1	41.2	15.0
I6-2	43.4	16.1
I6-3S	51.6	15.2
B-1	61.3	29.4

^aBased on residue.

One interesting feature of the concentration study done for all the coal extracts except I6-3S, is the fact that dilution down to about one-half the original concentration hardly

Fig. 2.9. SANS curves for the four coal extracts studied.

affects the scattering curve. The experimental points have been fitted to the Debye equation^{2,4}:

$$I(k) = I(o) \frac{1}{(1 + k^2 a^2)^2} + C$$

and the results of the fitting are grouped in Table 2.3 and in Fig. 2.10. As can be noted, the zero angle scattering intensity and the correlation lengths are essentially concentration independent over a wide range of concentrations. This fact implies that either the second virial coefficient is equal to zero, or that by a fortuitous cancellation of effects the concentration derivative of the zero angle scattering is null. The present data do not allow a definite conclusion concerning the possibility of obtaining weight average molecular weights of coal extracts by means of SANS experiments, although they seem to suggest that, from a pragmatic point of view, one might neglect the contribution of the second virial coefficient to the zero angle scattering

to get rough estimates of the size of the scattering centers.

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2.2 Chemistry of Coal Liquefaction

2.2.1 Hydrogen-Deuterium Exchange of Selected Aromatic Compounds Related to Liquefaction Solvents

(B. M. Benjamin, E. C. Douglas, S. Mesmer¹)

While the development of several one-stage processes (e.g., Solvent Refined Coal (SRC)) for

Table 2.3. Scattering results fitted to Debye equation

Coal Extract	Conc. (mg/ml)	I(o)	$a^2 \cdot 10^{-3}$	c
I6-1	41.2	62.0 ± 0.3	1.02 ± 0.02	4.4 ± 0.1
	34.2	65.0 ± 0.4	1.21 ± 0.01	3.4 ± 0.04
	27.2	70.1 ± 0.7	1.43 ± 0.01	2.9 ± 0.05
	21.8	62.1 ± 2	2.10 ± 0.5	2.7 ± 0.05
	17.3	46.0 ± 0.6	1.9 ± 0.3	1.5 ± 0.03
I6-2	43.4	155 ± 13	2.1 ± 0.2	5.8 ± 0.5
	39.1	159 ± 6	2.3 ± 0.1	3.8 ± 0.2
	32.6	169 ± 6	2.5 ± 0.1	3.4 ± 0.1
	21.7	160 ± 5	2.8 ± 0.1	2.6 ± 0.1
	7.38	61 ± 1	2.6 ± 0.1	1.40 ± 0.03
	5.64	59 ± 1	2.8 ± 0.1	1.56 ± 0.02
B-1	61.3	195 ± 7	1.6 ± 0.1	9 ± 1
	55.2	208 ± 14	1.7 ± 0.1	7.2 ± 0.7
	49.7	216 ± 13	2.0 ± 0.1	6.4 ± 0.6
	44.7	214 ± 14	2.1 ± 0.2	5.9 ± 0.5
	37.4	170 ± 9	2.0 ± 0.1	5.1 ± 0.4
	30.0	78 ± 2	1.5 ± 0.1	3.3 ± 0.1

Fig. 2.10. Least-square fitting parameters $I(o)$, a^2 , and C for the three coal extracts studied as a function of the concentration.

producing liquid fuels from coal are moving toward commercial feasibility, work has progressed on the concept of Advanced Two-Stage Liquefaction of coals consisting of a Short Contact Time (SCT) coal dissolution stage followed by a catalytic hydrotreating stage. SRC and SCT processing may require different characteristics of the recycle solvent. Regardless of the process, the recycle solvent must interact with the coal to give a fluid product from which the mineral matter can be separated. The solvents associated with SRC processes are usually discussed in terms of their H-donor content such as hydroaromatic compounds produced by partial hydrogenation of some part of the coal-derived product. By contrast, the SCT solvents may need to function especially as H-transfer agents rather than

H-donors. Key molecules for this purpose are believed to be the polynuclear condensed aromatic compounds.² Considering this viewpoint, which may be somewhat oversimplified, we decided to study a group of polynuclear aromatic compounds for their ability to undergo hydrogen exchange reactions, it being assumed that reactivity toward hydrogen exchange is related to hydrogen shuttling.

Some background experience on hydrogen exchange was obtained in earlier research. In that work, which was related to the fragmentation of coal, we were interested in the thermal cleavage of different kinds of C-C bonds³ and also in where the cleavage fragments derived their hydrogen in the primary process to become capped off to give products.^{4,5} In order to resolve the question,⁴ bibenzyl, completely deuterated in the dimethylene group, was heated with ordinary tetralin. After the first 1% of reaction (1 h at 400°C) the toluene derived from bibenzyl- d_4 had 1 hydrogen in the methyl group showing that all the H for capping the radical came from the tetralin. But after heating the mixture for 8 h the hydrogen was distributed through all the products and reactants. In fact, deuterium exchange between bibenzyl and tetralin had taken place some 3-4 times faster than C-C scission. We concluded that the chemistry of bibenzyl at 400°C is dominated by hydrogen exchange reactions. We then determined the activation energy for the H-D exchange of tetralin with two deuterated molecules, bibenzyl and diphenylmethane. The activation energy for exchange of the CD_2 deuteriums of bibenzyl- d_4 , 171 kJ/mole, is compared with the activation energy ~ 256 kJ/mole for scission of the central C-C bond. The activation energy for exchange of the CD_2 deuterium of diphenylmethane- d_2 is even lower, 134 kJ/mole. Diphenylmethane is stable toward C-C scission under the conditions.

It has been known for some time that coal heated in the presence of a donor solvent undergoes some 60-80% conversion on short contact time with very little consumption of H from the solvent. The solubility of coal is also increased by merely heating it for a very short time. The

changes have been ascribed to hydrogen shuttling^{6,7} within the coal itself. We were interested to know if we could study some of the aspects of hydrogen shuttling in the absence of a hydrogen donor solvent, but with a solvent that could easily undergo hydrogen exchange and was otherwise stable. Diphenylmethane seemed to meet the immediate requirements. Although the objectives of the earlier experiments were primarily aimed at observing the distribution of deuterium in coal extracts after heating the coal with diphenylmethane- d_2 , the principle was applied as well to determining the degree of exchange in pure compounds.

We observed⁴ that exchange of the aromatic hydrogens of alkyl-substituted benzenes occurred very slowly, if at all. However, exchange of naphthalene hydrogens was perceptible, 1.8% in two h at 400°C, and phenanthrene and anthracene exchanged more rapidly. It was noted also that in the presence of coal, H-D exchange was approximately ten times more rapid, and exchange could be observed in monocyclic aromatic systems.

Briefly, experimental conditions were as follows: The aromatic compound was mixed with enough diphenylmethane- d_2 so that the number of moles of exchangeable deuteriums in the $-CD_2-$ group equaled the number of moles of hydrogen on the aromatic molecules. The mixture was heated at 400°C in a stainless steel tube for the required length of time and then cooled. The contents were removed and separated so that the components could be analyzed by 1H NMR, 2H NMR, and GC-MS. Exchange data are presented in Table 2.4. These compounds were chosen to represent a variety of structural features. The list includes purely polynuclear aromatic hydrocarbons, phenols, and heterocyclic aromatics.

Three aspects of the data are immediately recognized: 1) Exchange rate is related to structure as in anthracene and phenanthrene; 2) exchange rate is related to stability as in naphthacene and α -phenanthrol; and 3) exchange appears to be positionally selective in some molecules such as phenanthridine and β -naphthol.

In general polynuclear aromatic hydrocarbons undergo hydrogen-deuterium exchange slowly. The

Table 2.4. Degree of hydrogen-deuterium exchange (%) of selected aromatic compounds with diphenylmethane- d_2 at 400°C

Compound	2 h	5 h
Acenaphthene	Unstable at 400°C	
Acenaphthalene	Unstable at 400°C	
Biphenyl	-	0
Diphenylether	-	0.4
1,2-Benzanthracene	3.92	13.9
Naphthacene	38.9 Decomposes	
Chrysene	0.93	2.20
Perylene	6.8	15.0
Triphenylene	2.02	3.2
Phenanthrene	0.12	1.56
Anthracene	10.06	16.91
Pyrene	1.20	5.40
Hexahydropyrene	6.03	18
β -Naphthol	9.0	12.8
9-Phenanthrol	21.1 Decomposes	22.75
β -Methylnaphthalene	5.34	7.73
Dibenzofuran	trace	trace
Dibenzothiophene	trace	trace
Carbazole	6.11	19.84
Phenanthridine	6.69	8.97

results with pyrene are of particular interest in view of the reports^{8,9} that pyrene is an efficient solvent for coal conversion. The implication is that pyrene functions as a good hydrogen transfer agent. The reaction pathways are not known in detail; however, hydrogen exchange through hydrogenation-dehydrogenation may well be involved. In our study, pyrene underwent exchange very slowly, only 1.2% in 2 h. We then observed that extensive exchange takes place, 30.7% in 2 h, when pyrene and diphenylmethane- d_2 are heated together in the presence of naphthacene, a compound which itself undergoes extensive decomposition and exchange under the experimental conditions. Because of this observation, we were curious to know if a pyrene-diphenylmethane- d_2 mixture would undergo rapid exchange when heated in the presence of a third component which

exchanges rapidly but is otherwise stable. The candidate for this experiment was phenol. Phenol itself⁴ undergoes exchange. When phenol, pyrene, and diphenylmethane-d₂ were heated for 2 h, the phenol was 14% exchanged but the pyrene was only 0.84% exchanged. Pyrene heated with bibenzyl-d₄ for 2 h at 400°C undergoes 2.9% exchange. The reisolated reaction mixture also contained small amounts of dihydropyrene and completely saturated pyrene. Bibenzyl slowly undergoes homolytic bond cleavage at a known rate¹⁰ under these conditions to produce free radicals. From this information above, it is tentatively proposed that pyrene functions as a hydrogen shuttling agent through reactions involving free radical intermediates.

Positional selectivity of H-D exchange was determined using ²H NMR at 47 kGauss for molecules for which spectral resolution permitted. The ²H NMR spectrum of 1,2-benzanthracene showed two strong peaks at $\delta = 9.13$ ppm and $\delta = 8.32$ ppm indicating exchange principally at H-9 and H-10. Smaller amounts of exchange were apparent in other positions as indicated by peaks at $\delta = 8.04$ ppm, 7.73 ppm, and 7.58 ppm. The almost complete absence of a peak at $\delta = 8.75$ ppm indicates that exchange is slowest at position H-1. Chrysene exchanges fastest at positions 1, 4, 5, 6. The 1-position of perylene exhibits faster exchange than the 2-position while almost no exchange occurs at the 3-position. Anthracene, as expected for previous work,⁴ exchanges most rapidly in the 9- and 10-positions whereas exchange in phenanthrene is nonselective. Hexahydropyrene and β -methylnaphthalene exhibit exchange primarily in the nonaromatic portion of the molecule. Of the two nitrogen-containing heterocyclics, phenanthridine displayed the most positional selectivity. Exchange was rapid in the 9-position and not observed in the other positions. Carbazole underwent exchange preferentially in the 2- or 3-position next to a lesser extent in the 1-position. β -Naphthol appeared to undergo exchange at the 1-, 2-, and 4-positions.

We have learned the following from the above experiments: 1) Hydrogen exchange in most pure hydroaromatic systems is slow; 2) Hydrogen exchange is positionally selective depending on

structure and is accelerated in certain positions by substituents; 3) Exchange is accelerated by compounds undergoing decomposition to form a coke-like residue; and 4) Exchange is accelerated by the presence of compounds which undergo fragmentation or decomposition reactions which are free radical in nature.

It appears that the reactions which give rise to hydrogen shuttling are initiated by free radicals formed by fragmentation when coal is heated; the higher the concentration of radicals, the more extensive are the exchange or H-shuttling reactions. It also appears that the kinds of reactions that lead to coke formation can also lead to more efficient hydrogen redistribution in coal.

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2.2.2 Assessment of Dihydroxybenzenes as Solvents for Coal Liquefaction

(B. M. Benjamin, M. S. Hendricks, J. W. Larsen)

We have been investigating the conversion of coals to soluble products by studying the thermal depolymerization and hydrogen redistribution which occurs when coals are heated with non-donor solvents. The first segment of this study using phenol as the solvent was reported by Larsen and Sams.^{1,2} Their criteria for phenol as a begin-

ning choice derives from several considerations. Phenols are polar compounds and interact strongly with coals. They are important components of steady-state recycle solvents in direct coal liquefaction processes and have been demonstrated to be beneficial to conversion yields.³⁻⁵ Phenols are cheap, readily available, and phenol itself can be prepared from benzoic acid. Thus it may be possible by using modifications of established chemical reactions to obtain phenolic compounds from aromatic acids derived from the oxidation of coals.

It was pointed out by Larsen that hydrogen donor solvents are not necessary for the conversion of coals to liquid products, or rather to pyridine-soluble materials. It is only necessary that the solvent participate in the reaction in such a way that hydrogen is redistributed from one part of the coal to another. Phenol was demonstrated to fulfill this requirement. It is particularly important to recognize from Larsen's work that a hydrogen-rich fraction could be obtained from coal in 60% yield without using hydrogen gas from an external source. In contrast, the liquid products from SRC-type processes are not as hydrogen-rich as the starting coal.

In view of the above observations we have conducted a set of experiments with the three isomeric dihydroxybenzenes to evaluate their effectiveness as coal conversion solvents and hydrogen shuttling agents. These experiments are in progress while parallel research is being conducted in the Chemical Technology Division on the oxidative decarboxylation of benzenepolycarboxylic acids to prepare polyhydroxybenzenes.

Initial reactions were done as a function of temperature. Experimental conditions were similar to those used by Larsen: One gram of coal was mixed with 10 g of solvent, either hydroquinone, resorcinol, or catechol, and the mixture was placed in a 19-ml tubing bomb. The sealed bomb was then heated while shaking in a fluidized sand bath at the predetermined temperature for 15 min. At the end of the heating period the bomb was cooled in a blast of air and then

quenched in cold water. The contents of the bomb were removed completely using tetrahydrofuran (THF) as a solvent. THF was removed on a rotary evaporator and soluble phenolic materials were extracted from the residue with hot water. The recovered coaly material was dried, weighed, and extracted with pyridine to determine the extent of conversion. Phenolic material was recovered from the water by continuous ether extraction. Finally the water was evaporated to recover soluble polymeric materials. Appropriate analytical work was done on all fractions. Results are recorded for Wyodak and Bruceton coals in Tables 2.5 and 2.6. The data are average results from duplicate runs. For comparison, in order to examine the stability of the three dihydroxybenzenes, they were thermolyzed alone under similar conditions. These data are presented in Table 2.7.

The initial scoping experiments were done as a function of temperature, second column in the Tables, in an effort to gain some perception of the best conditions for high conversion of coal to pyridine-solubles, low solvent incorporation into the coal-derived material, and efficient recovery of solvent. As can be seen in the third column, solvent incorporation was high (weights of water-insoluble material exceeding the 1 g of coal feed) in all cases except those conditions under which conversion was low as indicated by high pyridine-insoluble residues in column 4. Solvent recovery was generally poor and, in fact, all the solvent could not be accounted for. It is significant to realize that the dihydroxybenzenes, heated alone (Table 2.7), give small yields of polymeric water-insoluble materials.

The recovered solvents, that is, the ether extracts of the aqueous phases from the experiments with coal, were multicomponent mixtures. Only those mixtures derived from hydroquinone were examined in detail. Programmed GC analysis showed seven major peaks and numerous minor peaks for compounds in addition to the principle starting compound. The major compounds, with one exception, were identified using GC-MS, and their structures are shown:

Table 2.5. Conversion of Wyodak coal with dihydroxybenzenes

Feed is 1 g coal + 10 g solvent

Solvent	Temp.	Water-insoluble Pyridine-soluble Product	Pyridine- insoluble Residue	Recovered Water-soluble Product	Residue Recovered from Water
	(°C)	(g)	(g)	(g)	(g)
Hydroquinone	460	3.54	0.14	5.47	0.40
	441	2.06	0.32	6.92	0.15
	400	1.16	0.83	9.75	0.17
Resorcinol	460	6.03	0.61	3.11	0.04
	441	3.88	0.27	5.81	0.08
	400	2.98	0.96	7.65	0.08
Catechol	460	5.29	3.60	2.70	0.07
	441	2.07	0.70	8.56	0.13
	400	2.71	1.53	8.13	0.26

Table 2.6. Conversion of Bruceton coal with dihydroxybenzenes

Feed is 1 g coal + 10 g solvent

Solvent	Temp.	Water-insoluble Pyridine-soluble Product	Pyridine- insoluble Residue	Recovered Water-soluble Product	Residue Recovered from Water
	(°C)	(g)	(g)	(g)	(g)
Hydroquinone	460	2.50	0.18	7.25	0.20
	441	2.20	0.33	8.24	0.15
	400	1.82	0.55	8.95	0.53
Resorcinol	460	5.08	0.13	3.64	0.04
	441	6.17	0.27	4.56	0.06
	400	2.77	-	9.11	0.05
Catechol	460	4.54	2.18	4.69	0.04
	441	1.09	0.52	9.12	0.05
	400	1.86	0.38	8.42	0.06

Table 2.7. Effect of heating dihydroxybenzenes alone

Solvent	Temp. (°C)	Water Insoluble (g)	Pyridine Insoluble (g)	Recovered Solvent (g)	Residue Recovered from Water (g)
Hydroquinone	441	0.72	0.70	9.29	0.20
		-	-	9.86	0.13
Resorcinol	441	1.74	0.17	8.02	0.05
Catechol	441	0.37	0.006	9.51	0.01
		-	-	9.70	0.05

Phenol represents a degradation product while the remaining compounds are dimers derived from condensation and oxidation reactions. Attempts to isolate these condensation products for confirmation of their structures proved futile. Samples from fractional crystallization usually gave GC patterns resembling the original mixture. However, when these fractions were trimethylsilylated they usually showed only one principle peak and several smaller ones.

The phenomenon just described and further elaborated below, is a key to the chemistry of phenol dimers and it may be a key to the kind of chemistry applicable to releasing solvent-derived phenolic material incorporated in the coal-

derived products. These experiments are planned for future studies.

There is a paucity of information in the literature on the thermal reactions of dihydroxybenzenes, nothing for the temperature range in which we are interested here. At higher temperatures, 600-700°C^{6,7} decarbonylation of the compounds occurs as the major reaction and phenol is formed as a less important reaction. We do not expect decarbonylation to occur in the 400°C temperature range. Other reactions typical of phenols at ordinary temperature include oxidative coupling reactions.⁸ Those coupling reactions which form dimers, trimers, or higher molecular weight polymers can be initiated by oxygen and copper-amine catalysts or by single electron oxidizing agents such as potassium ferricyanide. Coupling reactions can also be initiated by stable free radicals. The products are carbon-oxygen coupled derivatives of aryloxy radicals. It was later shown⁹ that phenol dimers undergo similar reactions. The products consisted of higher polymers, trimers, and monomers. Mechanistic implications of these results led to the proposal that the reaction is a free-radical redistribution process or a disproportionation requiring a "quinol ether" intermediate. A similar disproportionation can be initiated thermally.¹⁰ The thermal process probably requires free radicals and may be responsible for the confusing GC results mentioned earlier.

The kind of chemistry described above is believed to take place when coal and the polyphenols are heated together, resulting in incorporation of the polyphenols into the coal products. The possibility that the thermal disproportionation reaction can be used to recover part of the incorporated phenolic solvent is the subject of subsequent research.

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2.2.3 Investigation of Solvent Losses during the Kerr-McGee Critical Solvent Deashing Process

(B. M. Benjamin)

One of the technical road blocks encountered in the development of direct coal liquefaction processes has been the separation of solid mineral matter and unconverted coal from the liquids. Because of the physical properties of the process stream, traditional rotary filtration and leaf filtration gave poor and uneconomical results. A newer technology, the Kerr-McGee Critical Solvent Deashing (CSD) process, has been successfully tested and is considered for design into a Solvent Refined Coal demonstration plant. Experience with the Critical Solvent Deashing process at the Wilsonville pilot plant has not demonstrated good solvent balance. It is important to find the source of solvent losses before final design decisions can be made. Possible sources

of solvent loss include not only mechanical losses through evaporation and leaks in valves and joints but also occlusion in, and reaction with, the product.

The objective of our project was to determine the degree to which Kerr-McGee solvents react with the coal-derived products under the conditions of the CSD process. The procedure makes use of carbon-14-labeling and isotope-dilution techniques.

Two Kerr-McGee proprietary solvents were used. These solvents will be referred to as A and B. Each solvent was synthesized from carbon-14-labeled precursors and, after preparation and distillation, their purities were confirmed by gas chromatography and their radioactivity content was determined. The coal-derived feed material was obtained from the Wilsonville Pilot Plant and was designated as follows: Kerr-McGee CSD Feed; Date: 03-31-80; Time: 1300; Run: 204-C-MB; Sample No.: 55254.

In a typical experiment, a weighed amount of radioactive solvent and Kerr-McGee feed were placed in a stainless steel tube bomb. Air was displaced by dry nitrogen and the bomb was closed. It was heated for a specified time at a specified temperature, while shaking, in a fluidized sand bath. All temperatures, residence times and ratios were previously agreed upon by Kerr-McGee, EPRI, and ICRC. The tube bomb was removed from the heat source, cooled first in a brisk stream of air and then by quenching in water. Before opening the tube, pressure was relieved by venting the gases into an aluminized bag. No gas was observed in any of the reactions. The liquid contents of the tube were washed into a millipore filter apparatus with methylene chloride and solid materials were removed from the tube by scraping the walls with a Teflon spatula while washing these materials into the filter apparatus with methylene chloride. Insoluble material was collected on a 5 micron filter element under nitrogen pressure and was washed thoroughly with methylene chloride. The filter cake was exhaustively extracted with methylene chloride to obtain a dark solution. The solids recovered in the three fractions were

dried in a vacuum at 65°C and assayed for their radioactivity content. Each fraction was then equilibrated with the appropriate nonradioactive solvent, recovered, dried, and assayed again. The quantitative determination of the amounts of solvents recovered unchanged was made by isotope-dilution techniques. The radioassays were performed on solid derivatives prepared from the solvents. The usefulness of these solvent balances is, however, marginal because of the difficulty in handling volatile solvents, weighing them into heavy tube bombs, and other problems such as evaporation during experimental manipulations.

Under the conditions of these experiments it was determined that only 0.04% of solvent A was permanently bound by chemical reactions to the coal-derived products. Absorption was less than 0.5%. The chemical retention of solvent B was approximately 0.05% of the starting solvent, but absorption was between 4% and 6%. Therefore, it was concluded that solvent loss because of chemically bound material was low and well within the process design value. However, attention will need to be paid to complete recovery of tenaciously absorbed solvent by steam stripping or other means.

2.2.4 Carbon-14 Tracer Study of the Fate of Tetralin under Simulated SRC-I Liquefaction Conditions

(M. L. Poutsma, E. L. Youngblood,¹ G. E. Oswald,¹ and H. D. Cochran¹)

In hydroliquefaction processes for coal, the process solvent plays a key chemical role of hydrogen donation to the degrading coal. To achieve closed-loop operation, its hydrogen content must be restored from molecular hydrogen at some later point in the process. It is generally considered that the interconversions between polycyclic aromatic hydrocarbons and their partially hydrogenated derivatives are the major chemical reaction involved. Model compound studies in several laboratories have used tetralin as a representative hydroaromatic hydrogen

donor.² Indeed, under conditions where coal model compounds are decomposed in tetralin, it serves as a hydrogen donor and is converted largely to naphthalene. However, several side reactions have been uncovered in model studies such as ring contraction to form 1-methylindane, ring opening to form *n*-butylbenzene, alkylation to form methylnaphthalenes, and probably grafting to larger coal-derived species.² The free-radical chemistry underlying these reactions is beginning to be understood. From a process viewpoint, these side reactions convert the hydrogen donor to a form which cannot be regenerated by hydrogenation and hence degrade solvent quality. The present experiment was designed to quantify the importance of such side reactions, for the example of tetralin, under realistically simulated liquefaction conditions.

A slurry of 28.4% of Illinois #6 coal in a typical recycle solvent from the Wilsonville pilot plant was doped with a low level (0.83%) of 1-¹⁴C-tetralin of high specific radioactivity. It was processed in the Coal Liquids Flow System in the Chemical Technology Division under simulated SRC-I conditions: 454°C dissolver outlet temperature; 0.92 kg m⁻³ s⁻¹ slurry space rate; and 1.6 × 10⁻⁴ std m³ s⁻¹ H₂ feed rate at 13.9 MPa pressure. The total reactor effluent was separated by a variety of solvent fractionation, distillation, and glpc techniques, and radioassays were performed to determine the fate of the labeled tetralin. Under the conditions chosen, one-half of the tetralin fed was consumed. Hence most of the hydrogen consumed was supplied by the recycle solvent and/or H₂ as desired while tetralin served both as a chemical and radiotracer of hydroaromatic behavior. Of the tetralin consumed, only 85% proceeded to naphthalene while 15% entered into side reactions. Approximately one-third of this "diverted" tetralin gave identifiable C₉-C₁₁ products while two-thirds became chemically grafted to much larger molecules derived from coal or the recycle solvent. The specific radioactivities of the oils, the asphaltenes, the preasphaltenes, and the insoluble organic matter were remarkably similar. Hence these grafting reactions of

tetralyl fragments to heavy products are not limited to certain specific functional groups in coal but rather occur quite indiscriminantly.

These results specifically document the importance of side reactions for the example of tetralin and demonstrate the power of ^{14}C isotopic tracer techniques to probe chemical questions underlying coal conversion processes under realistic conditions.

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2.2.5 Indirect Liquefaction Chemistry

(R. A. Strehlow, E. C. Douglas)

The selectivity of the Fischer-Tropsch synthesis is determined by the relative rates of chain lengthening reactions and of reactions which terminate chain growth. Chain lengthening reactions are now generally believed to proceed through adsorption, dissociation, and reduction of carbon monoxide to a methylidene group ($=\text{CH}_2$) on the catalyst surface. The methylidene group is then incorporated into a growing hydrocarbon chain which may desorb as an olefin or be reduced by hydrogen to a paraffin. Because carbon monoxide dissociation and reduction appears to dominate the overall course of the Fischer-Tropsch synthesis, studies of the reactions of intermediates which relate to selectivity have been sparse. The present work reports the occurrence of olefin chain lengthening (homologation) on an iron catalyst and discusses possible application to studies of selectivity in the Fischer-Tropsch synthesis.

Added olefins have been frequently used in studies of the course of the Fischer-Tropsch synthesis.¹ Generally, the results of these studies have been to add support for mechanistic descriptions of the synthesis which involve carbidic rather than oxygenated surface intermedi-

ates. More direct support for the involvement of the methylidene group was provided by the work of Brady and Pettit,² who used diazomethane as a source of methylidene groups in a study of product distribution and in a study with isotopically enriched carbon monoxide. However, the route by which insertion of methylidene or other surface bonded groups into growing chains occurs is not yet established. Table 2.8 lists some of the reactions associated with olefins as related to the Fischer-Tropsch synthesis.

Olefins have been reported as homologating to higher olefins in the presence of nickel,³ and paraffins through assumed olefin intermediates have been reported to homologate on tungsten films.⁴ We have found no report in the literature of this reaction being catalyzed by iron. An example, however, has been found of pentane producing benzene on Rh and Rh-Cu alloy films,⁵ which process indicates the occurrence of homologation followed by dehydrocyclization. In the course of this work, we have observed similar reactions of olefins on iron.

In the descriptive chemistry of some coordination complexes and mononuclear compounds of silicon, homologation reactions are commonly reported. Although it is not certain that the chemistry of complex compounds or cluster compounds have a significant relationship to the heterogeneously catalyzed Fischer-Tropsch reaction occurring on a surface, the case for the validity of the analogy has been strongly made.⁶ Methylidene insertion has been reported into coordination complexes of nickel, platinum, tungsten, and tantalum,⁷ as well as into Si-H and Si-R bonds of silanes.⁸ Two reports have been found of homologation by methylidene insertion in iron complexes.⁹ Supported iron clusters have been reported as active Fischer-Tropsch catalysts.¹⁰ The fact that similar insertion reactions occur on solid iron catalysts, clustered iron catalysts, and coordination complexes including iron and other metals provides evidence that a common mechanism for insertion may exist.

In this work we used a plug flow reactor containing a commercially available iron oxide

Table 2.8. Summary of olefin reactions possibly associated with the Fischer-Tropsch synthesis^{a,b}

Name of Reaction	Equation
I. Hydrogenation	$C_nH_{2n} + H_2 \rightarrow C_nH_{2n+2}$
II. Chain initiation and growth	
(i) Activated Adsorption	$C_nH_{2n} + * \rightarrow * - C_nH_{2n-1} + [H]_s$
(ii) Methylidene Insertion	$* - C_nH_{2n-1} + [CH_2]_s \rightarrow * - C_{n+1}H_{2n+1}$
(iii) Alkylidene Insertion	$* - C_nH_{2n-1} + [CHR]_s \rightarrow * - C_{n+1}H_{2n+1}R$
III. Incorporation in a growing chain	$* - C_mH_{2m-1} + C_nH_{2n} \rightarrow * - C_{m+n}H_{2m+2n-1}$
IV. Homologation	$C_nH_{2n} \rightarrow C_mH_{2m}; \text{ where } m > n \text{ (c)}$

^a[]_s = surface group.

^A = specific surface site, one or more atoms.

^bWe assume that a growing chain in the Fischer-Tropsch reaction has the character of a sorbed species, II(i)

^cThe source of the additional carbon atoms and other products are not indicated.

catalyst. The apparatus was designed to permit analyses to be made of products using an on-line mass spectrometer. After catalyst reduction with hydrogen, various olefins were injected into the hydrogen stream and allowed to flow through the reactor. Hydrogenation of the injected olefins competed with homologation to form higher olefins. The higher molecular weight olefins were themselves reduced to paraffins in each injection. From 1-butene, as an example, we obtained butane and the homologated products pentane, hexane, and octane. The extent of homologation relative to hydrogenation varied with the hydrogen partial pressure (which determined the hydrogen/butane ratio), space velocity, and temperature. Figure 2.11 shows the homologation of 1-butene to pentene as a function of space velocity at two temperatures. The homologation is measured as the ratio of pentane to butane formed in the competing reactions. The increase of homologation with space velocity implies the existence of a mass transfer effect resulting in an enhanced hydrogen-olefin ratio in the catalyst pores. We take these results to mean that homologation occurs at a rate comparable to that of hydrogenation and perhaps higher. The tempera-

Fig. 2.11. Yield of pentene from butene-1 as a function of space velocity at 200°C and 300°C.

ture variation of homologation is shown in Fig. 2.12 and indicated an apparent energy of activation about 10 kcal/mole (40 kJ/mole) greater than that for hydrogenation.

The occurrence of homologation by more than one carbon atom is indicated by experiments in which the amount of two-carbon-atom chain lengthening is compared to chain lengthening by one carbon atom for different isomers of butene. Table 2.9 shows the yield of butene homologated

Fig. 2.12. Temperature variation of homologation of butene to pentene.

with one carbon atom for three isomers and the yield of homologated product showing two carbon atom addition. In both cases the product was reduced to the paraffin and detected as such.

The single carbon atom addition does vary with the state of catalyst carburization, but we believe the differences shown to be representative of reactivity differences between the isomers. Since the single homologation occurs in competition with hydrogenation, the relative yields of single homologation would reflect the differences in intermediate reactivity for homologation if the intermediate were common to hydrogenation as well as homologation. The doubly homologated species as a fraction of the singly homologated product, shown in the final column of Table 2.9, shows that for *trans*-2-butene a larger relative amount of two-carbon-atom chain lengthening occurs than for the other

two isomers. This result indicates that *trans*-2-butene can homologate with the addition of a two carbon atom group.

Although no other data has been found bearing on the intermediates of the heterogeneously catalyzed homologation, we may turn to some of the speculations advanced for coordination compounds. Summer^{9b} postulates a di-iron five-membered ring in an ethylene insertion reaction into a methylidene-iron bond, which then rearranges with hydrogen transfer and elimination. McLain, Sancho, and Schrock^{7c} speculate based on their work with tantalum complexes that alkylidene ligands can form from olefins with incidental formation of homologated olefin. With ethylene, for example,

Although it is premature to relate the homologation reaction to the course of the Fischer-Tropsch synthesis, the similarities of the reaction are striking. It is not implausible that we are examining aspects of a reaction which shares common intermediates with the Fischer-Tropsch synthesis.

Hughes and others in their work on supported iron clusters^{10c} have proposed a metallo-cyclobutane intermediate for the Fischer-Tropsch synthesis. This type of intermediate could undergo the reactions involving rearrangement, hydrogen-

Table 2.9. Homologation of C₄ olefins over an iron catalyst

GHSV = 340 hr⁻¹; 300°C; H₂ at 35 psia (0.25 MPa); olefin/H₂ ≥ 1/2

Injected Compound	Ratio C ₅ H ₁₂ /C ₄ H ₁₀ (one carbon atom lengthening)	Ratio C ₆ H ₁₄ /C ₅ H ₁₂ (two carbon atom lengthening)
Isobutylene	0.025	0.078
1-Butene	0.014	0.057
Trans-2-butene	0.0069	0.13

ation, or decomposition. The relative rates of these reactions would determine the product selectivity. Studies using the homologation reaction reported here offer the possibility of determining with greater precision the chemical behavior of the proposed intermediates.

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2.3 Molten Salt Catalysis

2.3.1 Properties of Catalysts: Raman Spectra of $\text{SbCl}_3\text{-AlCl}_3$ Melts

(G. P. Smith, G. M. Begun, R. Huglen,^{1a,b}
G. Mamantov^{1b})

Liquid mixtures of SbCl_3 and AlCl_3 are solvents with unusual and useful properties.^{2,3} They are, for example, isomerization catalysts⁴ and they react with polycyclic arenes to form stable solutions of arenium ions.⁵ A mechanistic understanding of these properties requires information

on the molecular structure of the mixtures. In the present investigation Raman spectroscopy was used to clarify some important features of this structure although a complete structure determination was not achieved.

The pure components, SbCl_3 and AlCl_3 , melt to form molecular liquids. Liquid AlCl_3 consists of dimers (Al_2Cl_6) in which each Al is surrounded by a tetrahedron of Cl and the two tetrahedra share an edge.³ Neutron and x-ray diffraction data⁶ of liquid SbCl_3 at 80°C have been interpreted in terms of trigonal pyramidal monomers that are joined into chains with their dipoles pointing in the same direction along the chain axis.⁶

Liquid mixtures of Al_2Cl_6 and SbCl_3 show large negative deviations from volumetric additivity and from Raoult's law,⁷ indicative of intermolecular interaction. This interaction, however, does not lead to solid state compound formation,^{7,8} in contrast to the corresponding bromide system which forms a 1:1 compound that melts congruently.⁸

Aluminum chloride is a much stronger Cl^- acceptor than SbCl_3 , and it is often supposed² that in SbCl_3 -rich melts of these two chlorides the following reaction goes to completion

According to this model the Lewis acidity and, hence, most of the chemical reactivity of $\text{SbCl}_3\text{-AlCl}_3$ melts is due to SbCl_2^+ while AlCl_4^- is only a spectator ion. There is, however, no direct evidence that the species SbCl_2^+ and AlCl_4^- are formed in this case. On the contrary, the Raman spectrum⁹ of the equimolar $\text{SbCl}_3\text{-AlCl}_3$ melt does not contain the strong 186-cm^{-1} band of AlCl_4^- . This spectrum was interpreted as indicating either monomeric AlCl_3 or nearly planar SbCl_3 .

We have obtained Raman spectra for nine molten mixtures of SbCl_3 and AlCl_3 , as well as for the pure components. Also three molten mixtures of $\text{AlCl}_3\text{-NaCl-SbCl}_3$ were studied. Molten AlCl_3 contains molecular Al_2Cl_6 (D_{2h}) while molten SbCl_3 contains pyramidal (C_{3v}) molecules aligned head-to-tail. The Raman spectra showed the presence of Al_2Cl_6 molecules in molten $\text{SbCl}_3\text{-AlCl}_3$ mixtures containing 40 mol % or more AlCl_3 but

gave no evidence for the formation of SbCl_2^+ and AlCl_4^- . However, SbCl_3 is structurally modified by the addition of AlCl_3 as seen from the shift of the highest Sb-Cl stretching frequency. There is also spectral evidence that points to the formation of polymers that are different from those in pure SbCl_3 , and it cannot be ruled out that there may be a chloride deficient antimony species in the AlCl_3 -rich mixtures. The molecular nature of the observed modifications in these mixtures cannot be deduced solely on the basis of the recorded spectra.

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2.3.2 Properties of Catalysts: Vibrational Dynamics of Glassy and Molten ZnCl_2

(F. Aliotta,¹ G. Maisano,¹ P. Migliardo,¹ C. Vasi,¹ F. Wanderlingh,¹ G. P. Smith, and R. Triolo)

Zinc chloride has been intensively investigated as a liquid hydrocracking catalyst for the direct conversion of coal into reforming stock and high octane gasoline.² This molten halide has unusual physical and chemical properties that have been

the subject of wide ranging research in recent years.³ These unusual properties relate either directly or indirectly to its applications as a catalyst.

The present research was concerned with the very high viscosity of ZnCl_2 nears its melting point and the ease with which it can be super-cooled and glassified ($T_g = 375$ K). These properties have been rationalized by means of several, rather different, models, but direct evidence regarding structural relaxation processes has been wanting. This prompted us to undertake a refined Raman study of this substance in the molten and glassy states with particular emphasis on the low-frequency spectrum.

Polarized Raman spectra were obtained on the liquid phase near the melting point at 598 K and on the glassy phase at 293 K. Measurements were made to within 2 cm^{-1} of the exciting line. The results were accounted for in terms of a vibrational density of states that become Raman active through breaking the Raman-active momentum conservation rule.⁴

We found that the anisotropic reduced Raman spectrum in the $180\text{--}400\text{ cm}^{-1}$ region shows sharp features associated with a localization of modes that result from a decoupling of tetrahedral units from the remaining network in both the liquid and glassy phases. At very low frequencies ($2\text{--}180\text{ cm}^{-1}$) the collision-induced light scattering in both liquid and glassy phases gave rise to a central Lorentzian component in the spectrum that came from a structural relaxation process.

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2.3.3 Substrate-Catalyst Reactions: Hydride Abstraction from 9,10-Dihydroanthracene and 5,12-Dihydronaphthacene in $\text{SbCl}_3\text{-AlCl}_3$ Melts

(A. C. Buchanan, III, A. S. Dworkin, G. P. Smith)

We have recently reported several novel hydrogen transfer reactions in molten antimony trichloride.^{1,2} For example, anthracene in high-purity molten antimony trichloride undergoes a spontaneous catalytic disproportionation at temperatures as low as 100°C.¹ Some of the anthracene molecules are condensed to larger aromatics liberating hydrogen which is quantitatively captured by unreacted anthracene molecules to form hydroanthracenes. When 9,10-dihydroanthracene (DHA) is dissolved under the same conditions, it disproportionates to anthracene and 1,2,3,4-tetrahydroanthracene (THA). If the Lewis acidity and oxidizing power of the SbCl_3 solvent are increased by the addition of 10 mol % AlCl_3 , the dissolution of anthracene in this melt results instead in the prompt formation of stable solutions of the anthracenium ion (1) in 55-65% yields.² The proton source for this reaction is the condensation-dehydrogenation of a portion of the anthracene combined with a stoichiometric reduction of SbCl_3 .

We now report that DHA dissolved in high purity, aprotic molten SbCl_3 -10 mol % AlCl_3 at temperatures from 100-130°C also results in the prompt formation of 1. In this case, 1 is generated by a formal hydride abstraction from some of the molecules of DHA while the hydrogen abstracted is transferred to unreacted molecules of DHA to form a mixture of THA, 1,2,3,4,5,6,7,8-octahydroanthracene (OHA) and other hydroanthracenes and/or hydroarenes. The role of the Sb^{3+} as an oxidant is again evident in the recovery of stoichiometric amounts of Sb metal in the product mixtures. We have also found a similar reaction to occur for 5,12-dihydronaphthacene (DHN) producing the corresponding naphthacenium ion. The organic reaction products were identified by ^1H NMR, GC, GC-MS, and HPLC techniques and the Sb by atomic absorption spectrometry.

A simplified hydride abstraction-hydrogenation reaction in $\text{SbCl}_3\text{-AlCl}_3$ is shown in Equation (1)

for DHA in terms of one of its hydrogenation products, THA. Of course, the actual yield of 1 depends on the proportion of the various hydrogenated products formed varying from 67% as written above to 86% if we had written a simplified equation in terms of OHA. Our finding of $75 \pm 5\%$ yield of 1 is then consistent with our finding that the main hydrogenated products are a mixture of THA and OHA. However, the number of moles of Sb^0 produced should always be one-third that of the arenium ion generated, and that is what we find within experimental error.

The hydride abstraction reaction reported in this work does not occur in neat SbCl_3 where instead a catalytic disproportionation takes place. We had previously obtained substantial evidence that the effect of added AlCl_3 is to enhance the oxidizing power of the Sb^{3+}/Sb couple in molten SbCl_3 .² The evidence includes the observation of arene radical cations by ESR.³ Clearly these findings plus the isolation of stoichiometric quantities of Sb metal indicate that a redox process has taken place in this hydride abstraction reaction. Although we have no direct evidence,⁴ radical cations may be important intermediates for the net hydrogen transfer between arenes in this reaction.

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2.3.4 Reactive Intermediates in Catalysts: Spectroelectrochemical Study of the Formation of the Radical Cation and Dication of Perylene in Molten Antimony(III) Chloride

(G. P. Smith, M. Sørli,¹ E. Norvell,¹
G. Mamantov,¹ L. N. Klatt²

As part of a study of arene cations in molten SbCl_3 we have developed an electrochemical cell in which potentiometric, coulometric, and spectrometric methods may be used in concert to generate and characterize species formed by arene oxidation. This section describes the application of this cell to a clarification of the species formed by the oxidation of perylene (PeH) and its radical cation.

We have found that in molten SbCl_3 containing 0.038 *m* CsCl at 100°C, PeH is oxidized at 0.26 V relative to the SbCl_3/Sb , saturated CsCl reference electrode to form a stable solution of the radical cation $\text{PeH}^{+\cdot}$. The optical absorption spectrum (500-900 nm) of this cation has five maxima with the most intense at 545 nm ($\epsilon = 4.2 \times 10^4$). In molten SbCl_3 containing 0.079 *m* AlCl_3 at 100°C, PeH is spontaneously oxidized to $\text{PeH}^{+\cdot}$ by reduction of SbCl_3 . In this melt electrochemical oxidation of $\text{PeH}^{+\cdot}$ to form a stable solution of the dication PeH^{2+} at 135°C occurs at 0.97 V relative to the SbCl_3/Sb , saturated CsCl reference electrode. The optical absorption spectrum (400-800 nm) of PeH^{2+} consists of two overlapping bands with a peak at 533 nm ($\epsilon = 3.7 \times 10^4$).

The neutral perylene molecule is stable in the basic melt, SbCl_3 - CsCl , and the oxidation wave is due to the formation of the perylene radical cation $\text{PeH}^{+\cdot}$, thus:

In the acidic melt, SbCl_3 - AlCl_3 , perylene is chemically oxidized to form a stable solution of $\text{PeH}^{+\cdot}$ in the following way:

For this system the oxidation wave represents the oxidation of $\text{PeH}^{+\cdot}$ to the perylene dication PeH^{2+} thus:

According to prior investigations^{3,4,5} perylene is chemically oxidized in acidic melts by the reaction given in Eq. (2). Accordingly, when we prepared a melt containing 6.39×10^{-5} *m* perylene and 0.77 *m* AlCl_3 in SbCl_3 , the absorption spectrum (before electrolysis) was that of $\text{PeH}^{+\cdot}$. When this solution was electrochemically oxidized until absorption due to $\text{PeH}^{+\cdot}$ was gone, we obtained the spectrum of a quite stable species that is different from that which Bauer and coworkers⁶ reported for the dication formed by electrolysis of $\text{PeH}^{+\cdot}$ in SbCl_3 - AlCl_3 , but it is quite similar to that previously reported for PeH^{2+} in superacid media^{7,8} where its identity was established by proton-NMR spectroscopy.⁷ We believe that Bauer and coworkers did prepare PeH^{2+} because the $E_{1/2}$ value they found agrees with ours, but this dication must have subsequently reacted, possibly with impurities, prior to the time the spectrum was measured. It is interesting that the spectrum they reported as being that of PeH^{2+} is, in fact, rather like that of a different perylene cation, protonated perylene PeH_2^+ , but this may be a coincidence.

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2.3.5 Melt-catalyzed Reactions: Low Temperature Hydrogen Transfer and Cracking Catalysis in Molten $\text{SbCl}_3\text{-AlCl}_3$

(A. C. Buchanan, III, A. S. Dworkin, G. P. Smith)

We have examined the reaction behavior of naphthalene from 100-130°C in an acidic melt containing 90 mol % SbCl_3 and 10 mol % AlCl_3 by *in situ* ^1H NMR spectroscopy and by conventional quench and work-up procedures. At 100°C, NMR of a 4 mol % solution of naphthalene in $\text{SbCl}_3\text{-AlCl}_3$ showed that very little reaction had taken place over a period of 30 min. However, at 130°C naphthalene reacted very rapidly, and many overlapping resonances were observed in the aliphatic proton region from about 1.5 to 5 ppm. The aliphatic to aromatic proton ratio increased rapidly to a value of about 0.65 after 45 min. The *in situ* NMR results indicated the extensive formation of hydrogenated products.

Analysis of the organic products by capillary column GC demonstrated that at least 130 compounds had been formed. We found by GC-MS that naphthalene had been hydrogenated and isomerized in the melt to form methylindane, methylindene, and 1,2,3,4-tetrahydronaphthalene (tetralin).

The hydrogen used in the formation of these products was generated from the coupling of a portion of the naphthalene to form condensed aromatics such as binaphthalenes, benzofluoranthenes, and perylene. Furthermore, many of the

condensed products not only underwent similar catalytic hydrogenation and isomerization, but they were also severely cracked in this medium. The cracking ability of the catalyst was evidenced by the presence of compounds such as phenanthrene, phenylnaphthalene, acenaphthene, and methylnaphthalenes in the reaction mixture.

We also find that phenanthrene undergoes a reaction similar to that of naphthalene in an $\text{SbCl}_3\text{-AlCl}_3$ melt with the NMR showing extensive hydrogen redistribution reactions taking place. However, due to the complexity involved in analyzing the products from the naphthalene reactions, the phenanthrene product mixtures were not analyzed further.

The unusual feature of this reaction is the internal hydrocracking of many of the initially formed condensed arenes under extremely mild conditions (130°C) and no added H_2 gas. A few examples of these products were indicated above. There are also several major products with molecular weights of 256 and 258 identified by GC-MS. These products decay with increased reaction time (in favor of the cracked products) and appear to be the precursors for the hydrocracked products. These compounds probably represent partially hydrogenated binaphthalenes, benzofluoranthenes, etc., consistent with the ^1H NMR data. Some of the initial steps in one possible hydrocracking pathway for benz[j]fluoranthene are shown below, and are based on the

hydrocracking scheme proposed for fluoranthene in molten ZnCl_2 . Of course there are many possible hydrocracking routes for each of the condensed products initially formed, and this leads to the extremely complicated product mixture found. The source of hydrogen to form these hydrocracked products is again generated internally by the condensation and further polycondensation of some of the naphthalene.

We have found that molten $\text{SbCl}_3\text{-AlCl}_3$ provides an extremely active hydrocracking catalyst. The presence of AlCl_3 is necessary for the naphthalene reaction to occur, because naphthalene does not react in pure SbCl_3 in the temperature range of 80-175°C. The role of added AlCl_3 is to increase the catalytic activity of the melt by increasing the oxidizing power of the SbCl_3 . The addition of AlCl_3 also increases the Lewis acidity of the melt to a level necessary for isomerization and cracking reactions to occur under the low-temperature reaction conditions.

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2.3.6 Melt-catalyzed Reactions: Selective Hydrogenation of Anthracene and Naphthacene by Tetralin in Molten Antimony Trichloride

(A. C. Buchanan, III, A. S. Dworkin, G. P. Smith)

Tetralin is often used as a hydrogen donor solvent for thermally generated neutral radicals in coal liquefaction and model compound studies. In the present work, we investigate the possibility that tetralin may act as a hydrogen donor to some PAH's (polycyclic aromatic hydrocarbons) under extremely mild (80°C, no H_2) molten salt catalytic conditions in which PAH radical cations are believed to be present as reactive intermediates.

We have studied the reaction behavior of phenanthrene, pyrene, anthracene, and naphthacene (tetracene) with tetralin at 80°C in neat aprotic SbCl_3 by *in situ* ^1H NMR, and by determining the reaction stoichiometry via product analysis following quench and separation procedures.

Tetralin itself is unreactive in SbCl_3 (80-130°C), and anthracene also does not show any reaction in SbCl_3 at 80°C for a 30-min reaction period. At longer reaction periods, anthracene slowly undergoes Scholl condensation reactions.¹ This Scholl reaction is believed to proceed through the anthracene radical cation. In the presence of tetralin, however, anthracene does not undergo Scholl condensation but instead is rapidly hydrogenated by tetralin. GC analysis of the organic products from a reaction of equimolar anthracene and tetralin in SbCl_3 at 80°C for 30 min shows that 9,10-dihydroanthracene (DHA) is formed in 30% yield based on original anthracene. The DHA yield increases to 49% for a 165-min period. GC-MS shows that no other hydroanthracenes are produced; therefore, the transfer hydrogenation is selective. Surprisingly, the dehydrogenated tetralin does not yield naphthalene as expected, but, instead, two main products incorporating the tetralyl moiety are observed by GC-MS. One product (mass = 262) was collected by GC and identified by MS and ^1H and ^{13}C NMR as 1,2,3,4,5',6',7',8'-octahydro-1,2'-binaphthalene (1). The other product (mass = 308) was separated by HPLC and identified by MS and ^1H NMR as 2-(1,2,3,4-tetrahydro-1-naphthyl)anthracene (2).

Although the types of products do not change, the relative amounts of DHA, 1, and 2 formed depend on the concentration of tetralin initially present as shown for a 30-min reaction period in Table 2.10. Anthracene conversions range from 36% for an initial tetralin/anthracene mole ratio of 0.5 to 46% for an initial ratio of 4.0. The mole ratio of 1/2 varies dramatically as a function of initial tetralin concentration (Table 2.10) and increases with increasing concentration of tetralin. The overall reaction stoichiometry at any given tetralin/anthracene ratio can be represented as the sum of two limiting

Table 2.10. Influence of tetralin concentration on the anthracene-tetralin-SbCl₃ reaction^a

Anthracene (mmol)	Tetralin (mmol)	SbCl ₃ (mmol)	DHA Yield ^b (%)	1/2 ^c Mole Ratio
1.40	0	34.2	--	--
1.40	0.70	34.2	20	0.15
1.40	1.40	34.2	30	0.50
1.40	2.80	34.2	39	1.5
1.40	5.60	34.2	38	3.5
0.39	37.8	9.52	--	--

^aReactions were run at 80° for 30 min.

^bBased on original anthracene (±2%).

^cBased on GC area ratios.

equations. Reaction 1 predominates at high tetralin/anthracene ratios while reaction 2 predominates at low tetralin/anthracene ratios.

Products have also been identified from a naphthalene reaction performed at 80°C for 30 min with a tetralin/naphthalene mole ratio of 2 and the same molar concentration of naphthalene as was used in the anthracene experiments. The initial tetralin/naphthalene ratio chosen is the stoichiometry that maximizes the DHA yield in the anthracene reaction with tetralin (Table 2.10). Naphthalene is found to be much more reactive than anthracene, and GC and HPLC-UV analyses show a 97% conversion of the naphthalene. GC-MS analysis reveals that the transfer hydrogenation is again very selective with 5,12-dihydronaphthalene (DHN) the only hydronaphthalene detected.

Quantitative results from GC and HPLC-UV show that DHN is produced in $51 \pm 2\%$ yield based on initial naphthalene. The GC-MS results again show that no naphthalene is formed and that essentially all of the remainder of the organics can be accounted for by three compounds which incorporate the tetralyl moiety. These compounds include 1 and two isomers of a tetrahydronaphthyl-substituted naphthalene (3) (mass = 358). The mole ratio of 1/3 is about 0.12 rather than the 1.5 observed for 1/2 in the analogous anthracene reaction (Table 2.10). The reaction stoichiometry is therefore principally represented by eq. (3) even in the presence of excess tetralin.

Although anthracene and naphthalene are hydrogenated by tetralin in SbCl₃, phenanthrene and pyrene are unreactive. From a previous ESR study² we know that phenanthrene and pyrene are not oxidized by SbCl₃ to radical cations, whereas

the more easily oxidized PAH's, anthracene, and naphthalene, do form radical cations in SbCl_3 . These results, along with our previous observations of redox driven reactions in SbCl_3 in which Sb^{3+} acts as an oxidant,^{1,3,4} suggest that the unusual low-temperature hydrogenation reactions reported here proceed via reaction of the PAH radical cation with tetralin.

Space does not allow a detailed discussion of the mechanism of these transfer hydrogenation reactions. Briefly, these reactions can best be explained by a redox-initiated ionic mechanism involving the PAH radical cation and the 1-tetralyl (1,2,3,4-tetrahydro-1-naphthalenyl) cation as key intermediates. Two key steps in the reaction mechanism are the oxidation of the PAH to its radical cation by Sb^{3+} and the transfer of hydride from tetralin to the PAH radical cation. The resulting tetralyl cation then undergoes electrophilic aromatic substitution on unreacted tetralin and PAH molecules.

Our studies of the chemistry of model compounds for some of the structural units in coal in SbCl_3 melts have shown that SbCl_3 is a very active catalyst for transferring hydrogen from one molecule to another even at low temperatures and without added hydrogen gas. This ability to catalyze hydrogen shuttling could play an important role in the liquefaction of coal in molten SbCl_3 , especially in the presence of hydrogen donor solvents and at temperatures below those required for coal pyrolysis.

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2.4 Heterogeneous Catalysis

2.4.1 Photoelectron Spectroscopy of Molecular Sulfur Compounds Adsorbed on Cu(110) and Cu(111) Surfaces at 300 K

(P. A. Agron, T. A. Carlson, T. M. Thomas,¹ F. A. Grimm²)

The photoelectron spectroscopy of organic sulfur molecules adsorbed on Cu(110) and Cu(111) surfaces was studied because of the importance of sulfur interactions observed in catalysis studies. Angular resolved photoemission spectra (ARPES) of several sulfur-containing molecules, i.e., thiacyclobutane, thiacyclopentane, thiacyclohexane³ and phenyl mercaptan (benzenethiol, ϕSH)⁴ adsorbates were compared with their respective gas phase spectra (using HeI, 21.2 eV radiation).

Sulfur lone-pair orbital stabilization energies were obtained for the sulfur bond to the Cu(110) surface in the case of thiacyclobutane (1.4 eV), thiacyclopentane (1.1 eV) and thiacyclohexane (0.6 eV). The adsorbate relaxation energies are found to decrease in the order $4 > 5 > 6$ member ring. All adsorbates showed marked angular dependence, suggesting non-random orientation on the surface.

The analogous angular resolved photoelectron spectra study of benzenethiol (phenyl mercaptan, ϕSH) on a clean Cu(111) surface showed sharp spectra. In Fig. 2.13 are plotted the difference spectra for 10L of ϕSH adsorbed on the copper surface compared with that of the gas phase spectra. The correlation with the gas phase spectrum suggests that ϕSH bonds to copper by way of sulfur-containing orbitals rather than carbon π ring orbitals. Secondly, the angular dependence for the orbitals not involved in the bonding to the surface (namely, the phenyl group) shows that the molecule is oriented on the surface.

Orbital assignments⁵ of $\phi\text{SH}_{(g)}$ based on SPINDO calculations in which X_1 and X_3 represent π

ORNL-DWG 81-17695R

Fig. 2.13. Difference photoelectron spectra obtained with HeI (21.2 eV) of 10L of benzenethiol adsorbed on Cu(111) as a function of the polar angle θ at room temperature.

orbitals with substantial sulfur contributions, while X_2 is analogous to the $1e_{1g}$ π orbital of the phenyl group (Fig. 2.13). The orbitals of the adsorbate, A-D (Fig. 2.13) line up with the equivalent gas phase spectra, indicating that these orbitals are not involved in bonding to the copper surface. The gas phase bands X_1 , X_2 , and X_3 coalesce to a single broad band designated as X for the adsorbate spectra (Fig. 2.13). Energy shifts of the order of ~ 1.0 eV are observed for the S-p orbitals.

The most striking observation of the angular distribution studies is that the relative intensity of the C-band rises with decreasing emission

angle, θ . The X-band on the other hand, decreases in intensity with decreasing θ . The C-band can be identified with the bands associated with the $1b_{2u}$, $2b_{1u}$ orbitals of benzene. Since the angular dependence studies of benzene on Ni and Pd show the opposite behavior (benzene lies flat on Ni and Pd), it can be argued that ϕ SH must lie more perpendicular to the surface. (It should be pointed out that benzene does not adsorb on copper at room temperature.) The X-band includes contributions from orbitals containing sulfur 3p character. In our proposal, X_2 would remain nearly unaffected when ϕ SH is adsorbed on copper, while the X_1 and X_3 orbitals would be expected to split with part of the intensity shifting to the broad band X, with the remainder dispersed to higher and lower energies. The XPS analysis of the relative intensity of the Cu-2p, C-1s, and S-2p orbitals confirm the stoichiometry of the adsorbed molecule. A coverage of 0.63 monolayer of ϕ SH is indicated for the Cu(111) surface. This indicates that there is not sufficient room for the ϕ SH molecule to lie flat on the surface and supports the interpretation of the angular analysis of the photoelectron spectra.

In summary, we observe that ϕ SH adsorbs intact on Cu(111) as seen from both the XPS and UPS results. The bonding to the surface is through the π orbitals containing strong S-3p contributions and not the carbon π -ring orbitals. Both the large coverage observed and angular dependence of the orbital intensities as a function of the polar angle suggest that the phenyl ring is not parallel to the surface, but tilted away from the surface.

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3. T. M. Thomas, F. A. Grimm, T. A. Carlson, and P. A. Agron, J. Electr. Spectr., in press.

4. P. A. Agron and T. A. Carlson, J. Vac. Sci. and Techn., submitted.

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2.4.2 Interaction of Oxygen with Mo(100) Surface Studied by Low Energy Ion Scattering

(S. H. Overbury, P. C. Stair,¹ P. A. Agron, S. Datz)

Molybdenum in various forms has been used as a catalyst for numerous industrial reactions. It is known that addition of other metals, oxygen, or other impurities has a marked effect in altering the reactivity and selectivity of Mo as a catalyst. In surface experiments on well characterized Mo single crystal surfaces it has been shown that oxygen strongly alters the adsorptive behavior of Mo toward various molecules. A complete understanding of the mechanism by which oxygen affects adsorption, which is the crucial first step in any surface catalyzed reactions, requires a detailed knowledge about the location of the oxygen atoms at the surface and the effect that they have on the substrate surface structure. Current research emphasis has been directed at examining the interaction of oxygen with a Mo(100) single crystal surface using the structure sensitive technique of low energy ion scattering.

A new apparatus has been constructed during the last year which has the capabilities necessary to undertake such a study. The ultra high vacuum system which is capable of vacuums better than 2×10^{-10} torr, contains full capabilities for doing angle resolved low energy ion scattering using inert gas and alkali probe ions in the energy range from 100 to 3000 eV. The ability to do Auger electron spectroscopy (AES) and low energy electron diffraction (LEED) has been developed and applied. The system also contains a quadrupole mass spectrometer for identifying residual gases and monitoring admitted reactant gases. A sample mount has been built, tested, and used successfully to position the crystal and to adjust azimuthal and polar incidence angles accurately and reproducibly. It is also possible to sputter the crystal, heat it to 2000 K and perform controlled gas exposures. The apparatus therefore can clean, and characterize even a very reactive surface (e.g., clean Mo(100) has the unity sticking coefficient for

oxygen and carbon monoxide) and then perform controlled gas exposures to prepare a surface of known oxygen coverage for analysis by angle resolved low energy ion scattering.

Li^+ , K^+ , He^+ , and Ar^+ ion scattering measurements have been made for clean and oxygenated surfaces. Since, in general, ion scattering energy and angular distribution are still not yet fully understood, measurements on clean surfaces are necessary to interpret ion distributions from surfaces with oxygen or other adsorbates present. Because of reduced ion neutralization, measurements with alkali ions continue to be easier to interpret than measurements with inert gas ions. A comparison between K^+ and Ar^+ scattering from Au(110) clearly demonstrates that ion neutralization is dependent upon the details of the ion's trajectory. To determine structural information from inert gas ion scattering requires uncoupling the poorly understood effects of neutralization from the scattering probability. With K^+ , surface structure dependent neutralization seems to be eliminated. In the case of Li^+ on Mo(100) there is some neutralization of Li^+ that seems to depend only upon the work function of the surface and not upon details of the ion trajectory. The azimuthal dependence of the Li^+ scattering as a function of the work function of the Mo surface which was varied by exposure to oxygen supports this conclusion.

Strong focusing effects, resulting in intensity enhancement, have been observed in Li^+ scattering from Mo(100) which again demonstrates the importance of a surface multiple scattering mechanism that was found earlier in scattering of K^+ from Au(110). A similar focusing of K^+ by Mo has also been observed. The sensitivity of this enhancement to the presence of an adsorbate may be particularly helpful in determining its location. Another interesting discovery is that for some incident azimuths, sharp peaks in the back-scattered Li^+ energy distribution appear which apparently are multiple scattering features but which occur at energies below the single scattering energy, in contradistinction to the case with K^+ scattering.

This result indicates that inelastic losses are

important in the Li^+ case. Computer simulation techniques will be applied to determine if these features may be due to sub-surface channeling.

Li^+ , K^+ , and He^+ scattering results obtained for the oxygenated Mo(100) surface indicate that for coverages less than one monolayer, the oxygen is above the surface (as opposed to diffusing under the surface). The Mo surface does not seem to be reconstructed by the oxygen. K^+ results indicate that the oxygen atoms reside in four fold sites, and that the oxygen fills adsorption sites on the surface continuously up to about one monolayer. The height of the oxygen above the surface has not yet been determined; but with computer simulation and interpretation of angular distribution, this information may be determined.

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2.4.3 Adsorbent-Adsorbate Force Measurements

(E. H. Taylor, W. C. Waggener)

The technique which we are developing for the measurement of molecule-surface forces depends upon the deflection of a very thin ribbon of the metal of interest when one or another gas is adsorbed upon it. Adsorption is confined to one side of the ribbon by coating one side with gold, which does not chemisorb most gases. In preliminary experiments, crude but definitive, we were able to show that deflections did occur with various gases, and that the magnitude and even the sense of the bending differed from gas to gas.

Our first bending experiments in the ultrahigh vacuum system described last year revealed some problems that were not present in the original experiments. The latter were all conducted at atmospheric pressure, and desorption was accomplished (to the extent possible) by flowing helium over the sample. We need to use ultrahigh vacuum for cleaning and maintaining the surfaces clean prior to adsorption, but the change in pressure has introduced two artifacts. First, the pressure change produces enough asymmetric distortion of the vacuum system to cause appreciable movement of the end of the sample independent of any bending. Second, the difference in thermal conductivity between high vacuum and gas changes the temperature of the ribbon, either when the experiment is conducted at an elevated temperature or, even at room temperature, when the light used for observing the ribbon is too intense. (The ribbon, being bimetallic, bends as the temperature changes.) Both of these sources of spurious deflections have now been corrected, and we can make observations of deflections arising from processes on or in the ribbon itself.

During the year we lost our borrowed vacuum evaporator, and have had to renovate and put in service a different one. Although this has been a source of delay, we are now in better shape than before to produce vacuum evaporated thin ribbons. In particular, the new system should make it easier to attain our goal of preparing thin single crystals of adequate size for deflection experiments.

3. AQUEOUS CHEMISTRY AT HIGH TEMPERATURES

3.1 Thermodynamics of Solutions to High Temperatures

3.1.1 The Enthalpy of Dilution of Aqueous NaCl to 400°C

(R. H. Busey, R. E. Mesmer)

The enthalpy of dilution of aqueous NaCl has been determined over a wide concentration and temperature range to establish the performance of the recently developed heat and liquid flow calorimetric system briefly described last year.¹ Aqueous NaCl has become a standard for thermochemical measurements and its thermodynamic properties to 300°C have been correlated recently.² These measurements are unique in the field of solution thermodynamics; no other laboratory is making enthalpy of dilution observations to 400°C.

The calorimetric apparatus briefly described consists of a Calvet heat-flow microcalorimeter (1000°C model) equipped with two specially designed heat-exchangers made of platinum. One Ruska differential proportioning pump delivers precise water flows to one of the heat-exchangers (the reaction cell) and to a pusher containing the electrolyte solution under study. The pusher is simply a high pressure squeeze bottle containing the solution in a teflon bag with a platinum capillary line from it to the reaction cell with a platinum-core valve interposed. A second Ruska pump delivers a water flow to the other heat-exchanger (reference cell) in the Calvet calorimeter equal to the total flow (solution + water) to the reaction cell. The effluent from both heat-exchangers is collected in a high pressure receiver with an argon pressure at the desired pressure of the experiment. A 450 junction thermopile surrounding the reaction cell is in opposition to a 450 junction thermopile surrounding the reference cell; the signal resulting gives a measure of the power generated by the enthalpy of dilution.

The great advantages of this calorimetric system over a conventional autoclave-type high temperature calorimeter are: (1) no vapor space so that evaporation during reaction is not a

problem, (2) solutions at high pressures are readily confined in thin wall capillary tubing without substantial increase in equilibration time, (3) a volatile solute presents no difficulty, (4) pressure coefficients of a reaction are readily determined, and (5) the calorimeter does not have to be brought back to room temperature in order to perform a new experiment.

From an analyzed 5.178 m NaCl stock solution 1, 0.2, and 0.1 m NaCl solutions were prepared by weight. At each temperature of the dilution measurements a series of dilution were made on the 5.178 m, 1.000 m, and 0.2000 m (0.1000 m above 300°C) solutions which provided a dilution curve with evenly placed data points covering the concentration range 5.178 m to about 0.03 m (0.016 m above 300°C). The differential proportioning pump allowed 1:1, 1:2, 1:3, 1:4, and 1:5 dilutions (as well as 2:1, 3:1, etc.). Below 300°C measurements were made at a constant pressure of ~66 bars, at 105 bars at 300°C, about 200 bars at 350°C, and about 400 bars at 400°C. At each temperature below 400°C, a series of 4 to 5 data points were obtained at about 400 bars to provide pressure coefficient data required to convert the enthalpy data to saturation pressure.

Figure 3.1 presents the results of the measurements. The apparent molal enthalpy of the final or resulting solution, $\phi_L (m_f)$, relative to that of the most concentrated solution, $\phi_L (5.178 \text{ m})$, is plotted against $m_f^{1/2}$. The light lines labeled DHLL represent Debye-Hückel limiting law slopes. Figure 3.2 is representative of the pressure coefficient measurements. Again, the light line represents the Debye-Hückel limiting law slope, obtained from Bradley and Pitzer,³ which is employed as an aid in drawing the curves.

Pitzer's ion-interaction model has been used to fit the enthalpy data to arrive at values of ϕ_L , ϕ , and $\gamma_{\pm}$ (apparent molal enthalpy, osmotic coefficient, and mean activity coefficient, respectively) as a function of molality and temperature. The precision of the isothermal fits is about 1.5% for 100° and 150°, 2% for 200°, 2.5% for 250° and 300°, and 3% for 350° and 400°C. No precise value for the Debye-Hückel slope for the

ENTHALPY OF DILUTION OF AQUEOUS NaCl

Fig. 3.1. Enthalpy of dilution of NaCl. The apparent molal enthalpy relative to that of a 5.178 m solution is plotted against $m^{1/2}$. The Debye-Hückel limiting law slope is shown as a light line (DHLL).

apparent molal enthalpy, A_H , is available at 400°C and 400 bars. In fitting the 400°C data, A_H was made an adjustable parameter and the value 403.4 kJ/mol was obtained. To assess how good this value may be, A_H was made an adjustable parameter with the 300° and 350° data where reliable values are available.³ The results of the calculations gave values of A_H which agreed with Bradley and Pitzer³ to 6% and 4% respectively, well within the uncertainty of the literature values.

For the purpose of deriving osmotic and activity coefficients from the enthalpy data and 25°C values of $\gamma_{\pm}$ and ϕ , it is necessary to have a fit to a function of temperature. For the 50°-250° data at 66 bars, a fit with agreement to 2.3% was obtained. Using our observed pressure coefficients all the data to 350°C was corrected to 200 bars. It was not possible to obtain a good fit when all the data, 50°-to-350°C at 200 bars, were included. When the 350°C data were removed the fit was still poor (3.5% with the 300°C

PRESSURE COEFFICIENT OF ENTHALPY OF DILUTION OF AQUEOUS NaCl

Fig. 3.2. Pressure coefficient for the dilution of NaCl. The coefficient expressed as cm^3/mol is plotted against $m^{1/2}$. The Debye-Hückel limiting law slope is shown as a light line (DHLL).

poorly fit). The agreement was again 2.4% for the 50°-to-250°C data at 200 bars. The enthalpy data at the higher temperatures (above 250°C) clearly demonstrate the need for revision or modification of the model.

Likke and Bromley⁴ have determined the heat capacity of NaCl solutions from 80° to 200°C at molalities of 0.713, 1.488, and 2.333 m. A comparison between their data and our enthalpy data is possible using the following thermodynamic relation:

$$\phi L(m, T_2) - \phi L(m, T_1) = \int_{T_1}^{T_2} (\phi C_p - \phi C_p^\circ) dT \quad (1)$$

where ϕC_p and ϕC_p° are the apparent partial molal heat capacity of the NaCl in a m molal solution and at infinite dilution, respectively. All data is along the saturation curve. The integral is evaluated from Likke and Bromley's data to be 7.09 kJ/mol at $m = 0.713$, 9.56 kJ/mol at $m = 1.488$, and 11.57 kJ/mol at $m = 2.333$. The enthalpy results are 7.34, 9.77, and 11.59 kJ/mol respectively, giving an agreement of 3.6, 2.2 and 0.2%.

A more definitive comparison is that to the results of Silvester and Pitzer¹ who have tabulated enthalpy values, ϕL , at saturation pressure as a function of molality and temperature using the ion-interaction model fit to all the available thermodynamic data. Their values above 100°C are primarily based upon vapor pressure measurements of Liu and Lindsay⁵ and Gardner⁶ together with the heat capacity data⁴ mentioned above. Apparent molal enthalpies at saturation pressure are computed from our values at 66 and 200 bars assuming a linear relationship. The agreement is quite satisfactory: an average agreement of 1.0% at 100°C over the concentration range 0.1 to 5 m , 1.3% at 150°C, 2.5% at 200, and 1.4% at 250°C.

For a given solution in one of the pushers of the calorimetric apparatus, the precision (repeatability) of an enthalpy of dilution measurement is about 0.5% or 20 J/mol whichever is larger. However, with another loading of the same solution in the pusher at a later date, the agreement with the previously 0.5% precise result may be only 1.5 to 2%. Since these measurements were made several improvements in the apparatus have been made which should insure a consistent precision of 0.5% or better.

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3. D. J. Bradley and K. S. Pitzer, *J. Phys. Chem.* **83**, 1599(1979).

4. S. Likke and L. A. Bromley, *J. Chem. Eng. Data* **18**, 189(1973).

5. C. Liu and W. T. Lindsay, *J. Soln. Chem.* **1**, 45(1972); C. Liu and W. T. Lindsay, *J. Phys. Chem.* **74**, 341(1970).

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3.1.2 The Enthalpy of Mixing of Methanol and Water to 300°C

(Daniel J. Bradley,¹ R. H. Busey)

Solutions of electrolytes and water at high temperatures and pressures have been the subject of considerable interest in the past 10 years. The development of flow calorimetry and accurate isopiestic measurements has allowed a rapid expansion of the data base for these systems. In contrast, little new information about the properties of non-electrolyte solutions at elevated temperatures and pressures have been obtained. This lack of information is unfortunate considering their importance both from an industrial and a basic science perspective. This investigation was undertaken to fill a small portion of this knowledge gap and at the same time complement work already proceeding on electrolyte solutions.

Methanol was chosen as a starting point for the study of non-electrolyte-water solutions for three primary reasons: (1) the complete miscibility in water at temperatures and pressures of interest, (2) the small molecular size, and (3) the highly polar electronic structure.

The first was considered important only in that it made the experiments much simpler. The second and third were made requirements because it seemed desirable to be able to compare the results with those for electrolyte solutions at temperatures where considerable association was thought to be occurring.

Enthalpies of solution and dilution for compositions ranging from 0.02 to 0.9 mole fraction methanol were measured at 50° temperature intervals from 100 to 300°C at 69 and 207 bars. The results of these experiments are presented in Fig. 3.3 in terms of the enthalpy of mixing (ΔH_m) plotted on a per mole of solution basis. As can be seen in Fig. 3.3, the minimum of the enthalpy of mixing, is skewed substantially to the water rich side at 25°C with the minimum occurring at

Fig. 3.3. Enthalpy of mixing of methanol and water on a per mole of solution basis.

approximately 0.3 mole fraction methanol. At higher temperatures, however, the peak moved toward the alcohol rich direction and the sign of the enthalpy changes from negative to positive. In fact, the enthalpy of solution, at infinite dilution, at 250°C is equal to that at 25°C, but has the opposite sign. The effect of increasing the pressure was found to be small and positive.

The results at 300°C show that the enthalpy continues to increase in magnitude and becomes skewed to the alcohol rich side. These results, however, are not considered to be as precise as those at lower temperatures. For reasons not yet clear but possibly related to mixing of solutions of substantially different densities, the calorimeter failed to reach a steady state at 300°C for solutions with high concentrations of methanol.

A more complete analysis, which would hopefully explain the gross changes in the size and symmetry of the enthalpy of solution curve, will be completed in the next few months.

1. ORAU summer participant (1981) from Montana College of Mineral Science and Technology.

3.1.3 The Enthalpy of Dilution of Aqueous CaCl_2 by Flow Calorimetry

(R. H. Busey, R. E. Mesmer)

The need for an isopiestic standard at high temperatures which can give low water activities has prompted the measurements of the enthalpy of dilution of aqueous CaCl_2 over an extended temperature and concentration range. Osmotic coefficients determined^{1,2} at 25°C may be extended to higher temperatures using apparent relative molal enthalpies derived from enthalpy of dilution data and the thermodynamic relation:

$$\phi(T, m) - \phi(298.15, m) = \frac{m^{\frac{1}{2}}}{2\nu R} \int_{298.15}^T \left(\frac{d(\phi L)}{dm^{\frac{1}{2}}} \right) d\left(\frac{1}{T}\right) \quad (1)$$

where $\phi(T, m)$ is the osmotic coefficient at temperature T and molality m , ν is the number of moles of ions formed from 1 mole of electrolyte (3 for CaCl_2), R is the gas constant, and ϕL is the apparent relative molal enthalpy ($\phi L = \frac{L}{m}$, L is the relative enthalpy of the solution). It is also of intrinsic scientific interest to observe the dilution behavior of a (2-1) type electrolyte over a wide concentration and temperature range.

A stock solution of 7.259 m CaCl_2 was analyzed gravimetrically by precipitating and weighing AgCl . One molal, 0.2 molal, and 0.1 m solutions were prepared by weight from the stock solution. At each temperature of the dilution measurements, a series of dilutions were made on the 7.259 m, 1.00 m, and 0.200 m (0.1000 m above 300°C) solutions which provided a dilution curve with evenly placed data points covering the concentration range 7.259 m to about 0.03 m (0.016 m above 300°C).

Enthalpy observations were made using the heat and liquid flow microcalorimeter.^{3,4} The temperatures of the observations were 25°, 50°, 75°, 100°, 150°, 200°, 300°, and 400°C. Additional measurements at temperatures of 250 and 350°C will be made later to complete the data. Below 300°C measurements were made at a constant pressure of ~70 bars, at 105 bars at 300°C, and about 400 bars at 400°C. At each temperature below 400°C, 4 to 5 data points were obtained at about 400 bars to provide pressure coefficient data

required to convert the enthalpy data to saturation pressure.

Figures 3.4 and 3.5 give the results of the measurements. The apparent molal enthalpy relative to the most concentrated solution, 7.259 m CaCl_2 , is plotted against the square root of the molality. The light lines labelled DHLL represent the Debye-Hückel limiting law slope. An interesting feature of these curves compared to those for NaCl above is the S-shape character of the curves at the lower temperatures. It is most evident at 25°C but has almost disappeared at 200°C. The initial steep drop of the curves from the 7.259 m reference point represents an enthalpy associated with hydration of the ions which are apparently undersaturated in the most concentrated solutions.

Fig. 3.4. Enthalpy of dilution of CaCl_2 , 25° to 150°C. The apparent molal enthalpy relative to that for the 7.259 m solution is plotted against $m^{1/2}$. The Debye-Hückel limiting law slope is shown as a light line (DHLL).

Fig. 3.5. Enthalpy of dilution of CaCl_2 , 150° to 400°C. The apparent molal enthalpy relative to that for the 7.259 m solution is plotted against $m^{1/2}$. The Debye-Hückel limiting law slope is shown as a light line (DHLL).

The data in its present form (Fig. 3.4) is of limited use since ϕL values are required by Eqn. 1. When the data is completed, an extrapolation of the data to zero molality and derivation of an analytical expression for the temperature and molality dependence will be derived using Pitzer's ion-interaction model.⁵

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3. Chem. Div. Annu. Prog. Rep. Feb. 29, 1980, ORNL-5665 (July 1980), p. 35.
4. See Section 3.1.1.
5. L. F. Silvester and K. S. Pitzer, *J. Phys. Chem.* **81**, 1822(1977) and preceding papers in this series.

3.1.4 Thermodynamics of Alkali Metal Chloride Solutions from 0 to 250°C

(H. F. Holmes, R. E. Mesmer)

The most common family of strong electrolytes is the alkali metal chlorides which almost universally serve as models for theories and predictions. NaCl(aq) is certainly the most studied electrolyte at elevated temperatures and serves as the standard for our isopiestic measurements. We have previously measured the osmotic coefficients of LiCl(aq), KCl(aq), and CsCl(aq) from 110 to 200°C. We have now extended the measurements on these three electrolytes to 250°C. The osmotic coefficient (and the derived activity coefficients) of all three systems continued the trend observed in the range of 110 to 200°C, i.e., they continued to decrease with increasing temperature and become less dependent on molality above about one mol kg⁻¹. A least-squares fit of the ion-interaction model to the osmotic coefficient results at 225 and 250°C gave the parameters—with a standard error of fit ranging from 0.0006 to 0.0012 in the osmotic coefficient—needed for the calculation of activity coefficients.

Figure 3.6 was constructed from our results at 200°C for LiCl(aq), KCl(aq), and CsCl(aq), literature data for NaCl(aq) at 200°C, and tabulated activity coefficients for all four salts

at 25°C. Although the reduction in the activity coefficient on going to 200°C is much more noticeable in the case of LiCl(aq) and NaCl(aq), the activity coefficients of all four salts are decreasing at about the same rate at 200°C on a percentage basis. The statement is often made that electrolytes lose their individual character at elevated temperatures. Results for NaCl(aq), KCl(aq), and CsCl(aq) support this proposition as do the activity coefficients of the four common alkaline earth metal chlorides which are even more nearly alike at 200°C. However, this statement is clearly not true when one considers LiCl(aq) at temperatures up to, and including, 250°C. The individuality of LiCl(aq) may be related to hydration and/or ion size effects but no one has yet developed an adequate theory based on these two factors. With the exception of LiCl(aq), it now appears that the assumption of the same activity coefficient for all members of a given family of electrolytes (also reasonably independent of molality at high concentrations) is a good estimate at high temperatures, at least for the two families that we have studied.

In comparing our results for LiCl(aq), KCl(aq), and CsCl(aq) with existing literature data for these salts it became apparent that there was sufficient information available that it would

Fig. 3.6 Activity coefficients ($\gamma_{\pm}$) of the alkali metal chlorides in aqueous solutions as a function of molality (m) at 25 and 200°C.

be worthwhile to make a thermodynamic analysis and comparison of the various types of results for these three electrolytes. The thermodynamic information available for these three solutions can be classified into the three general categories of free energy, enthalpy, and heat capacity. The basic thermodynamic relationships between these three groups are:

$$L = -T^2(\partial(G^{\text{Ex}}/T)/\partial T)_{P,m} \quad (1)$$

where L is the relative enthalpy and G^{Ex} is the excess free energy, and

$$J = (\partial L/\partial T)_{P,m} \quad (2)$$

in which J is the total relative heat capacity. It is necessary to assume a model to provide mathematical equations on which the operations of (1) and (2) can be performed. Because of our success in using it isothermally, we have chosen to use the ion-interaction model. Having chosen the model, it is then necessary to provide an acceptable temperature dependence for the three parameters of the ion-interaction model. With a few exceptions we have used the analytical forms for the temperature dependence that were employed by Silvester and Pitzer¹ in their analysis of the NaCl(aq) system.

Adjustable parameters of the model were fixed by a simultaneous least-squares fit of the various types of thermodynamic data to mathematical expressions from the ion-interaction model, the assumed temperature dependence, and eqns. (1) and (2). Included in the final data set for each salt were results from various kinds of experiments including isopiestic, vapor pressure, freezing temperature, cell potential, heat of dilution, heat of solution, and heat capacity. Somewhat surprisingly, the LiCl(aq) system proved to be the simplest to describe, with two of the ion-interaction parameters being simple linear functions of temperature. The CsCl(aq) system was intermediate with KCl(aq) being the most complex, possibly because the heat capacity results at 5°C were difficult to fit. Overall, with a few exceptions, the osmotic coefficients

were fit to about 0.3 per cent, which is probably better than the absolute accuracy of the results. The activity coefficients data did not fit quite as well because the precision of the measurements was not as good at temperatures other than 25°C. Fits of various enthalpy results were highly variable, ranging from very precise to systematic differences so large that the given set of results was excluded from the final least squares analysis. With the exception of one systematically high set, the heat capacities fit the model to $4 \text{ J mol}^{-1} \text{ K}^{-1}$, or better, a very acceptable result. The equations, parameters, and tables of calculated thermodynamic properties will be included in a forthcoming publication.

The derivatives of equations (1) and (2) are at constant pressure while the available thermodynamic results are either at saturation pressure or one atmosphere. There are thermodynamic methods for correcting the results to a constant pressure with the required input being the volumetric properties of the solutions. Most of the high temperature PVT measurements have been made on NaCl(aq) but even in this case the precision of the results is not quite satisfactory as first and second derivatives of the volume are required. In the present case—with pressures limited to 40 bars or less—estimates of the correction, based on the NaCl(aq) data, show that it is smaller than the uncertainty in the property being corrected. This will not be the case for temperatures much above 250°C and highlights a void in our knowledge of electrolyte solutions at high temperatures.

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3.1.5 Osmotic Coefficients of $\text{MgSO}_4(\text{aq})$ and $\text{NiSO}_4(\text{aq})$ at 110°C

(H. F. Holmes, R. E. Mesmer)

The peculiarities of higher charged electrolytes such as the divalent metal sulfates were well known before the advent of the Debye-Hückel theory. Difficulties involved in satisfactorily

treating experimental results for this class of salts (e.g. obtaining activity coefficients from osmotic data) were not alleviated with the Debye-Hückel theory. It has subsequently been shown that an adequate solution can be obtained by assuming specific ion association equilibria although the equations are somewhat cumbersome and require iterative calculations. More recently, it has been demonstrated that the ion-interaction model is capable of providing, in a relatively simple manner, satisfactory treatment of the experimental results for 2-2 and more highly charged electrolytes without the assumption of an association equilibrium.

In order to obtain additional information concerning this important class of electrolytes, we have measured the osmotic coefficients of $\text{MgSO}_4(\text{aq})$ and $\text{NiSO}_4(\text{aq})$ at elevated temperatures by isopiestic comparison with $\text{NaCl}(\text{aq})$. The results are shown in Fig. 3.7 with several aspects needing some explanation. Our normal range of operating temperatures is from 110 to 250°C. The four points at 140°C were the only ones ob-

tainable for these two electrolytes in this specific experimental sequence because of solubility limitations. At temperatures above 140°C both salts remained completely insoluble under our operating conditions. It is known that these two salts have retrograde solubilities but we did not expect this type of difficulty, especially at 140°C. Obviously there were kinetic and/or irreversible chemical changes occurring at 140°C, otherwise we would have been able to obtain results for $\text{NiSO}_4(\text{aq})$ at low molalities.

The measurements at 110°C were normal, reproducible, and completely reversible with changes in molality. Published osmotic coefficients for $\text{MgSO}_4(\text{aq})$ ¹ and $\text{NiSO}_4(\text{aq})$ ² have been included in Fig. 3.7 for purposes of comparison. Two features of the results—decreasing osmotic coefficients with increasing temperature and a shift of the minimum in the ϕ - m relationships to higher molalities—are quite similar to the behavior of other electrolytes at elevated temperatures. Lines drawn through the 110°C results in Fig. 3.7 were calculated from a least squares fit of the ion-interaction model to our experimental osmotic coefficients. The fit was quite good with a standard error of fit equal to 0.0037 and 0.0025 for $\text{NiSO}_4(\text{aq})$ and $\text{MgSO}_4(\text{aq})$, respectively.

Equations of the ion-interaction model contain four adjustable parameters for 2-2 electrolytes in contrast to the normal three for salts in which at least one of the ions is univalent. Unfortunately, the fourth parameter has a negligible contribution to the osmotic coefficient above 0.1 mol kg^{-1} —a concentration below the accessible range of isopiestic experiments. To make the situation even more difficult, the fourth parameter does make a significant contribution to the activity coefficient at all concentrations. Since we can determine only three of the four parameters from our results we cannot calculate activity coefficients directly from our osmotic coefficients as was the case with 1-1 and 2-1 electrolytes. However, there are available freezing temperature measurements for $\text{MgSO}_4(\text{aq})$ from which one can determine the

Fig. 3.7. Osmotic coefficients (ϕ) of $\text{MgSO}_4(\text{aq})$ and $\text{NiSO}_4(\text{aq})$ as a function of molality (m) and temperatures.

fourth parameter. In addition there are enthalpy results (from 25 to 150°C) from which one can calculate the temperature coefficients of all four parameters. Thermodynamic relationships between the various functions make it possible, at least in principle, to calculate the activity coefficients for $\text{MgSO}_4(\text{aq})$.

For purposes of mathematical modeling, the four parameters of the ion-interaction model were assumed to be quadratic functions of temperature. In view of the rather large uncertainties associated with much of the enthalpy data a more complicated function is not justified. A simultaneous least-squares fit of the isopiestic, freezing temperature, and enthalpy data gave a set of 12 parameters (three for each of the four ion-interaction parameters) which can be used to calculate activity coefficients in the temperature range of the experimental results. The computer program (ORGLS) used for the least squares calculation also gave values for the standard errors and correlation coefficients associated with the 12 parameters. These quantities made it possible to calculate the standard errors associated with the computed activity coefficients. Table 3.1 is an abbreviated listing of the calculated activity coefficients for $\text{MgSO}_4(\text{aq})$ along with the corresponding standard errors. Certainly the most striking feature of

Table 3.1 is the magnitude of the activity coefficients. They are quite small and decrease with increasing temperature with the minimum in the γ - m relationships shifting to higher molalities—two traits in common with non-associated electrolytes. Published values¹ of γ for MgSO_4 at 25°C agree with our calculated values within the estimated uncertainty (~2%) of the literature data. The standard errors increase with increasing molality and removal from 25°C—which is to be expected as both factors increase the contribution (and therefore the uncertainty of γ) of the 12 parameters. At 110°C and high molalities, the errors are such that the calculated values of γ can only be regarded as rough estimates. There are two reasons for this situation. One is the lack of data at 0.1 mol kg⁻¹ and below and the other is the very large uncertainties in the high temperature enthalpy data.

In the case of $\text{NiSO}_4(\text{aq})$ the thermodynamic data necessary for this type of calculation do not exist. However, one would certainly expect similar behavior.

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Table 3.1 Calculated activity coefficients (γ) for $\text{MgSO}_4(\text{aq})$ and their associated standard errors (σ)

m mol kg ⁻¹	t/°C									
	0		25 ^a		25		75		110	
	γ	σ	γ	σ	γ	σ	γ	σ	γ	σ
0.1	0.1749	0.0026	0.1613	0.1645	0.0009	0.1338	0.0040	0.1081	0.0056	
0.3	0.1034	0.0028	0.0948	0.0971	0.0006	0.0764	0.0042	0.0589	0.0058	
0.5	0.0801	0.0028	0.0733	0.0752	0.0006	0.0580	0.0044	0.0434	0.0058	
1.0	0.0578	0.0033	0.0529	0.0540	0.0005	0.0399	0.0049	0.0281	0.0063	
1.5	0.0510	0.0042	0.0464 ^b	0.0472	0.0005	0.0332	0.0059	0.0222	0.0074	
2.0	0.0507	0.0056	0.0451	0.0460	0.0006	0.0307	0.0076	0.0195	0.0091	
2.5	0.0549	0.0079	0.0477 ^b	0.0485	0.0007	0.0305	0.0100	0.0184	0.0117	
3.0	0.0637	0.0117	0.0532	0.0543	0.0010	0.0318	0.0135	0.0182	0.0156	
3.5	0.0783	0.0181	0.0637 ^b	0.0639	0.0014	0.0344	0.0188	0.0188	0.0214	

^aFrom Reference (1).

^bInterpolated.

3.1.6 The Application of the Ion-Interaction Model to Ion Pairing and Non-Electrolytes in Aqueous Solutions

(Daniel J. Bradley,¹ R. E. Mesmer)

Aqueous solutions containing both ionic and neutral solutes are a broad and important class of systems. They can be easily subdivided into two groups based on the relationship between the solutes. In Group I, the neutral and ionic species are related through an association reaction and in the other only by the fact that both solutes are in the same solvent. An example of Group I would be an acetic acid solution. A mixture of methane, water, and sodium chloride could be considered typical of Group II.

There has been a great deal of controversy concerning Group I as to how associated an electrolyte must be to be considered a weak electrolyte. Chemists have generally been of the opinion that a salt should be considered a strong electrolyte unless its properties fail to conform to those of "known" strong electrolytes. They have generally dismissed as unnecessary the attempts to describe seemingly strong electrolytes in terms of an association equilibrium. Geologists have tended in the other direction. There are data which can be interpreted as support for some degree of association in almost all aqueous salts, even at 25°C. As a result, association constants for almost all salts have been obtained in the literature.

The purpose of this investigation was to develop a set of equations which could be used to describe associated systems and to determine what information could be obtained about the different species using available experimental techniques. The equation of Pitzer² for the excess Gibbs free energy was chosen as a starting point because of its simplicity and wide usage for fitting electrolyte solution data.

For a solution containing n solutes, the equation has the following form:

$$\frac{G^{EX}}{RT} = n_w f^{GX} + \frac{1}{n_w} \sum_{ij} \lambda_{ij} n_i n_j + \frac{1}{n_w^2} \sum_{ijk} \mu_{ijk} n_i n_j n_k \quad (1)$$

where:

- n_w = number of kg of water
- n_i = number of moles of species i
- $f^{GX} = -A_\phi (4I/b) \ln(1 + bI^{1/2})$
- λ_{ij} = binary interaction parameter between species i and j
- μ_{ijk} = ternary interaction parameter between species i , j and k
- I = ionic strength
- A_ϕ = Debye-Hückel parameter for the osmotic coefficient
- b = ion size parameter (normally fixed at 1.2 Å by Pitzer and others) .

In terms of molality we can rewrite the equation:

$$\frac{G^{EX}}{n_w RT} = f^{GX} + \sum_{ij} \lambda_{ij} m_i m_j + \sum_{ijk} \mu_{ijk} m_i m_j m_k \quad (2)$$

For the case of a system containing two ions and a neutral species, the activity coefficient of salt (MX) and the neutral molecule (k) are written as follows:

$$\ln \gamma_{MX} = v \ln \gamma_{\pm} = |Z_M Z_X| f^Y + 2m v_M v_X B_{MX}^Y + 6m^2 (v_M v_X)^{3/2} C_{MX}^{GX} + 6v_M v_X m m_k \Delta_{MXk} + 3m_k^2 \Gamma_{MXk} + 2m_k \Delta_{MXk} \quad (3)$$

$$\ln \gamma_k = 2m \Delta_{MXk} + 2m_k \lambda_{kk} + 6m m_k \Gamma_{MXk} + 3v_M v_X m^2 \Delta_{MXk} + 3m_k^2 \mu_{kkk} \quad (4)$$

for 1-1 salts, m is the molality of M^+ or X^- .

The notation of Pitzer³ has been followed for parameters he has previously identified.

Given these equations, the question now becomes: what type of data are available and what information can be calculated for the various species. The situation for the first type of solution is summarized in Table 3.2. Table 3.2 lists for the case of ion association ($M^+ + X^- \rightleftharpoons MX$) what is usually known or can be determined by experiment. Normally the equilibrium constant for the association reaction and the

Table 3.2 Ion Association of a 1-1 Electrolyte

Unknowns	Observations	Knowns
		Equations
m_{M^+}	ϕ	$m_{M^+} = m_{X^-}$
m_{X^-}	K_A	$m_k + m_{M^+} = m_M$
m_k		$K_A = \gamma_k m_k / \gamma_{\pm}^2 m_{M^+} m_{X^-}$
γ_k		Gibbs-Duhem eqn.
$\gamma_{\pm}$	$\therefore$ 5 unknowns and 4 equations	

osmotic coefficient over a range of concentration are the only experimental variables that can be measured. The concentrations and activity coefficients of the associated and unassociated salt can only be determined in special cases such as when a reversible EMF cell exists for one of the ions or the neutral species is volatile. Weak acids, such as acetic or phosphoric, form the largest class of electrolytes where $\gamma_{\pm}$, the mean ionic activity and coefficient, can be determined directly from experiment. In the case for associated salts where the association constant and the osmotic coefficient are observable then one is left with five unknowns and four equations when attempting to model the excess thermodynamic quantities. All that can be determined is the product of the activity coefficients.

Neutral-strong electrolyte mixtures are more tractable. No chemical reactions are occurring in solution and, therefore, the concentration of all the species are known from the initial conditions. The activity coefficient of the neutral molecule (k) and the solvent can normally be measured directly. The only unknown then is $\gamma_{\pm}$, which can be obtained through the Gibbs-Duhem equation.

The equations presented earlier can be used equally well to describe the thermodynamics of both types of solutions. It is apparent, however, that except in a few special cases, necessary experimental data are not available for associated systems. The concentration and activity coefficients of the solutes cannot be individually determined. Approximations such as assuming that $\gamma_k = 1$ or that $\gamma_{\pm}$ is equal to the Debye-Hückel

limiting law value, are possible, however, they defeat the purpose of explicitly including the association reaction in the equations. The simpler equations where association is ignored seem more appropriate.

It is recommended that the association approach only be used in cases where the simpler approach is not sufficient. The equations will be useful only in the study of Group II solutions or special sub-groups of Group I, such as weak acid solutions (see Pitzer, et al.⁴). This analysis also shows that most speciation calculations in weak electrolyte systems rely on an unverifiable assumption about the activity coefficient of one of the species. The results of such calculations cannot be expected to closely approximate the true state of the system.

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3.2 Equilibrium and Speciation Studies

3.2.1 Analysis of the Kinetics and Equilibria of Iodine Hydrolysis Reactions

(D. A. Palmer, M. H. Lietzke)

In order to establish an effective scenario on the release of volatile iodine species (e.g., I_2 and possibly HOI) during a nuclear accident, a detailed understanding of the kinetics and equilibria of all the known, and postulated, iodine species is necessary. The aqueous system is complex due to the number of oxidation states available to iodine at ambient conditions.

Equilibrium Model. The following ten equilibria were considered in this model:

The equilibrium expressions for these equations were solved simultaneously using a modified version of the Newton-Raphson method, based on an initial iodine concentration, $[\text{I}_2]_0$, between 10^{-3} and 10^{-6} M over a pH range of 0 to 11 (depending on the value of $[\text{I}_2]_0$). A typical distribution of species is shown in Fig. 3.8 for $[\text{I}_2]_0 = 10^{-3}$ M, where I_2 is the dominant form at low pH (<6), while IO_3^- and I^- are stable at higher pH values. At lower total iodine concentrations, and at higher temperatures—the temperature dependencies of the equilibrium expressions were either estimated from existing data or ap-

proximated up to temperatures of 125°C—the stability field of the non-volatile, and therefore environmentally innocuous IO_3^- and I^- species extends to lower pH values. Furthermore, the potentially hazardous HOI form represents less than 2% of the total iodine concentration under all the conditions described above.

This model was validated as far as the major species are concerned from a limited number of experimental measurements.

By solving those equilibrium expressions which do not contain iodate, it is possible to predict the distribution of iodine species prior to the relatively slow disproportionation into IO_3^- and I^- . The calculations indicated that the major species would be I_2 , I^- and HOI/OI^- depending on the pH of the solution. The relative stability fields of the species are very sensitive to the initial I_2 concentration.

Kinetic Model. To gauge the time frame over which the two distributions exist, the rate laws for the reactions

Fig. 3.8 Equilibrium concentrations of iodine species as a function of pH at $[\text{I}_2]_0 = 10^{-3}$ M and 25°C.

and

were solved numerically using the Runge-Kutta method as a function of the initial iodine concentration and pH at 25°C. Two different sets of experimentally obtained rate laws for the second reaction were treated and gave essentially the same results over the pH range (7-13) investigated. An example of these calculations is given in Fig. 3.9 for $[\text{I}_2]_0 = 10^{-3}\text{M}$ and pH = 10 where the rate of formation of IO_3^- virtually reaches a maximum. The first reaction is clearly complete within one second and this applies to the entire pH range. On the other hand, the second reaction is complete within a few hours, but takes several days at lower pH values (i.e., <7) and lower initial iodine concentrations. No experimental data exist at the present time on the temperature dependence of these rate constants.

A detailed description of all these calculations will be included in the report ORNL-5824 and subsequent reports.

3.2.2 The Kinetics of Reactions of Iodine and the Spectral Characterization of the Hypoiodite Ion

(D. A. Palmer, R. van Eldik¹)

Kinetics. The rate of hydrolysis of molecular iodine according to equation (1) has been studied previously on at least four different occasions,²⁻⁵ and although it is generally agreed that this reaction is fast, the half-lives reported vary from 2ms to 3 min. If the reaction were complete within seconds, then the kinetics of this reaction will have virtually no impact on predictions of the behavior of iodine during a LWR accident. However, if the reaction occurs over a matter of minutes, this may provide sufficient time for I_2 to escape from the solution phase into the atmosphere of the containment building.

ORNL-DWG 81-12628

Iodine Hydrolysis Kinetics, pH 10

Fig. 3.9 Change in species concentration vs time for the hydrolysis of I_2 at $[\text{I}_2]_0 = 10^{-3}\text{M}$, 25°C and pH = 10.

Rapid mixing of an acidified solution of I_2 (I_2 being stable with respect to disproportionation at low pH) and a solution containing sufficient NaOH to destabilize I_2 in a stopped-flow spectrophotometer clearly demonstrated that reaction (1) must have been virtually complete within the "mixing time" of the instrument (i.e., ca. 2ms). Similar attempts to observe the reverse reaction showed it to be complete before measurements could be made. Thus, even the reported half-life of 2s appears to be conservative by more than three orders of magnitude.

A relaxation technique (*viz.* temperature-jump spectrophotometry) was investigated as it allows reactions which occur in the 1 μs to 1 s range to be monitored. By using this method with equilibrated I_2 solutions, a ΔT of +10°C, and a wavelength setting of 350nm, which corresponds to the absorption maximum of the I_3^- species, two distinct consecutive reactions were observed over the pH range 4.5 to 6.0. The first reaction, which involved a decrease in absorption, was observable over a far greater pH range of 2.5 to 7.7. The second reaction, involving an increase in absorption, could be directly attributable to equation (1) based on the known ΔH value of +15 kcal mol⁻¹ (6) for this reaction and the sign of the absorption change. Furthermore, in contrast to the earlier conclusions of Kustin and Eigen,² the observed rate constant (1700 s⁻¹ at 25°C and an ionic strength of 0.1 M, NaNO₃) is attributable almost entirely to k_1 in equation (1). This corresponds to a half-life of 0.4ms, which is far faster than previously reported and is consistent with our failure to observe the reaction by stopped-flow methods with its limitation that reaction times must be >2ms.

The initial decrease in absorption can be rationalized in terms of the following equation:

for which $\Delta H = +3.8$ kcal mol⁻¹ (6). The overall reaction is therefore driven to the right. By

studying this reaction at higher pH over a long period of time, I_2 , and/or HOI, slowly disproportionate to IO_3^- and I^- according to equations (3) and (4) allowing the rate of reaction (2)

to be measured as a function of iodide concentration, providing the pH is kept constant. Thus, a plot of the observed rate constant versus $[\text{I}^-]$ yields the value of k_2 as the intercept and k_{-2} as the slope. For example, at pH = 7.7, k_2 and k_{-2} were determined to be $4.3 \times 10^{-3} \text{ s}^{-1}$ and $6.6 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$, respectively, at 25°C and an ionic strength of $10^{-3} \text{ M}(\text{NaNO}_3)$.

All of the above mentioned rate constants are tentative values and more kinetic data are now being accumulated in order to obtain more definite numbers.

Spectral Characterization. A combined stopped-flow/rapid-scan spectrophotometer was used in an attempt to obtain a reproducible spectrum of the HOI/OI⁻ species. This work will continue when a suitable light source is found for the instrument, but preliminary results show the existence of a peak at, or slightly below, 370nm which may be ascribed to OI⁻, in keeping with some earlier reports.⁷ This result was obtained by mixing an acidified I_2 solution with sufficient basic solution to give a final pH of >11. At lower pH's, where the HOI species could be expected to exist, the presence of trace amounts of I_3^- formed by the hydrolysis reactions completely dominates the <400nm region of the spectrum making the assignment of an absorption band to the HOI species impossible by this technique.

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3.2.3 Predictions of Amorphous Silica Solubilities in Aqueous Mixed Electrolyte Solutions up to 300°C¹

(W. L. Marshall, C.-T. A. Chen²)

Natural waters are generally multicomponent and complicated solutions. Thus, solubility data for amorphous silica in single salt-water solutions may not easily be applied to aqueous systems in the natural environment. In a preceding study,³ the amorphous silica solubilities in separate NaCl, Na₂SO₄, MgCl₂ and MgSO₄ aqueous solutions from 25 to 300°C were shown to fit the straight line relation of the Setchenow equation,

$$\log s^{\circ}/s = Dm \quad (1)$$

where s° and s are molal solubilities of amorphous silica in water and in the salt solution, respectively, m is the molality of added salt, and D is a parameter that varies only with tem-

perature and salt type. In the present study, we show that amorphous silica solubilities in mixed aqueous electrolyte solutions can be estimated from the solubilities in the several single salt solutions.

It was assumed that the D parameter for amorphous silica solubilities at a constant temperature in salt solutions is a characteristic of the particular salt. It was also assumed that the D parameters for various salts at the same temperature are additive. For example,

$$D(\text{NaCl}) - D(\text{KCl}) = D(\text{NaNO}_3) - D(\text{KNO}_3) \quad (2)$$

or

$$D(\text{MgSO}_4) = D(\text{MgCl}_2) + D(\text{Na}_2\text{SO}_4) - 2D(\text{NaCl}). \quad (3)$$

With the D parameters at 25°C obtained from evaluations of the previous studies (Table 3.3),³⁻⁶ the left side of eq. (2) agrees with the right side to within 0.01. Similarly $D(\text{NaCl}) - D(\text{LiCl})$ agrees with $D(\text{NaNO}_3) - D(\text{LiNO}_3)$, and $D(\text{NaCl}) - D(\text{NaNO}_3)$ agrees with $D(\text{KCl}) - D(\text{KNO}_3)$ or $D(\text{LiCl})$

Table 3.3 Values of the D parameter describing solubilities of amorphous silica in several salt solutions at various temperatures

Added Salt	D (kg/mol)*					
	25°C	100°C	150°C	200°C	250°C	300°C
NaCl	0.0803	0.0619	0.0515	0.0427	0.0353	0.0295
Na ₂ SO ₄	0.0394	0.0113	-0.0129	-0.0413	-0.0742	-0.1113
MgCl ₂	0.254	0.216	0.187	0.154	0.119	0.0796
MgSO ₄	0.159	0.094	0.069	(0.027)**	(-0.025)**	(-0.091)**
NaNO ₃	0.0722	0.0574	0.0479	0.0387	0.0298	0.0212
KCl	0.028					
KNO ₃	0.025					
LiCl	0.143					
LiNO ₃	0.132					

* Calculated with the sets of three parameters in Table 7 of Chen and Marshall³ and their eq. (1) with E equal to zero.

** Estimated using eq. (3).

— $D(\text{LiNO}_3)$ to within 0.01. Other additive equations at 25°C for 1-1 salts also agree within 0.01 units. Those for 1-2, 2-1, and 2-2 salts are additive to within 0.02 to 0.03 units.

A further test of additivity is the determination whether the following equation is valid:

$$\log s^{\circ}/s(\text{mixture}) = \sum_i (D_i m_i) \quad (4)$$

where s (mixture) is the molal solubility of amorphous silica in a mixed electrolyte solution, and D_i and m_i are the D parameter and molality, respectively, of an individual electrolyte i . Solubilities of silica at 100-300°C in selected aqueous mixtures of $\text{NaCl}-\text{Na}_2\text{SO}_4$, $\text{NaCl}-\text{MgCl}_2$, $\text{NaCl}-\text{MgSO}_4$, $\text{Na}_2\text{SO}_4-\text{MgCl}_2$, $\text{Na}_2\text{SO}_4-\text{MgSO}_4$, and $\text{MgCl}_2-\text{MgSO}_4$, determined in this study, were estimated by using eq. (4) and the D parameters in Table 3.3. The average deviation between all estimated and measured values was 12%, or just 2 or 3% greater than the precision of the data. This good agreement shows that we are now able to predict, with reasonable accuracy, the solubility of amorphous silica in natural waters, brines, and their concentrates at temperatures of geochemical, geothermal, and oceanographic (including submarine hot waters) interest. This ability should have wide, practical applications.

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2. Oak Ridge Associated Universities Faculty Research Participant, 1980. Permanent address: School of Oceanography, Oregon State University, Corvallis, OR 97331.

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3.2.4 High Temperature Aqueous Sodium Phosphate Solutions — Immiscibility Boundaries and Critical Phenomena, 275-400°C¹

(W. L. Marshall)

High temperature aqueous sodium phosphate solutions of very low concentrations (0-100 ppm) have been applied to reducing scale formation in power plant steam generators.² However, in recent times a particular corrosion of steam generator tubes in nuclear pressurized water systems (the corrosion commonly defined as "thinning") was attributed in part to sodium phosphate additives. Consequently, their use in nuclear pressurized water power plants was greatly reduced, which appeared to diminish this problem. In some steam generators corrosion subsequently occurred to form oxides in the holes of support plates through which steam generator tubes passed. Continued corrosion has "dented" steam generator tubes, and has even necessitated costly replacement of some of the steam generators.

After the discovery by Broadbent et al.³ that aqueous solutions of disodium hydrogen phosphate form two immiscible liquids at temperatures near 300°C, Garnsey² proposed that the resulting concentrated and strongly corrosive solution, possibly produced by boiling concentration, may have corroded the steam generator tubes to cause "thinning". Recently, the analogous dipotassium hydrogen phosphate-water system has been studied at this Laboratory at temperatures from 100 to 400°C,⁴ motivated by the earlier work of Broadbent et al.,³ by the proposals by Garnsey,² and by knowledge that potassium salts generally are more soluble than the analogous sodium salts. Immiscibility was also discovered in the $\text{K}_2\text{HPO}_4-\text{H}_2\text{O}$ system but with a minimum temperature of 360°C, approximately 85°C higher than for Na_2HPO_4 solutions.³ Use of potassium phosphate would therefore prevent the formation of a second liquid phase in the region of operation (275-325°C) and might again make phosphates useful in eliminating particular problems of corrosion (for example, "denting") as suggested earlier.⁴ The present study on aqueous sodium phosphate solutions extends our knowledge in quantitatively

describing immiscibility boundaries for mole ratios, Na/PO_4 , varying from 1.0 to 2.0.

Figure 3.10 shows the boundaries of two-liquid formation for solutions of several constant mole ratios, Na/PO_4 . Shown also are values from Broadbent et al.³ The liquid-vapor critical temperatures (t_c) represent behavior for the dilute liquid at a composition estimated by extrapolating each immiscibility curve upward to our determined values of t_c (on Fig. 3.10 at the left terminus of the horizontal dashed straight lines). The concentrated liquid becomes more concentrated with rising temperature, and remains as a liquid at least up to a temperature of 410°C.

The Three Component Nature of the System. The several boundaries shown in Fig. 3.10 represent slices at several constant mole ratios in a three-dimensional figure for the system, $\text{Na}_2\text{O}-\text{P}_2\text{O}_5-\text{H}_2\text{O}$. The CSP (point of disappearance of immiscibility at which compositions of both phases become identical) for each curve in Fig. 3.10 appears to be at a slightly higher tempera-

ture (and composition) than the minimum temperature of immiscibility. A three-component system would not require the CSP to be at the minimum temperature. A CSP temperature higher than the minimum even substantiates the necessity for description by three or more components. It may, however, appear that the boundaries approximate behavior as separate two-component systems. For example, all critical temperatures for the dilute phases from different solution compositions of a given mole ratio, Na/PO_4 , are nearly the same. This suggests that each slice can be treated approximately as a two-component system.

Expected Behavior at Ratios above 2.0. Presently, the very large reactivity of the fused silica tubes (used for the experiments) toward solutions of high alkalinity has precluded measurements at mole ratios, Na/PO_4 , much greater than 2.0. However, immiscibility was found for solutions of ratio 2.16, with a minimum temperature of 279°C for a 37.5 wt. % sodium phosphate solution. At higher ratios, solids were the saturating phases as described in several papers in the literature. The present study should be applicable to any further consideration of phosphate additives to steam generator systems.

Fig. 3.10. Two-liquid-phase regions for condensed aqueous solution mixtures of NaH_2PO_4 and Na_2HPO_4 ; $\text{Na}/\text{PO}_4 = 1.00$ to 2.00 , 290 – 400°C .

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3.2.5 Hydrolysis of Metal Ions by the Solubility Method

(F. H. Sweeton, R. E. Mesmer)

The ions that are now being studied by this method are Al^{3+} and Co^{2+} ; the corresponding oxides being used for the solubility studies are $\text{Al}(\text{OH})_3$ (gibbsite) and $\text{Co}(\text{OH})_2$. These studies are being carried out in NaCl solutions of several concentrations in order to determine the effect of ionic strength.

The gibbsite studies at low temperatures are being made with apparatus that allows eight slurries to be equilibrated simultaneously, since this particular oxide is very slow to equilibrate. The gibbsite being used in these tests has been treated by sedimentation methods to give particle diameters in the 10-20 μ m range; this is to avoid the appreciable increase in solubility that could come from using very small particles. The slurries contain about 30% solids by volume; this high ratio serves to lower the equilibration time. During equilibration, the cylindrical Teflon bottles holding the slurries are rotated at about 2 revolutions per minute; this low rate is sufficient to bring the solids into effective contact with the solution in a semi-suspended state and minimizes the generation of fines from internal

Following equilibration, samples of the supernatant are used for determination of pH and Al concentration after being filtered through Millipore membranes with 0.22 μ m pores. The Al concentration is determined by means of an atomic absorption spectrophotometer operating in the graphite furnace mode; this mode is necessary in order to get the high sensitivity needed for many of the samples (some of the concentrations are in the 0.01 to 0.1 μ molal range). The Al is extracted into toluene using 8-quinolinol; this separates the Al from the NaCl and at the same time can reduce the volume in which the Al is held by a factor of as much as forty. As a result the sensitivity of the Al analysis can be increased forty-fold.

The extractions are carried out in tubes of silica glass sealed with Teflon stoppers. Early use of extraction tubes made of plastic and regular glass was discontinued because of appreciable background readings of Al. The ammonium hydroxide and acetic acid which are used for pH control during extraction have been specially distilled to remove traces of Al. The extracts are stored in small stoppered Pyrex tubes pending analysis. In order to increase the precision of the AA readings, parallel standards are extracted along with the unknowns, and several readings of each extract are taken for averaging.

Measurements have been made at 25°C for three NaCl concentrations in the pH range 4-6. The results at the lower pH readings appear self-consistent and reproducible, but at higher pH's the results have increased scatter. The following table shows the initial values of log Q_{s10} and log Q_{s11} that have been calculated from these data.

	NaCl Concentration (molal)		
	0.1	0.4	1.0
log Q_{s10}	8.25	8.61	8.98
log Q_{s11}	3.8	3.4	3.6

As the first part of the Co(OH)_2 study, approximately 120 grams of the hydroxide was prepared by the slow addition of a 2 M solution of CoCl_2 to 50% NaOH at 90°C under argon. The resulting preparation has particles in the 2-20 μ m range.

A sample of this material was equilibrated with a 1.0 m NaCl solution at 25°C under argon. The filtered equilibrated supernatant had a measured pH of 8.53 and a Co concentration of 189 μ m. This is equivalent to a value of 13.3 for the value of log Q_{s10} for the reaction $\text{Co(OH)}_2 + 2\text{H}^+ = \text{Co}^{2+} + \text{H}_2\text{O}$, but this is an upper limit because of possible hydrolysis.

3.2.6 On the Treatment of Pressure Effects on Ionization Constants in Aqueous Solution

(W. L. Marshall, R. E. Mesmer)

The ability to predict accurately the ionization behavior of salts (and other electrolytes) present in natural and other waters under wide conditions of temperature and pressure is highly important for applications in steam generators chemistry, geothermal energy, geochemistry, and chemical oceanography. In this respect, Fisher and Fox² recently presented molal ionization constants (K_m) of several sulfate salts in aqueous solution at pressures (P) from 1 to 2000 atm and at temperatures from 15 to 30°C. In their treatment of pressure dependency, they used the well known equation of Owen and Brinkley.³ This

equation describes changes in K_m as a function of pressure by two terms, $\Delta \bar{V}_m^o(1)$ and $\Delta \bar{K}_m^o$, which are differences at 1 atm in partial molal volumes and compressibilities between products and reactants in their standard states, respectively. Several years ago, it was shown that use of density (ρ) rather than pressure provided a simpler description and predictability of ionization behavior.⁴ The highly precise ionization constants of Fisher and Fox are applied in further demonstrating a reduction in required parameters by using density.

The equation involving density may be written in the form,

$$\log (K_m/K_m(1)) = (k-1) \cdot \log (\rho/\rho(1)) \quad (1)$$

where $K_m(1)$ and $\rho(1)$ are the molal ionization constant and the density, respectively, at 1 atm and k is a parameter defined previously.⁴ With the use of molar ionization constants, $(k-1)$ is replaced by k . The Owen-Brinkley equation applied by Fisher and Fox (their Table III) has the form,

$$\log (K_m/K_m(1)) = A \cdot (P-1) + B \cdot (P-1)^2 \quad (2)$$

where A and B are equal to $-\Delta \bar{V}_m^o(1)/(2.303 RT)$ and $0.5 \Delta \bar{K}_m^o/(2.303 RT)$, respectively, in which R is the gas constant and T is absolute temperature. Generally, $\Delta \bar{V}_m^o(1)$ and $\Delta \bar{K}_m^o$ are obtained from eq. (2), whereby A and B may be considered parameters. Equations (1) and (2) are one and two parameter equations, respectively.

Values by Fisher and Fox of K_m for $MgSO_4$, $CaSO_4$, and $NiSO_4$ over the above ranges of pressure and temperature were evaluated by least squares to obtain the parameters, standard deviations, and variances of fit for eqs. (1) and (2). The average standard deviations for all $\log K_m$ values with unit weights were 0.0048 and 0.0028 with eqs. (1) and (2), respectively, and both deviations approximate the random error in the reported values. Figure 3.11 shows deviation plots ($\log K_m(\text{calcd.}) - \log K_m(\text{obs.})$) for $MgSO_4$ at 25°C using eqs. (1) and (2), with no significant difference. This agreement is typical for the other sets of values.

Fig. 3.11. Calculated minus observed values of $\log K_m$ for $MgSO_4$ at 25°C and 1-2000 atm using the one and two parameter eqs. (1) and (2).

Advantages in using density. The values of Fisher and Fox at 15 to 30°C are for densities changing by only 7% where the two parameter eq. (2) will easily fit the data. In the Owen-Brinkley equation, $\Delta \bar{K}_m^o$ is taken to be approximately constant but is a variable over wide ranges in density.³ That is, additional parameters must be added to eq. (2) for accurate descriptions. The straight line relation of eq. (1), not restricted to the constancy of $\Delta \bar{K}_m^o$ and with no additional parameters, has been shown to describe ionization constants for densities changing by 2.5 times.⁴

Descriptions in dioxane-water solutions are excellent where, in agreement with the solvent-solute mass action equilibrium model for eq. (1), the "densities" or concentrations of water in the dioxane-water solutions are used.^{4b-d} Earlier values of Fisher⁵ for $MgSO_4$ ionization in water at 25°C and pressures up to 2000 atm together with those of Dunsmore and James⁶ in dioxane-water solutions at atmospheric pressure are described by a single straight line.^{4d} The ionization of sodium chloride in dioxane-water solutions at 100 and 300°C is described similarly as a function both of solvent composition and pressure to 4000 atm.⁷ The Owen-Brinkley equation or any other equation involving simply pressure cannot describe ionization constants varying with solvent composition, and accordingly cannot correlate these values with those varying with hydrostatic pressure.

If a single value of $\Delta\bar{V}_m^\circ$ can be obtained at atmospheric or any other pressure, the parameter k can be obtained by the relation,

$$\Delta\bar{V}_m^\circ = -(k-1)RT\beta \quad (3)$$

where β is the coefficient of compressibility of the solvent. Values of $\Delta\bar{V}_m^\circ$ at other pressures and temperatures may then simply be calculated from the pressure-volume-temperature properties of the solvent. For applications mentioned above, the relation of eq. (1) with use of density should be applied where possible for its simplicity and accuracy of prediction.

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4. GEOSCIENCES

4.1 High Temperature-High Pressure Silicate Studies

(M. T. Naney)

A high pressure (414 MPa), high temperature (1400°C) hydrogen-service internally heated pressure vessel and associated gas intensifier system are currently being installed at ORNL. System tests and initial experiments will be conducted in the fall of 1981. This apparatus will be used to simulate P-T conditions in the earth's crust to a depth of 15 km. A principal use of the equipment will be the investigation of physical properties (phase equilibria, crystallization kinetics, chemical partitioning) of model magma systems. Prototype furnace assemblies have been successfully tested to 1400°C at 100 KPa (1 atm).

4.1.1 Melting Relations and Crystallization Kinetics of Two Synthetic Basalts(M. T. Naney, J. M. Parks¹)

Two iron-free synthetic basalt compositions, B1 and B2 (Table 4.1), modeled after a quartz dolerite and a high alumina basalt, respectively² were subjects of experiments made at 100 KPa (1 atm) to investigate crystallization kinetics of basaltic magmas.

Prior to conducting crystallization experiments, the equilibrium behavior of each composition was determined in the melting interval. The liquidus temperatures for compositions B1 and B3 are 1352 ± 3 and 1375 ± 3 °C, respectively. The phase assemblage field forsterite + silicate liquid extends below the liquidus 90°C and 75°C for compositions B1 and B3 respectively. The results of equilibrium experiments were used as a guide for conducting the subsequent study of forsterite crystallization kinetics.

Samples homogenized at the liquidus temperature for 150 min were subjected to temperature drops ranging from 10°C to 90°C. Following the temperature drops samples remained at the new isotherm for periods ranging from 1 second to 5×10^3 minutes before quenching to room temperature.

Table 4.1 Composition and normative mineralogy of experimental starting materials

		Quartz Dolerite B1	High Alumina Basalt B3
wt %	SiO ₂	59.86	51.19
	Al ₂ O ₃	14.44	18.47
	MgO	13.89	15.91
	CaO	8.28	11.52
	Na ₂ O	3.05	2.82
	K ₂ O	0.47	0.09
	TOTAL	99.99	100.00
norm	or	2.78	0.56
	ab	25.70	23.60
	an	24.48	37.56
	di	12.99	15.16
	en	28.52	0.80
	fo		22.24
	qtz	5.53	
	TOTAL	100.00	99.92

Abbreviations: or, orthoclase; ab, albite; an, anorthite; di, diopside; en, enstatite; fo, forsterite; qtz, quartz.

These experiments were designed to determine crystal nucleation delay times and crystal growth kinetics as functions of bulk composition and undercooling ($\Delta T = T_{\text{liquidus}} - T_{\text{growth}}$).

Crystal nucleation delay times were determined by noting the absence or presence of crystals in a series of timed experiments. Forsterite nucleation delay times in experiments made with composition B1 were observed to vary more than 100 minutes at the same isotherm. This pattern yields a ΔT vs time plot (Fig. 4.1) in which nucleation and non-nucleation fields are separated by a time-probability field in which nucleation may or may not take place.

A similar series of experiments with composition B3 yields a ΔT vs time plot (Fig. 4.2) showing an apparently much more restricted time-probability field between nucleation and non-nucleation fields. This contrast in nucleation predictability is thought to be a function of melt viscosity. Melt viscosities were calculated using the method of Shaw.³ Composition B3 has a

Fig. 4.1. Forsterite nucleation delay (minutes) as a function of undercooling for composition B1. (Filled circles = glass; open circles = crystals.) Dashed curve marks onset of nucleation; solid curve indicates limits of predictable nucleation field.

Fig. 4.2. Forsterite nucleation delay (minutes) as a function of undercooling for composition B3. (Filled circles = glass; open circles = crystals.) Dashed curve marks onset of nucleation; solid curve indicates limits of predictable nucleation field.

relatively low liquidus viscosity ($\eta_{1648^\circ\text{K}}=36$ poise); while composition B1, exhibiting a broader time probability field, has a higher liquidus viscosity ($\eta_{1626^\circ\text{K}}=237$ poise).

Diffusivity (D) and viscosity (η) are inversely proportional as shown by the Stokes-Einstein hydrodynamic equation: $D = mRT/\eta$, where m is a function of particle size and jump distance. This relationship suggests that in liquids of low viscosity, diffusion rates will be rapid enough so that the crystallization process is not hindered. However, in higher viscosity silicate liquids diffusion may be sufficiently slowed to significantly influence crystallization. The observed behavior is thought to result from a competition between two rate limiting steps: one being diffusion controlled and the other the re-establishment of thermal equilibrium. Kinetic behavior of this type also explains the disappearance of the time-probability field for experiments of long duration (Figs. 4.1 and 4.2). For experiments of short duration and high undercooling the competition of these two processes tends to randomize nucleation. The longer the duration of an experiment, the less influence diffusion has on limiting the nucleation process.

Studies of olivine⁴ and plagioclase feldspar⁵ nucleation delay times from natural basaltic compositions show a similar correlation with melt viscosity. Olivine nucleation delay in basalts having viscosities in the range 5-53 poise (Donaldson⁴) show a sharp transition at the onset of nucleation similar to that observed for composition B3 in this study. In contrast, the nucleation delay of plagioclase observed by Gibb⁵ shows a time-probability interval similar to that observed for olivine crystallization from composition B1.

Crystal growth rates parallel to the c crystallographic direction for forsterite were calculated from observed crystal sizes and the duration of growth isotherms corrected for nucleation delay times observed in Fig. 4.1 and 4.2. A plot of growth rate versus growth isotherm duration shows that growth rate decreases from initial values as high as 1×10^{-3} cm/sec to growth rates in the range 10^{-7} to 10^{-6} cm/sec

for experiments of 24 hours (8.64×10^4 sec) duration with composition B3. A similar growth rate versus growth isotherm duration relationship was observed for experiments made with composition B1.

Growth rates obtained at the same undercooling in general appear as linear trends in Fig. 4.3, and growth rates for experiments made at large ΔT in general are greater than those made at

Fig. 4.3. Change of forsterite growth rate as a function of experiment duration, composition B3. Linear least squares fits are shown for each isotherm investigated.

smaller ΔT . The observed growth rate changes may be produced by either the approach of the system to an equilibrium distribution of crystals and liquid, or diffusion limitations on growth.

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4.1.2 Melting and Crystallization Kinetics of a Two-Pyroxene Andesite

(M. T. Naney, S. E. Swanson¹)

High temperature controlled atmosphere experiments were conducted at one atmosphere to investigate melting and crystallization kinetics of porphyritic andesite from Dennison Volcano, Alaska. The rock contains phenocrysts of plagioclase (Pl, 24%), hypersthene (Opx, 5%), and augite (Cpx, 4%) together with an opaque phase (1%) in a groundmass composed of Pl, Opx, Cpx, and opaque microlites plus interstitial glass (L). All experiments were conducted in a CO + CO₂ atmosphere such that f_{O_2} was maintained at 1.75 log-units above the QFM buffer curve, analogous to a trend observed for many calc-alkaline rocks.

Melting experiments bracketing the liquidus show that the reaction $Pl + L \rightarrow L$ takes place at $1242.5 \pm 2^\circ C$. The Pl + L field extends approximately $30^\circ C$ below the liquidus. The stable phase assemblage below $1207 \pm 6^\circ C$ is Pl + Opx + L.

A series of experiments at $1243^\circ C$ were conducted to investigate melting kinetics. These experiments indicate that a crystal-free glass (R.I. = 1.535) is produced when samples are held at this isotherm for times greater than 1050 minutes. Experiment durations in excess of 2300 minutes were required for air bubble migration and elimination from sample interiors. The time required for equilibration of samples to the f_{O_2} imposed by the furnace CO + CO₂ atmosphere was determined using the same set of experiments. Colorimetric determinations of the ferrous and ferric iron contents of these samples indicate that redox equilibrium is reached in approximately 1440 minutes (Fig. 4.4).

A series of experiments were conducted to investigate groundmass textural development in andesitic rocks. Isothermal crystallization experiments were made to determine the growth rate of Pl as a function of undercooling ($\Delta T = T_{liquidus} - T_{growth}$). Samples were initially held at $1243^\circ C$ for 360 minutes to produce a liquid containing residual Pl crystallites. Temperature was subse-

Fig. 4.4 FeO equilibration kinetics for andesite of Dennison Volcano, Alaska at liquidus (1242.5°C) and $\log f_{O_2} = -6.05$. Data fitted to equation: $y(\text{FeO}) = 4.31772 (1 - 0.74978 e^{** - 129787 t})$; t in hours.

quently lowered to a new isotherm to initiate crystal growth in the presence of Pl nuclei. The presence of Pl crystallites eliminated the problem of sluggish nucleation often observed in silicic system. Crystal growth rates for Pl varied from 2.3×10^{-8} cm/sec. for $\Delta T = 20^\circ\text{C}$ to 3.6×10^{-7} cm/sec for $\Delta T = 65^\circ\text{C}$.

1. University of Alaska, ORAU visiting scientist.

4.2 Hydrothermal Geochemistry of Natural Materials at Elevated Temperatures and Pressures

4.2.1 Solubilities and Reaction Kinetics of Quartz with Aqueous Salt Solutions at 300°C and 20 MPa

(F. W. Dickson)

Quartz and amorphous silica were reacted with aqueous solutions from 300 to 325°C as part of our program on mineral-solution interactions. The reactions were done in 2 types of equipment. Rocking titanium alloy pressure vessels of 58 cm³ capacity described by Gill and Marshall,¹ were used for studies at the vapor pressures of the solutions. A static flow-through titanium

pressure vessel, also of 58 cm³ volume, with connections in the base and the top that permitted fresh fluid to be pumped in the bottom while reacted fluid was taken out at the top, was used to study the reactions of quartz with H₂O.

Coarse natural sand (Ottawa), leached by HNO₃ to remove iron coatings and with NaOH to remove fines or sharp edges, was used in the experiments rather than finely powdered quartz which tends to produce anomalous data. Commercial amorphous silica was repeatedly shaken in distilled H₂O, and the fines were decanted until rapid settling produced clear supernatant liquid. Stock solutions, H₂O and NaNO₃-H₂O, were prepared from distilled H₂O and reagent NaNO₃.

Internally filtered samples of solution were withdrawn from the equipment at regular intervals and analyzed for SiO₂ by a silico-molybdate colorimetric procedure,² with the use of a Bausch and Lomb Spectronic 710 spectrophotometer. The Spectronic 710 was stable and produced data reproducible to 1 part in 800. NaNO₃ was determined gravimetrically, by weighing as NaNO₃ or as Na₂SO₄ after conversion of the NaNO₃. Both methods gave equivalent results.

Table 4.2 presents some results of the reactions of Ottawa quartz with H_2O and NaNO_3 solutions at 300°C and solution vapor pressures. Quartz reacts with H_2O by the following equation:

H_4SiO_4 weakly dissociates to H^+ and H_3SiO_4^- , but H_4SiO_4 remains the dominant species, as an uncharged molecule. The addition of NaCl has been shown experimentally to decrease quartz solubility at 300°C but to increase it at 350°C and above.⁴ No prior study of the effect of NaNO_3 at elevated temperatures exist for comparison. The data of Table 4.2 show that NaNO_3 increases quartz solubility to a maximum of 11.8 millimolal SiO_2 at about 1.5 molal NaNO_3 . Clearly a solubility

Table 4.2 Reaction of 1 g Ottawa quartz sand with 34 g H_2O and NaNO_3 solutions at 300°C and vapor pressures of the solutions for 12 days.

NaNO_3 molal	SiO_2 millimolal
0.00	10.99
0.51	10.97
1.10	11.74
1.97	11.62
2.97	11.57
5.09	10.76
5.93	9.57

enhancing reaction is dominating over the salting-out effect at low NaNO_3 concentrations. Controlled investigations are needed to deduce the compositions of solution species. Reactions with either sodium ion or nitrate ion must be considered along with the changes that occur in the density of the solution due to the presence of electrolyte. Our value for the solubility in pure H_2O , 10.8 millimoles SiO_2 , is 8% higher than some values in the literature, 10.00⁵ but lower than Kennedy's original value of 11.5.⁶

The reactions of 100 g of Ottawa quartz with about 21 g H_2O at 20 MPa at 300°C and 326°C for several days yielded solubility values of 11.77 and 12.25 millimolal, respectively. These compare very well with literature values of 11.78

and 12.02 millimolal SiO_2 for the same temperatures.

Four grams of amorphous silica was reacted for 14 hours with 34 g of 1 molal NaNO_3 solution at 300°C and at the solution vapor pressure for 14 hours in rocking titanium equipment. Internally filtered liquid samples were withdrawn into hypodermic syringes and each was subdivided into two portions, one filtered further through a 0.22 μm millipore filter, and the other analyzed without filtering. Table 4.3 shows the results of the experiment. The amorphous silica reacted rapidly. The solution reaches a slowly varying SiO_2 concentration by 1.67 hours. No significant

Table 4.3 Concentrations of SiO_2 in 1 molal solution of NaNO_3 reacted with 4 g amorphous silica at 300°C and solution vapor pressure in rocking titanium vessel equipment.

Lapsed Time Hours	SiO_2 millimolal	
	Filtered	Unfiltered
0.17	15.00	15.32
0.67	18.15	18.70
1.67	19.50	19.43
4.0	19.30	19.18
14.0	19.03	18.70

differences are apparent between unfiltered and filtered samples, except for the ones taken at 0.67 hours, which show anomalous overshoot in silica of the filtered solution and an equally anomalous undershoot of the silica of the unfiltered solution. The steady values of about 19.2 millimolal most likely is the best value for the solubility of amorphous silica from the batch prepared for this study. Marshall reported a value of 22.8 millimolal SiO_2 for 1 molal NaNO_3 .⁷ The cause of the difference is not clear; however, amorphous silica is notoriously variable in its properties from batch to batch. No changes in the solid phase were detected by microscope and x-ray diffractometer examinations. Recrystallization to cristobalite happened in other experiments permitted to react for 300 hours or more.

The reactions of amorphous silica with aqueous solutions should proceed differently from the quartz reaction because of the presence of water in amorphous silica:

Further studies of the solubility of amorphous silica in aqueous NaNO_3 are being made at 300°C to clarify the water dependency of this reaction.

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4.2.2 Basalt-Seawater Reactions at 400°C and 500°C , 1000 bars

(D. C. Pohl,¹ F. W. Dickson)

The recognition that seawater flows through sea-floor basalts at surprisingly fast rates at spreading centers has developed over the past few years from a growing body of experimental, mineralogical, trace element and isotopic data. Times required for a volume of seawater equal to all the oceans pass through the earth's spreading centers have been calculated to be 3 to 10 million years. This recognition, coupled with the knowledge that the basalt crust of the ocean floors is renewed in 200 million years or so, cause data on basalt-seawater reactions over geologically applicable ranges of temperatures and pressures to be important in working out geochemical balances for the crustal-seawater system.² Basalts of the sea floor have in places been altered by Na-rich solutions at temperatures up to 500°C and higher. Therefore, basalt-seawater reactions were done at 400°C and 500°C , 1000 bars, to extend existing experimental coverage.³⁻⁶

Seawater (Table 4.4) was reacted with -100 mesh powdered natural basaltic glass (Table 4.4) at initial mass ratio of seawater to basalt (W/R) of 10/1 for up to 33 days in rocking gold cell equipment in the Hydrothermal Laboratory, Geology Department, Stanford University. Internally filtered liquid samples withdrawn from the gold cell at regular intervals were analyzed for major and minor components. The solids in the cell removed at the close of each experiment were examined by microscope, x-ray diffractometer, and electron-microprobe methods.

Solid phases produced by the 400°C reaction were anhydrite, smectite, alkali-montmorillonite, prehnite and tremolite. Solids that formed at 500°C were the same except that prehnite and alkali-montmorillonite were absent, and inter-layered chlorite-montmorillonite and minor hematite were present. The solids formed at both temperatures were for the most part those found in basalts altered by Na-rich solutions at moderate to high grades of metamorphism.

Table 4.4

Chemical compositions of Juan da Fuca basalt glass and Cerops II seawater used in experiments

Basalt Glass ¹		Seawater ²	
Component	wt. %	Component ³	ppm ⁴
SiO_2	50.10	Na	10463
Al_2O_3	14.80	K	394
FeO	12.61	Ca	400
MgO	7.00	Mg	1240
CaO	11.10	Sr	8.1
Na_2O	2.57	Cl	19760
K_2O	0.14	SO_4	2695
TiO_2	1.28	Ba	280*
MnO	0.22	Mn	1.25
Ignition Loss	0.10	Zn	0.3
TOTAL	99.20		

¹Analysis by Seyfried and Bischoff (1977).

²Collected during Cerops II expedition.

³Asterisk indicates ppb.

⁴Si, Al, Fe, Cu, Ni below detection.

Seawater reacted rapidly with the basalt glass at both 400°C and 500°C, with most solution components achieving steady or slowly changing concentrations in 3 days. Figures 4.5 and 4.6 show the time dependencies for some solution components and H^+ activities measured at room conditions for 400°C and 500°C, respectively. The acidities of the reacted solutions increased from the 6.3×10^{-9} of seawater to 3.2×10^{-5} at 400°C and 3.2×10^{-4} at 500°C, showing a dependence on temperature. The causes of the

Fig. 4.5. 400°C, 1000 bars. Time dependencies of solution components in reaction of basalt glass with seawater. Numbers below component symbols are dividers chosen for convenience in plotting. Meaning of symbols: $\blacksquare$, $H^+ \times 10^5$; $\blacktriangle$, $SiO_2/100$; $\bullet$, $Na/100$; $\blacklozenge$, $K/100$; $\bullet$, $Mg/10$; $\square$, $Sr/10$; $\blacktriangle$, Fe ; $\circ$, $Mn/10$; $\diamond$, $Ca/100$; $\circ$, Al .

increased acidities rest in the formation of solid phases, a process which consumes OH^- or O^{2-} of solution H_2O to create hydroxy or oxy layers in mineral structures. Mg and SO_4 concentrations dropped sharply because of the formation of clays and the precipitation of Mg hydroxy sulfate and $CaSO_4$. Sodium dropped slightly at 500°C; because of the high concentration of Na in seawater, a slight decrease implies that the reaction could create significant Na fluxes. K, and

Fig. 4.6. 500°C, 1000 bars. Time dependencies of solution components in reaction of basalt glass with seawater. Numbers below component symbols are dividers chosen for convenience in plotting. Meaning of symbols: $\blacksquare$, $H^+ \times 10^4$; $\blacktriangle$, $SiO_2/100$; $\bullet$, $Na/100$; $\blacklozenge$, $K/100$; $\bullet$, Mg ; $\square$, $Sr/10$; $\blacktriangle$, Fe ; $\circ$, Mn ; $\diamond$, $Ca/1000$; $\circ$, $Al/10$.

eventually Ca, values rose; about 50% of the low level of K in the rock was solubilized. These elements are involved in mineral-solution reactions and surface-dominated processes which require a net loss from the rock of K and Ca. SiO_2 concentrations rose to above quartz saturation levels in the H_2O . The overall reaction transformed the alkaline seawater solution, dominated by Na, Mg, Ca, K, Cl, and SO_4 , to acid solutions of Na, Si and Cl enriched in Ca and K. The chemical nature of the reacted solutions is similar to solutions responsible for mass transport and deposition in natural metamorphic and hydrothermal systems of the earth's crust.

Minor constituents were selectively leached from the rocks. Typically, solutions were enriched 100-fold in Cu and Zn, and 200-fold in Fe and Mn. The Fe to Mn ratio, 2:1 at 400°C, was 12:1 at 500°C. Ba and Sr were at about the same level at 400°C and 500°C, with Na having increased 3-fold over the seawater level and Sr having decreased to 1/3 of seawater values. H_2S contents of the solutions was temperature de-

pendent, 20 ppm at 400°C and 80 ppm at 500°C. The heavy metals and sulfide contents of the solutions were high enough to account for heavy metal precipitates at vents on the spreading centers and the formation of large base metal deposits of the Troodos type. The implied fluxes of H^+ , K, Na and Ca aid mass exchange calculations in the basalt-seawater system.

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4.2.3 Reactions with Glassy Basalt with H_2O , $Na_2CO_3-H_2O$, and $NaHCO_3-H_2O$ at 300°C and 50 MPa

(Yishan Zeng,¹ J. G. Liou,² F. W. Dickson)

As part of a continuing series of experiments on the reactions of basalt with aqueous solutions in the Hydrothermal Laboratory, Geology Department, Stanford University,¹⁻⁴ the reactions of basalt glass with aqueous carbonate solutions, with and without NaCl, were studied by rocking Dickson gold-cell and static sealed gold capsule techniques, at 300°C and 500 bars, and at a solution to rock mass ratio of 10. Solution compositions were: 0.14 and 0.5% $NaHCO_3$; 0.5% Na_2CO_3 ; 0.076% NaCl + 0.0088% $NaHCO_3$; and 0.046% NaCl + 0.077% $NaHCO_3$; 0.1% NaCl; and simple H_2O . Seven gold-cell experiments using the different solution types were duplicated by 7 sealed gold tube experiments. Major and minor element concentrations, Cl and total CO_2 contents, and room temperature pH values were determined. The solids resulting from the experiments were identified and analyzed by microscope, x-ray diffractometer, electron microprobe and scanning electron microscope methods.

Solutions reacted rapidly with the basalt glass, and slowly changing states were achieved

in about 3 days. Table 4.5 presents a summary of the experimental data; under each component is listed in sequence the initial concentration, the range of concentrations during the reaction, the average steady state values with the number of data points included in the averaging (in parentheses to the right), and the concentration in the rest fluid in the gold-cell after cooling to room temperature (at constant pressure). The pH values of all solutions except H_2O drifted to slightly acid values (as measured at room conditions); a pH of 8.7 developed in the simple H_2O solutions. SiO_2 rapidly grew in concentration to steady values from 924 to 1340 ppm, which exceed H_2O solubility of quartz at the conditions. Values of K rose to 17 to 42 ppm, by dissolution of glass and cation exchanges. The Al values showed large maxima at first samplings, from 18.5 to 92.4 ppm, and steadied to 2 to 6 ppm. The Na in the solution was consumed during the reactions, and dropped to 88 to 7% of the original values, except for Na in the reaction with pure H_2O , which rose to 61 ppm. The Na was incorporated in the clays and zeolites, and possibly in a Na- CO_2 -containing solid phase. Total CO_2 remained nil in the pure water solution, but rose to 20 ppm in the 0.10% NaCl solution. Presumably CO_2 in the basalt was more effectively extracted by the slightly acid dilute NaCl solution. The total CO_2 in other solutions dropped to steady values that ranged from 5% to 72% of original CO_2 contents of solution. The changing solution concentrations reflect processes of glass hydration, formation of transitory phases, ion exchange on surfaces, precipitation of minerals from solution, and conversion of glass to alteration silicate solid phases. The system did not reach overall equilibrium but some solution parameters (Na and K) approached ratios that exist for equilibrium at 300°C.

At the close of experiments solutions and solids remaining in the gold-cell were brought to room temperature at 500 bars while not rocking. The process took from 0.5 hours to several hours. So called "quench" samples were withdrawn for analysis to gain estimates of the extents of back reactions during cooling. The last figure in each set of numbers in Table 4.5 is the

Table 4.5 The experimental data on the reaction of powdered basalt glass, -100 to -325 mesh, with aqueous solutions at 300°C, 500 bars and 10 to 1 initial solution to rock mass ratios for 21 to 36 days, in rocking gold-cell hydrothermal equipment. All concentrations are in ppm. Each entry is divided into four parts: original concentration/range in concentration during the reaction/average steady concentration (number of data points used in averaging)/concentration in quenched fluid in gold-cell at room temperature and 500 bars.

Solution Type	Time Days	No. of Samplings	pH	SiO ₂	K
1. H ₂ O	30	5	6.7/7.8-8.7/8.7(5)/9.2	0/184-1293/1290(2)/812	0/14-19/17(5)/15
2. 0.10% NaCl	36	7	7.5/6.6-8.1/6.9(6)/8.2	0/175-1183/1161(6)/671	0/20-42/42(6)/21
3. 0.14% NaHCO ₃	21	6	8.6/7.8-5.9/5.9(2)/6.2	0/443-1248/1108(3)/285	0/12-21/18(5)/25
4. 0.50% NaHCO ₃	28	5	9.3/9.1-6.7/6.7(4)/7.5	0/551-1042/994(4)/794	0/10-19/17(4)/33
5. 0.50% Na ₂ CO ₃	32	5	11.2/11.0-6.4/6.8(4)/7.1	0/637-924/902(4)/861	0/11-20/19(4)/14
6. 0.008% NaHCO ₃ + 0.076% NaCl	27	8	7.6/8.6-6.4/6.7(5)/6.6	0/330-1344/1340(2)/1203	0/22-53/42(7)/49
7. 0.077% NaHCO ₃ + 0.046% NaCl	35	9	8.6/8.0-6.2/6.3(8)/6.4	0/285-1100/1063(8)/1033	0/8-37/31(8)/41

Solution Type	Al	Na	ΣCO ₂
1	0/92.4-4.5/6.4(3)/6.9	0/18-64/61(4)/57	0/0/0/0
2	0/20.1-1.1/2.1(6)/0.4	393/368-313/313(1)/315	0/15-23/20(7)/18
3	0/37.8-2.2/2.4(2)/1/9	393/273-80/90(5)/162	753/532-79/79(1)/286
4	0/92.7-5.3/6.6(4)/3.9	1369/1263-107/115(3)/186	2619/1230-120/129(3)/365
5	0/87.5-6.3/6.6(3)/5.0	2170/1890-120/124(3)/151	2075/1528-167/180(3)/304
6	0/18.5-1.7/2.4(4)/2.5	329/323-289/294(4)/291	46/46-26/33(7)/33
7	0/35.2-2.6/3.3(7)/0.7	393/373-184/199(8)/233	405/376-139/161(8)/390

quench value. Most constituents showed significant changes. SiO₂, for example, dropped to an average of 73% of the steady state values, but it ranged widely, from 26% to 97%. Sodium showed drops, increases and constancy. Total CO₂ increased the most, 208% on the average, and ranged from 90% to 362%. The solutions, therefore were not only unquenchable, but were highly variable in their departures from quenchability. The implications are that back reactions during quenching are to be expected, even for constituents such as SiO₂, which is known to display slow solution reactions. Some of the back reactions are caused by dissolution of solids with retrograde solubility (carbonate), and others reflect reversals in ion exchange processes on solids.

Minor elements appeared in solution at geochemically significant levels. The NaCl dominated solutions and H₂O solutions were especially effective in extracting ppm levels of Fe, V, Mo, Cu, Zn, and 0.1 ppm levels of Ag. The overall reaction of the dilute solutions with basalt glass produced SiO₂ charged solutions of types found in geothermal systems which have been thought to have been involved in ore deposition.

The basalt glass altered during long experiments to the same solid phases regardless of the chemical compositions of the starting solutions. A characteristic sequence of formation of the solid phases was observed: Fe-smectite, Ca-rich montmorillonite, a Na-Ca zeolite (analcime-wairakite solid solutions), and calcite for high

CO₂ solutions. Chabazite formed in the sealed tube experiments within a few hours to several days as a transitory phase, which subsequently transformed to analcime-wairakite. The individual solid phases showed solid solution compositional variability which appeared to have been controlled by differences in solution composition.

The changes in solution compositions and the parageneses of the solids were similar for all experiments, demonstrating the indifference of the reactions to initial solution composition over the small ranges of concentration involved. The H₂O in the solutions had an important role in the alteration of basalt. Early in the reaction, beginning during the initial heating stages, H₂O migrated into the glass (hydration reaction) and converted components of the glass into Fe-smectite. Components such as Si, Ca, Al, Na, and K not consumed by the reaction tended to migrate into aqueous solution; some solids were subsequently produced by combined precipitation and further reactions with glass and previously formed alteration products. The original non-rock components in solution, Na, HCO₃, CO₃, had little control on the nature of the solids formed, except for calcite and possibly some Na, CO₃-containing phase.

The initial compositions of the solutions appear to have affected the ratio of constituents in solids showing solid solution behavior. For example, Ca-poor zeolite formed in contact with Na-rich solutions and Ca-rich zeolite was formed in experiments with the simple H₂O and dilute Na solutions.

The assemblages of solids produced in the experiments are similar to assemblages found by other researchers.⁶⁻⁹ Such differences as exist can be explained by the higher concentrations and different compositions of solutions used by other workers.

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4.3 Equilibrium Measurements and Thermodynamic Modeling at High Temperatures

4.3.1 Association Constants for Magnesium Chloride and Calcium Chloride in Aqueous Solutions at Temperatures from 25 to 600°C and Pressures to 4000 Bars^{1,2}

(J. D. Frantz,³ W. L. Marshall)

Knowledge of the ionization behavior of electrolytes in aqueous solutions at high temperatures and pressures is important to understanding and thereby predicting transport phenomena, solubility equilibria, and hydrolytic behavior in multicomponent natural waters including supercritical steam. We have now obtained the ionization constants of two salts, CaCl₂ and MgCl₂, which are greatly important but which were not yet studied. Electrical conductances of these two salts in dilute aqueous solutions were measured at high temperatures and pressures. The results show that CaCl₂ and MgCl₂ at low concentrations exist primarily as Ca²⁺, Mg²⁺, and Cl⁻ ions at temperatures below 400°C and densities greater than 0.75 g cm⁻³. At higher temperatures significant ion-pairing was detected. With the first and second ionization constants for each salt obtained from these measurements, the distributions of aqueous species can now be calculated over wide ranges of temperature, pressure, and concentration.

By methods described in the paper,¹ the first (K₁) and second (K₂) ionization constants of CaCl₂ and MgCl₂ were obtained at temperatures up to 600°C and pressures to 4000 bars. For CaCl₂, the two constants describe the equilibria.

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Analogous equilibria exist for MgCl_2 . Plots of $\log K_1$ and $\log K_2$ for CaCl_2 and MgCl_2 against $\log d(\text{H}_2\text{O})$ at several temperatures are shown in Figs. 4.7 and 4.8. In these plots, where $d(\text{H}_2\text{O})$ is the density of the solvent H_2O , we observe the straight line relations observed earlier in the description of ionization constants of many electrolytes.⁴ Moreover, the value of

Fig. 4.7. The logarithms of the first (Part A) and second (Part B) ionization constants (molal units) of CaCl_2 in aqueous solution plotted against $\log$ density (g/cm^3) of water; 400-600°C and at pressures to 4000 bars.

Fig. 4.8. The logarithms of the first (Part A) and second (Part B) ionization constants (molal units) of MgCl_2 in aqueous solutions plotted against $\log$ density (g/cm^3) of water; 400-600°C and at pressures up to 4000 bars.

all slopes for $\log K_1$ vs $\log d(\text{H}_2\text{O})$ is 10, the same number that is obtained for 1-1 salts.⁴ The determined values of K_1 and K_2 for MgCl_2 behave similarly.

The equations for describing K_1 and K_2 as a function of density and temperature, obtained from least squares fits of the values, are given as follows:

$$\log K_1 (\text{CaCl}_2 \text{ or } \text{MgCl}_2) = -3.21 + 2407/T + 10.6 \log d(\text{H}_2\text{O}) \quad (3)$$

$$\log K_2(\text{CaCl}_2) = -5.05 + 3112./T + 16.5 \log d(\text{H}_2\text{O}) \quad (4)$$

$$\log K_2(\text{MgCl}_2) = -4.80 + 3415./T + 19.2 \log d(\text{H}_2\text{O}) \quad (5)$$

where T is absolute temperature, $d(\text{H}_2\text{O})$ is the density of water in g cm^{-3} , and the constants (K_1, K_2) are in units of molality.

Hydrolysis and precipitation of $\text{Mg}(\text{OH})_2$ (brucite) or MgO (periclase) at temperatures of 500°C and above prevented the determination of the first ionization constants of MgCl_2 at densities below 0.55. It was possible, however, to calculate constants from measurements taken from solutions at higher densities. The results of these calculations for MgCl_2 agreed well with those of CaCl_2 , and thus it was assumed that the first ionization constants of MgCl_2 and CaCl_2 were identical, as described above by eq. (3). This assumption is especially reasonable in view of the similarities found among the ionization constants of 1-1 electrolytes.⁴

Conclusions. This study quantitatively describes the ionization behavior of the aqueous 2-1 electrolyte salts MgCl_2 and CaCl_2 at high temperatures and pressures. With the behavior of BaCl_2 presented earlier by Ritzert and Franck,⁵ three 2-1 salts have now been studied under supercritical conditions. Several new conclusions can be made from the present study. First, not only do isothermal plots of $\log K$ vs. $\log d(\text{H}_2\text{O})$ produce straight lines for both the first and second ionization constants of each salt, the slopes for K_1 have essentially the same values as for the 1-1 electrolytes studied earlier.⁴ Both are independent of temperature above 300°C. Moreover, the actual values of $\log K_1$ at a given density and temperature are within 0.5 logarithmic unit of the values for the 1-1 electrolytes. Thus, the first ionization constant of MgCl_2 and CaCl_2 (which actually represents the ionization of a pseudo 1-1 electrolyte salt) follows essentially the same quantitative trends as the simple 1-1 electrolyte salts.

Second, the simplicity of the observed ionization behavior of both 2-1 and 1-1 electrolyte

salts at temperatures above 300°C provides a form of equation that should yield reliable values of ionization constants in regions of temperature and pressure outside those of the experiments. The ionization constants for a given equilibrium above 300°C are calculated from three parameters that are independent of temperature and density as summarized previously for the 1-1 electrolyte salts.⁴ Combination of the ionization constants for MgCl_2 and CaCl_2 with those of the 1-1 electrolytes will now yield quantitative descriptions at elevated temperatures and pressures of ionization equilibria in mixed aqueous salt systems containing alkaline earth elements. These calculations may be used for the prediction of properties mentioned above, especially for applications to geochemistry, geothermal energy, hydrothermal oceanography, and steam generator chemistry.

1. Summary of paper in press: Amer. J. Sci. (1981). This paper will also be summarized in Annual Report of the Director of the Geophysical Laboratory 1980-81 (Carnegie Institution of Washington, Yearbook 80). The first part of the study is summarized in Chem. Div. Annu. Prog. Rep. ORNL-5665, p. 43.

2. Work co-sponsored by Carnegie Institution of Washington, Geophysical Laboratory, Washington, D.C. A portion of this study was sponsored by the Earth Sciences Section, National Science Foundation, NSF Grant EAR-7814274.

3. Guest scientist from Carnegie Institution of Washington Geophysical Laboratory, Washington, D.C.

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4.3.2 Amorphous Silica Solubilities in Pure Water and Aqueous Sodium Chloride, Sodium Sulfate, Magnesium Chloride, and Magnesium Sulfate Solutions up to 300°C¹

(C.-T. A. Chen,² W. L. Marshall)

It has commonly been assumed by geochemists that the solubility of silica in aqueous solutions does not change greatly from that in water for low concentrations of dissolved salts. Without quantitative information, silica solu-

bilities in pure water thus have been used frequently as an approximation for geochemical calculations in natural waters. Recently at ORNL, the solubility of amorphous silica was measured in aqueous NaNO_3 solutions (25 to 300°C)³ and in a number of other aqueous salt solutions at 25°C.⁴ It was found for all the solutions studied that the solubility of amorphous silica decreased with increasing concentration of dissolved salt. We have now determined solubilities at temperatures up to 300°C in separate salt solutions of NaCl , Na_2SO_4 , MgCl_2 , and MgSO_4 . Solubilities in these solutions, containing the major components of seawater and other natural waters are of interest to geochemistry, geothermal energy and chemical oceanography. There should be significance in evaluating silica behavior in the recently discovered regions of hydrothermal seawater.

The molal solubilities of amorphous silica in pure water and in aqueous NaCl , Na_2SO_4 , and MgSO_4 solutions at temperatures up to 300°C are shown in Fig. 4.9. The solubilities in NaCl solutions (Fig. 4.9a, filled triangles) are close to those in NaNO_3 (Fig. 4.9a, open triangles) as expected previously.^{3,4} Solubilities in Na_2SO_4 solutions decrease slightly at high salt concentrations at 25°C, but remain essentially constant at 100°C. These solubilities increase gradually with salt concentration at 150°C and increase sharply at temperatures above 250°C. Solubilities in MgCl_2 solutions all decrease sharply at high salt concentrations. There is indication that some cristobalite (one crystalline form of SiO_2) was formed at temperatures below 300°C in MgCl_2 solutions. This may have contributed to the scatter of the data. The solubility measurements in MgSO_4 solutions

Fig. 4.9. The molal solubility of amorphous silica in aqueous NaCl , Na_2SO_4 , MgCl_2 , and MgSO_4 solutions, 25-300°C.

covered a small concentration range because of the hydrolytic instability of MgSO_4 in water solutions at high temperatures.⁵ These data show that MgSO_4 also depresses the solubility of amorphous silica.

The solubility values in each salt were fitted to the following empirical equation:

$$\log s = \log s^\circ - Dm - Em^2 \quad (1)$$

where s and s° are the molal solubilities in the salt solutions and in pure water, respectively, m is the molality of the salt, and D and E are functions of absolute temperature,

$$D = a + bT + cT^2 \quad (1a)$$

$$E = d + eT + fT^2 \quad (1b)$$

The terms a , b , c , d , e , and f are constants. $\log s^\circ$ was described previously as a function of temperature,³ and parameters for eq. (1) for NaCl , Na_2SO_4 , MgCl_2 , and MgSO_4 solutions are given in Table 4.6 along with the standard deviations of the fit.

Activity Coefficients. Activity coefficients for dissolved silica can be defined as s°/s based on either molality or molarity (this definition incorporates into γ any explicit dependence on water activity and any changes in the solid phase as the solution composition is varied).^{6,7} Thus, the molal activity coefficients may be related to the salt molality as follows:

$$\log \gamma = Dm + Em^2 \quad (2)$$

The logarithms of molal activity coefficients ($\log \gamma$) in NaCl , Na_2SO_4 , MgCl_2 , and MgSO_4 solutions are plotted against molality in Fig. 4.10

These were calculated by eq. (1). The plots show clearly that the dissolved silica activity coefficients in all four solutions increase with increasing salt molality at 25°C and that the activity coefficients decrease with increasing temperature. For those in Na_2SO_4 , the values of $\log \gamma$ become negative at temperatures higher than 100°C. In a later study we will postulate a 1:1 solution complex of Si(OH)_4 and SO_4^{2-} to account for this behavior.⁸

The results of this study have been combined with another study at ORNL on the solubility of amorphous silica in aqueous mixed salt solutions at temperatures up to 300°C.⁹ Correlation of these two studies by the assumption that salt effects are additive now allows us to predict the solubility of silica in natural waters of widely varying compositions and over a wide range of temperatures. There should be substantial application to environmental behavior.

1. Summary of paper in press: *Geochim. Cosmochim. Acta* (1981); *Chem. Div. Annu. Prog. Rep.* on related studies: this report, part 3.2.3; *Chem. Div. Annu. Prog. Rep.* ORNL-5665, p. 38; ORNL-5485, p. 33; ORNL-5297, p. 22.

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Table 4.6

Parameters for eqn. (1) describing the effect of salt on the solubility of amorphous silica (based on molality)

	$10a$	10^4b	10^7c	10^2d	10^4e	10^7f	Std. dev.: %
NaCl	0.31949	4.6982	-8.7442	3.1961	-1.8951	2.4453	6.4
Na_2SO_4	0.7087	3.8692	-13.648	-0.61449	-1.2489	3.1330	4.4
MgCl_2	4.4621	1.7798	-16.354	-2.7712	-0.4324	2.0922	23.6
MgSO_4	-9.6086	59.306	-78.775	35.959	-15.729	14.690	5.8

Fig. 4.10. Log γ for solubility of amorphous silica in aqueous NaCl, Na₂SO₄, MgCl₂, and MgSO₄ solutions vs. salt molality at 25 to 300°C.

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4.3.3 Gas Solubilities in High Temperature Aqueous NaCl Solutions

(S. E. Drummond)

The solubilities of CO₂ and H₂S have been measured in 0-6 m sodium chloride solutions to 400°C by a P-V-T mass balance method. Most of the solubility measurements were at low partial gas pressure (<100 atm CO₂ and <30 atm H₂S) and

easily normalized to infinite dilution Henry's Law constants by:

$$\ln K_H^\circ = \ln K_H^P - (\bar{V}_{\text{gas}} \cdot P_{\text{gas}}/RT)$$

where K_H° is Henry's Law constant in the limit of infinite gas dilution, expressed as fugacity (atm)/molality, K_H^P is the f/m ratio at any given experimental gas pressure, $\bar{V}_{\text{gas}}$ is the partial molal volume of the gas in solution, and P_{gas} is the gas partial pressure. Values of K_H for CO₂ and H₂S were regressed to the following equations:

$$\begin{aligned} \ln K_H^\circ (\text{CO}_2) = & 20.44 - 9016323T - 1.0312 X - 3629.7/T \\ & + 0.4445/X + 0.0012896XT + 255.9X/T \\ & - 0.001606T/X \quad (R^2 = 98.7\%) \end{aligned}$$

$$\ln K_H^{\circ}(\text{H}_2\text{S}) = 11.416 - 0.007013T + 0.2905X \\ - 2067.7/T + 0.5705/X - 0.0001574XT \\ - 46.2X/T - 0.001777T/X \quad (R^2 = 98.5)$$

where T is Kelvin and X is the NaCl molality plus 1.0. These data are plotted in Figs. 4.11 and 4.12.

Carbon dioxide solubility decreases (i.e., K_H° increases) sharply from 25° to 150°C, levels off to a broad minimum centered around 200°C, and then increases gradually and continuously with increasing temperature. The solubility minimum shifts from 175°C in pure water to about 220°C in 6 m sodium chloride solutions. The position of the solubility minimum has about 10° uncertainty due to the broad, flat nature of the minimum and uncertainty in the experimental values ($\pm 0.12 \ln K_H^{\circ}$ at the 90% level). The most significant trend shown in Fig. 4.11 is the strong salting-out effect of sodium chloride which decreases CO_2 solubility by a factor of four for a 6 molal solution. Above 1 molal sodium chloride $\ln K_H^{\circ}$ increases linearly with increasing salinity at all temperatures. However, there is a dispropor-

tionately large salting-out effect, particularly at the higher temperatures, between pure water and 1 molal sodium chloride solutions making the commonly used Setchenow relationship (for the linear dependence of $\ln K_H^{\circ}$ with salt concentration) invalid for the entire range of salinities.

Hydrogen sulfide solubility decreases rapidly with increasing temperature below 150°C, approaches a broad minimum around 240°C, and then continuously increases at higher temperatures (Fig. 4.12). The aqueous solubilities of H_2S and CO_2 follow the general trend for all gases of increasing minimum solubility temperature with increasing overall gas solubility. Similar to CO_2 , H_2S shows an apparent shift in the solubility minimum from 210°C in pure water to about 260°C in sodium chloride solutions. The salting-out effect of sodium chloride increases slightly with temperature. The solubility of H_2S in a 6 molal sodium chloride solution is lower by a factor of two at 25°C and by a factor of three at 350°C than in pure water. Above 1 molal sodium chloride $\ln K_H^{\circ}$ increases almost linearly with increasing salinity at all temperatures.

Fig. 4.11. Solubility of CO_2 at infinite dilution in aqueous NaCl solutions. The solubility is expressed in terms of Henry's Law constant, K_H° (units = fugacity (atm)/molality).

Fig. 4.12. Solubility of H_2S at infinite dilution in aqueous NaCl solutions. The solubility is expressed in terms of Henry's Law constant, K_H° (units = fugacity (atm)/molality).

Paralleling CO_2 solubility behavior, between 1 molal sodium chloride and pure water, the salting-out effect for H_2S is two or three times greater than above 1 molal. Consistent with its greater polarity, H_2S is generally about three times more soluble in aqueous sodium chloride solutions than CO_2 .

4.3.4 High Temperature pH Measurements with Stabilized Zirconia Membrane Electrodes

(S. E. Drummond, R. E. Mesmer)

Conductivity of O^{2-} ions by stabilized zirconia has facilitated high temperature oxygen fugacity measurements for some time. For this application, the reaction $1/2\text{O}_2 + 2\text{e}^- \rightleftharpoons \text{O}^{2-}$ across a zirconia membrane can be used to sense oxygen potentiometrically above 500°C where the O^{2-} conductivity is appreciable. In aqueous system, however, the conductivity of O^{2-} ions is coupled with the proton activity of the systems via the reaction $\text{O}^{2-} + 2\text{H}^+ \rightleftharpoons \text{H}_2\text{O}$. Neidrach¹ showed in some preliminary studies that the conductivity of O^{2-} ions across stabilized zirconia membranes is pH dependent up to 300°C and that yttria stabilized zirconia might be used as a membrane for a high temperature pH electrode. Our recent studies have been designed to experimentally determine the response of zirconia membrane electrodes to pH over a range of conditions and to evaluate the potential of developing these electrodes for precise pH measurements at elevated temperatures.

The membrane is a $1/4 \times 6$ inch 92% ZrO_2 -8% Y_2O_3 closed-end tube. A Ag-AgCl electrode immersed in a 0.10 N HCl solution comprises the internal element of the electrode. A standard hydrogen electrode is used for reference. Normally the HCl-NaCl reference solution for the hydrogen electrode is separated via a liquid junction from the HCl-NaCl or NaOH-NaCl test solution with the ZrO_2 membrane. The entire cell can be represented by

Below 150°C the conductivity of O^{2-} ions through the ZrO_2 membrane is low (less than $\approx 10^{-8} \Omega^{-1} \text{cm}^{-1}$) and the response of the cell is unstable. Above 250°C problems arise from the thermal expansion and flowing of the teflon that seals the ZrO_2 tube to the vessel and isolates the internal element from the test solutions. Consequently, most of the experiments to date have been at an intermediate temperature ($\approx 200^\circ\text{C}$).

The most notable and troubling observation of these experiments so far is a consistent drift in the response of the ZrO_2 electrode. This long-term drift is best demonstrated when the liquid junction is removed from the cell so that the ZrO_2 electrode and the hydrogen electrode reference are in the same solution. In this configuration at 200°C and 50 bars of H_2 pressure the response of the cell typically drifts from about 350 mv to 270 mv at rates of between 0.5 mv/hr to 2.0 mv/hr over a period of several days. The drift rate decreases with time until after 4-5 days the EMF of the cell gradually stabilizes at around 270 mv. Tsuruta and MacDonald² have also reported a similar drift in ZrO_2 membrane pH electrodes and attribute the drift to pH changes by ZrO_2 dissolution. This explanation is unsatisfactory since <0.1 ppm Zr is observed in any of the solutions in our cell whereas ≈ 100 ppm would be required to cause such large apparent pH changes in the solutions. In addition, the response of two H_2 electrodes in two cells (one with zirconia present) separated by a liquid junction is constant over several days. All of this evidence is inconsistent with Tsuruta and MacDonald's explanation and indicates that the drift is due to another inherent property

of the zirconia membrane. It is interesting to note that the drift is similar for all of the membranes tested so far and is similar for the same membrane in successive tests.

Acid-base titration from a pH of 2.0 to 8.7 shifts the relatively stable EMF less than 4.0 mv per pH unit which is within 4% of the Nernstian response at 200°C. Although further testing is needed, preliminary titration with the liquid junction separating the hydrogen electrode reference solutions from a test solutions with a different composition confirm the near-Nernstian EMF-pH response of the ZrO_2 membrane electrode in strong acid and strong base at 200°C.

As suggested by Neidrach the stabilized zirconia membrane does seem to have some potential as a pH sensor. However, before precise pH measurements can be facilitated with this membrane electrode, several problems must be addressed:

1. What causes the drift and how can it be minimized?
2. Is the pH response Nernstian or just nearly so?
3. How can the conductivity be increased so that low temperature pH measurements might also be made?
4. How can the membrane be fitted to a reaction vessel for temperatures above 300°C?
5. At what temperature in aqueous systems does the membrane become responsive to the oxygen fugacity of the environment?

1. L. W. Neidrach, J. Electrochem. Soc. **127**, 2122(1980).

2. T. Tsurutu and D. A. MacDonald, J. Electrochem. Soc. in press, (1980).

4.3.5 Effects of Boiling on Mineral Precipitation from Hydrothermal Solutions

(S. E. Drummond)

In the past thirty years a large body of evidence has accumulated in the literature indicating that many hydrothermal ore forming systems have maintained a two-phase fluid and that partitioning of components from the liquid to the vapor phase (boiling) is genetically associated

with mineralization. This study was designed to quantify the effects of boiling on aqueous mineral solubilities by a numerical model capable of simultaneously considering not only the complex chemical equilibria in a multicomponent-multiphase system but also the most significant physical variables operative in natural systems. Aside from the wide range of intensive variables that were considered, other system variables incorporated in the model were: heat budget - conservation of heat or an isothermal process; physical constraints on mass - a system that is either open or closed to mass; redox equilibria - controlled by carbon, sulfur, or other equilibria; heterogeneous mineral-solution equilibria - fluid constrained to be in equilibrium with various solid phases during the boiling process.

Several generalizations concerning the effects of boiling on mineral deposition and solution chemistry were derived from modeling hundreds of hypothetical and real natural boiling hydrothermal systems.

1. The most significant chemical effect is a result of the partitioning of acidic volatile gases (CO_2 , H_2S , etc.) into the vapor phase and raising the pH (as much as 3-4 units) of the solution.

2. This gas partitioning is most effective in open systems when heat is conserved (i.e., when boiling is accompanied by cooling) and when the temperature is lowest.

3. Reduced volatile species (CH_4 , H_2S , etc.) are more volatile than their oxidized counterparts (CO_2 , SO_4^{2-} , etc.) so that boiling tends to oxidize hydrothermal fluids.

4. The pH of boiling hydrothermal solutions increases most when the acidity of the solution is due to a volatile component-i.e., when both the initial CO_2 content and pH of the solution are relatively high. A general rule of thumb is that the pH of the solution must be at least as high as the square root of the product of the CO_2 concentration and the pK_1 for H_2CO_3 dissociation in order for boiling to be effective in increasing the solution pH.

5. The most favorable conditions for oxide, sulfide, and native metal mineralization from boiling solutions are: when the system is open (particularly for oxides), is isoenthalpic, and has a high CO_2 content and a relatively high initial pH.

6. The initial oxidation state of the fluid is relatively unimportant in determining the effect of boiling on solution chemistry and mineral solubilities except at high f_{O_2} where SO_4^{2-} - HSO_4^- equilibria buffers pH somewhat.

7. Particularly in open systems, small amounts of vaporization can produce dramatic effects on the chemistry of the solution and on mineral solubilities.

8. The order of minerals most-to-least likely to precipitate as a result of boiling is as follows: oxides-native metals-sulfides-carbonates-sulfates.

9. There is no particularly favorable temperature for mineralization during boiling. However, the temperature largely determines the mode of interaction and relative importance of the other variables as well as the amount of vaporization needed to produce a significant effect.

10. Initial CO_2 content and the open or closed constraints are more important at the lower temperatures.

11. Heat budget is most significant for the higher temperature systems.

12. Initial solution pH is the most important overall factor determining the effect of boiling on mineralization at all temperatures.

13. Since the volatility of the gases relative to water decreases markedly with increasing temperature, more vaporization is required to produce the same effect at the higher temperatures.

14. Boiling can be a viable and possibly dramatic mechanism for mineral deposition in most but not all natural hydrothermal systems.

15. Boiling is a complex process that involves the interactions of many physical and chemical variables. Without a quantitative numerical model neither the above generalizations nor the evaluation of specific boiling systems would be possible.

4.3.6 Modeling of Speciation in the System

NaHSO_4 - NaHS - H_2O

(F. W. Dickson, M. H. Lietzke)

Knowledge of sulfur isotopic fractionation factors between sulfide and sulfate sulfur in aqueous solutions provides ways of determining temperatures of formation of mineral pairs, such as pyrite, FeS_2 , and barite, BaSO_4 . Fractionation factors for ^{34}S and ^{32}S as a function of temperature have been calculated from theoretical models.⁴ Recently attempts have been made to measure fractionation factors experimentally.¹⁻³ Sakai and Dickson⁴ studied the isotopic exchange reaction

at 300°C and 1000 bars (10 MPa). Their approach was to heat $\text{Na}_2\text{S}_2\text{O}_3$ solutions of known concentrations to 300°C to generate equimolar solutions of NaHSO_4 and NaHS by the breakdown of thiosulfate to sulfide and sulfate ions which occurs above 200°C

Immediately upon the chemical decomposition of the thiosulfate to sulfate and sulfide the isotopes of sulfur began to partition according to eqn. (1). The equilibrium fractionation factor at 300°C and 1000 bars, $+20.0 \text{ permil} \pm 0.01 \text{ permil}$ (parts per thousand), turns out to be significantly smaller than other experimental and theoretical values. Sakai and Dickson determined the time dependency of the isotopic exchanges and reported half-lives of 8.2 to 3.4 days that depended on total sulfur concentrations and pH.⁴ The geochemical applications of Sakai and Dickson were based largely on a temperature versus pH diagram on which were plotted constant half-life curves.

The experimental data were used to calculate the distribution of aqueous species at 300°C and vapor pressures of the solutions by use of the computer program of Barnes and Kharaka.² The following reactions were considered:

It was pointed out to Sakai and Dickson⁵ that the equilibrium constant for reaction (5) was incorrect, introducing order of magnitude uncertainties to the calculated distribution of species. Therefore, the species distribution have been newly calculated at ORNL, using appropriate data, by a method that requires minimal assumptions. Reactions (5) and (6) were not used; any effects caused by them were attributed to ionic strength effects. The solution model therefore was simplified to

$$Q_1 = [\text{H}^+][\text{SO}_4^{2-}]/[\text{HSO}_4^-], \quad (8)$$

the HSO_4^- dissociation quotient; and

$$Q_2 = [\text{H}^+][\text{HS}^-]/[\text{H}_2\text{S}], \quad (9)$$

the H_2S dissociation quotient. The quantities in brackets are concentrations in molal units (mols per kg H_2O). Variations in Na_2SO_4 and H_2SO_4 concentrations also were included. Ionic strengths dependence of Q_i was expressed as

$$\ln Q_i = \ln K_i + S_i^0 \sqrt{I} / (1 + A_i \sqrt{I}) \quad (10)$$

in which K_i represents the thermodynamic infinite dilution equilibrium constants; S_i^0 are the appropriate Debye-Hückel limiting slopes, A_i was taken as 1.5; and the ionic strengths, I , were calculated from $I = 1/2 \sum m_i Z_i^2$, in which m_i and Z_i are the molality and charge on each ionic species, respectively.

The calculations solved the equations for Q_1 and Q_2 simultaneously, using the Newton-Raphson method, for a given set of initial conditions. After each iteration, the values of Q_i were recalculated using an updated value of the ionic strength. In all cases, the convergence to equilibrium values was rapid. Table 4.7 shows

results for calculations performed at regularly spaced initial conditions.

The values calculated at the solution concentrations of the Sakai and Dickson experiments are listed in Table 4.8, together with other data. The major differences between the newly calculated results and the former are the elimination of NaSO_4^- as an important species and pH values that are higher by 1.5 and 2.0 pH units.

Difficulties in the kinetic interpretations experienced by Sakai and Dickson have been diminished or eliminated by the use of the newly calculated distribution of species. The half-life of run 1, 8.2 days, was the same as that of run 2, in spite of the fact that run 1 was lower in total sulfur and higher in pH. Both factors should lead to a larger half-life for run 1, as much as ten-fold higher. Analysis of the experimental data in light of the recent calculations made clear that a large uncertainty exists in the experimental data of run 1 and that the reported half-life should be disregarded.

Sakai and Dickson were puzzled by an apparent anomaly in runs 2 and 3. Both were the same in total sulfur, but the ratio of the previously calculated acidities $[(\text{aH}^+)_3/(\text{aH}^+)_2]$ of 10 would require a 10-fold difference in $(t_{1/2})_2$ as compared to $(t_{1/2})_3$; the newly calculated ratio of acidities is 1.8, closer to the ratios of half-lives of 2.4. The geochemical interpretations of Sakai and Dickson are based on their Fig. 4, constant $t_{1/2}$ curves on the pH versus temperature diagram. Re-plotting the diagram, using the newly calculated data and keeping the coordinates the same, shifts the curves toward slightly smaller half-lives for given pH-temperature combinations. The conclusions as to residence times of sulfur-containing natural fluids remain almost unchanged. The newly calculated pH values from 5.4 to 6.0 span neutrality at 300°C and are more reasonable in terms of pH of natural solutions.

1. S. A. Igumnov., *Geochimaya*, 4, 497(1976) (in Russian).

2. Y. K. Kharaka and I. Barnes., U.S. Geol. Surv. Rep. No. USGS/WRD-73-002 (1973).

3. B. W. Robinson., *Earth Planet. Sci. Letters*, 18, 443(1973).

Table 4.7

Calculations for aqueous NaHSO_4 - NaHS - Na_2SO_4 - H_2SO_4
solutions at 300°C and at the vapor pressure of the solutions¹

Initial Concentration (mmoles/kg H_2O)				Equilibrium Concentrations (moles/kg H_2O)				
NaHSO_4	NaHS	H_2SO_4	Na_2SO_4	300°C				
				HSO_4^-	HS^-	H_2S	H^+	SO_4^{2-}
10	10	0	0	6.97-4	6.96-4	9.30-3	1.04-6	9.30-3
10	10	1	0	2.22-3	2.19-4	9.78-3	3.44-6	8.78-3
10	10	10	0	1.95-2	1.49-6	9.999-3	4.61-4	4.58-4
10	10	100	0	1.10-1	1.58-8	1.00-2	9.01-2	5.65-5
10	10	0	1	7.19-4	7.18-4	9.28-3	1.04-6	1.03-2
10	10	1	1	2.73-3	2.33-4	9.77-3	3.36-6	9.77-3
10	10	10	1	1.98-2	3.66-6	9.996-3	1.95-4	1.19-3
10	10	100	1	1.11-1	1.60-8	1.00-2	8.91-2	5.82-5
10	10	0	10	8.55-4	8.54-4	9.15-3	1.12-6	1.92-2
10	10	1	10	2.32-3	3.25-4	9.68-3	3.09-6	1.87-2
10	10	10	10	2.00-2	2.25-5	9.98-3	4.29-5	1.00-2
10	10	100	10	1.20-1	1.86-8	1.00-2	8.01-2	7.60-5
10	10	0	100	1.26-3	1.26-3	8.75-3	1.83-6	1.09-1
10	10	1	100	2.64-3	6.38-4	9.36-3	3.84-6	1.08-1
10	10	10	100	2.01-2	8.32-5	9.92-2	3.08-5	1.00-1
10	10	100	100	1.98-1	1.20-6	9.999-3	1.79-3	1.18-2
50	50	0	0	2.43-3	2.44-3	4.76-2	3.24-6	4.76-2
50	50	1	0	3.64-3	1.65-3	4.84-2	4.87-6	4.74-2
50	50	10	0	2.02-2	2.64-3	4.97-2	3.04-5	3.98-2
50	50	100	0	1.50-1	1.67-7	5.00-2	5.02-2	1.93-4
50	50	0	1	2.45-3	2.45-3	4.76-2	3.26-6	4.86-2
50	50	1	1	3.66-3	1.66-3	4.83-2	4.89-6	4.84-2
50	50	10	1	2.02-2	2.67-4	4.97-2	3.04-5	4.08-2
50	50	100	1	1.51-1	1.71-7	5.00-2	4.92-2	2.00-4
50	50	0	10	2.54-3	2.54-3	4.75-2	3.44-6	5.75-2
50	50	1	10	3.74-3	1.75-3	4.83-2	5.08-6	5.73-2
50	50	10	10	2.03-2	2.96-4	4.97-2	3.02-5	4.97-2
50	50	100	10	1.60-1	2.16-7	5.00-2	4.03-2	2.76-4
50	50	0	100	3.09-2	3.09-3	4.69-2	4.77-6	1.47-1
50	50	1	100	4.27-3	2.27-3	4.77-2	6.60-6	1.47-1
50	50	10	100	2.04-3	4.72-4	4.95-2	3.26-5	1.40-1
50	50	100	100	1.99-1	2.02-5	4.998-2	6.73-4	5.07-2

¹Table entries are in exponential form, e.g., 1.50-5 = 1.50×10^{-5} .

4. H. Sakai and F. W. Dickson, Earth Planet. Sci. Letters, 39, 151-161 (1978).

5. H. Ohmoto, private communication, 1979.

4.4 The Response of the Oceans to Increasing Atmospheric CO_2

(C. F. Baes, Jr.)

During the reporting period, a study was performed for the Oak Ridge Associated Universities Institute for Energy Analysis critically reviewing the present state of knowledge of the response of the oceans to increasing atmospheric CO_2 . The following is an abstract of a report¹ prepared as a result of this review:

The rate at which the oceans take up excess atmospheric carbon dioxide from the burning of fossil fuels is an important factor in determining the rate of increase in the atmospheric concentration of carbon dioxide and the maximum value it will reach. In this review are considered the relevant physical and chemical features of the oceans, the observational evidence of its response to increasing atmospheric carbon dioxide, and the uncertainties involved in modeling this response.

The deep oceans are near saturation with calcite (the least soluble form of calcium carbonate). While the pressure dependence of this solubility and ocean circulation tend to

Table 4.8

Comparison of Sakai and Dickson's data on sulfur isotope fractionation with Dickson and Lietzke's calculations at 300°C at the vapor pressure of the solutions

Concentrations are in millimolal (D&L) and millimoles per kg of solutions (S&D).

	Run 1		Run 2		Run 3		Run 4	
	S&D*	D&L [†]	S&D	D&L	S&D	D&L	S&D	D&L
pH	4.2	6.04	4.5	5.65	3.5	5.40	3.4	5.59
SO ₄ ²⁻	0.0047	7.55	0.01	29.68	0.01	28.09	0.009	23.99
HSO ₄ ⁻	0.22	0.59	0.11	1.72	1.08	2.98	1.31	1.99
NaSO ₄ ⁻	7.61	----	30.7	-----	30.08	-----	25.08	-----
HS ⁻	0.001	0.59	0.013	1.72	0.0013	0.92	0.00058	0.75
H ₂ S	7.8	7.55	30.7	29.68	30.09	28.40	17.53	16.81
Δ (1)	5.0	8.7	4.8	6.0	4.2	6.1	4.1	7.6
ΣS (2)		8.14	31.4			30.7		18.1
ΣSO ₄ ²⁻ (3)		8.14	31.4			32.0		26.6
t1/2 (4)		8.2	8.2			3.4		4.5

(1) $\Delta = -\log t1/2 + \text{pH} - \log (\Sigma\text{SO}_4^{2-} + \Sigma\text{S}^{2-})$.

(2) Total sulfide sulfur.

(3) Total sulfate sulfur.

(4) Half life in days.

* Sakai and Dickson, S&D, 1978.

† Dickson and Lietzke, D&L, this paper.

produce calcite supersaturation of the upper ocean, these effects cannot account for the far greater supersaturation of the surface waters. This condition is probably maintained by the effects of photosynthesis and the biogenically controlled precipitation of calcium carbonate. Since the calcite-supersaturated surface waters are approximately at equilibrium with the carbon dioxide content of the atmosphere, the biological processes in the oceans may strongly influence the carbon dioxide content of the atmosphere. The capacity of the well-mixed surface layer to react with excess atmospheric carbon dioxide is limited; and the rate of uptake is determined largely by the nature and rate of ocean circulations, particularly in the first thousand meters of depth.

After correcting for the expected effects of biological processes on the composition of seawater, several investigators have found evidence that the increasing carbon dioxide content of the atmosphere has already detectably affected the distribution of carbon in the upper ocean. While there are some complications and uncertainties from mixing effects, there seems reason to hope that this signature of excess carbon may soon become a valuable tracer for monitoring ocean response. One direct effect of increasing atmospheric carbon dioxide on the mixed layer will be a decrease in the pH of about 0.25 pH unit per doubling of the atmospheric concentration. The release of carbon dioxide induced by ocean warming is estimated to be a minor feedback effect. A more significant feedback may

be produced by the coupling of climate warming, reduced ocean circulation (from the decreased temperature difference between pole and equator), and reduced biological productivity, resulting in a change in surface water composition and a redistribution of carbon dioxide between ocean and atmosphere.

The most widely used carbon dioxide ocean models are one-dimensional (depth) arrangements of boxes and water flows. The capacity of such model oceans to take up carbon dioxide depends substantially on the number of boxes used to represent the upper ocean and on the relative importance assigned to advective (largely horizontal mass) flow versus diffusive (largely vertical mixing) flow of water. A variation of

as much as 0.15 in the airborne fraction of excess carbon is found for the more realistic models. It remains to be seen how two-dimensional (latitude $\times$ depth) box models will alter this uncertainty when tested against the available tracer data. Finally, it will be necessary to simulate in models the effect of the biological processes on the distribution of carbon between ocean and atmosphere and the feedback that this may entail when ocean and atmosphere models are combined to predict the climatic impacts of increased carbon dioxide.

1. C. F. Baes, Jr., The Response of the Oceans to Increasing Atmospheric Carbon Dioxide, Oak Ridge Associated Universities Report ORAU/IEA-A-81 6(M), Aug. 1981.

5. HIGH-TEMPERATURE CHEMISTRY AND THERMODYNAMICS OF STRUCTURAL MATERIALS

5.1 Permeation of Construction Materials by Hydrogen Isotopes

(J. D. Redman)

The tritium permeability of seven non-oxidized (i.e., clean) alloys was measured between 550 and 1025 K and isothermally over tritium pressures of 2×10^{-9} to 1×10^{-7} Pa. The seven alloys studied were stainless steel types Sanicro 32, HT 9, 21-6-9, SR 18, and 310; nickel-base Hastelloy X; and, an ordered alloy, Fe-39.5% Ni-22.4% V-0.4% Ti, which was developed and prepared by C. T. Liu of ORNL's Metals and Ceramics Division.

All of the specimens studied in this program except the 21-6-9 and the sintered refractory alloys were annealed at 1050°C in pure H_2 after working, and prior to the measurements. Arrhenius-type equations were derived to express the permeabilities, DK_s , in terms of a permeability constant or pre-exponential term (DK_0) and an apparent activation energy (ΔE). Data for tritium permeabilities of 16 non-oxidized alloys (including the seven examined during this reporting period) are shown in Fig. 5.1. A curve for Hastelloy X is not shown in Fig. 5.1 because it is almost identical to that of SS 310. Our studies show that permeation rates through these alloys are grouped according to the respective alloy lattice structure and, within that group, the rates are dependent upon composition, lattice

diffusion, and grain boundary diffusion. We have found that for the body-centered cubic structured ferritic steels the ΔE value increases as the iron content of the alloy decreases except for the aluminum containing alloys SR 18 (2% Al) and SS 406 (4% Al) which are reversed in position with respect to the iron composition. For all of the face-centered cubic austenitic steel alloys, except for the 21-6-9 specimen, ΔE increased with decreasing chromium content of the alloy. [The 21-6-9 specimen may have behaved differently because it was cold worked rather than annealed.] The sintered W-Ni-Fe alloys, which are primarily austenitic, show increasing ΔE values for increasing W content. That the permeation mechanism involves both lattice diffusion, which is reflected by the temperature dependent ΔE value, and grain boundary diffusion, which is in part determined by the permeation constant, was shown by permeability measurements of annealed and cold worked specimens of ferritic HT9 and austenitic Sanicro 32. For both materials the permeability of the cold worked specimen was about 50% higher than for the annealed specimen although the respective ΔE values were similar. This is shown in Fig. 5.2 for Sanicro 32. In micrographs of the specimens the grain size of the worked specimens was 40% smaller than the grain size of the annealed specimen. The results from the alloy 21-6-9 experiment were unusual; the permeability of the annealed specimen was not linear with respect to reciprocal temperature. A change in slope in the Arrhenius plot occurred between 400 and 570°, possibly because of changes in the lattice structure caused by the annealing at 1050°C. This speculation is based on the knowledge that high manganese steels such as alloy 21-6-9 (10% Mn) undergo structural instability with loss of ductility above 800°C. Data for the 21-6-9 specimen which was not annealed showed no break in the Arrhenius plot. The ordered Fe-Ni-V-Ti alloy yielded inconclusive permeability data because of alloy surface oxidation attributable to the titanium in the alloy.

Fig. 5.1. Tritium permeation through clean steel and sintered refractory alloys.

Fig. 5.2. Tritium permeation through clean Sanicro 32, annealed and cold worked.

However, sufficient permeation data were collected to show that an Arrhenius plot was non-linear and was similar in shape to the annealed 21-6-9 specimen, but with the break occurring at the order-disorder critical temperature, 690°C. The dependence of the rate of permeation on tritium pressure in all the cases studied was found to be one-half power dependent.

Studies of the effects of oxidation by steam at pressures near 96 kPa (0.95 atm) to form oxide films on high strength steel alloys and to reduce tritium permeation through these materials

have continued. Compared to the values determined for non-oxidized metals, the permeation rates were significantly reduced by oxidation by subatmospheric steam. We have recently measured the steam oxidation effect for five high temperature structural alloys: SS 316-Ti (standard 316 type with a 1% Ti addition), SR 18, SS 310, Sanicro 32, and 21-6-9. The results of these five long-term experiments (2-4 months each) are summarized with our earlier experiments in Table 5.1. The test temperature and pressure of 660° and 96 kPa are standard for these experiments because we had learned initially from the Incoloy 800 experiments that these conditions led to the greatest lowering of the permeability. Typical parabolic permeation rate curves were obtained. Since the composition of Incoloy 800 and SS 310 are similar, and since their rate curves are similar, the surface oxides formed may also be similar; the oxide formed on Incoloy 800 was primarily MnCr_2O_4 . However, the oxide films formed on the SS alloys are quite complex and only a few could be identified by x-ray diffraction. The major oxide components formed on SS 406 were Al_2O_3 and an unidentified silica compound; on SS 316 and SS 316-Ti, the respective major oxides were Fe_2O_3 and an Fe-Cr spinel with lattice parameters close to Fe_3O_4 and MnCr_2O_4 ; and, on alloy 21-6-9 the major oxide was also an Fe-Cr spinel, but having a higher chromium

Table 5.1 Factors by which permeation rates were decreased by oxide coatings on alloys at 935°K by 96 kPa pressure steam

Alloy	Initial DK _s [$\frac{\text{cm}^2 \cdot \text{Pa}^{-1/2}}{\text{min} \cdot \text{m}^2 \cdot \text{Pa}^{1/2}}$]	Factor by which permeation was reduced after (days)				
		1	6	24	40	65
SS 316	7.62×10^{-6}	2	2.5	3.5	4	5
SS 316-Ti	7.62×10^{-6}	1	2	3.5	4	8.5
Sanicro 32	5.37×10^{-6}	4	9.5	16.5	20	22.5
SR 18	32.87×10^{-6}	2	8	29	32	34.5
21-6-9	7.79×10^{-6}	9	20	47	57	69
Incoloy 800	8×10^{-6}	21	55	111	131	165
SS 310	8.66×10^{-6}	14	57	171	194	226
SS 406	13.9×10^{-6}	71	150	293	428	706

content than the spinel oxide formed on SS 316-Ti plus an unknown oxide.

5.2 Tritium Permeation of Steam Generator Materials Under High-Temperature, High-Pressure Dynamic Steam Conditions

(P. Berlinski)

It is important from an ecological standpoint to prevent tritium loss from fusion power reactors systems. An extremely vulnerable area of the system is that of the steam generator since tritium permeating into the steam generator would be irrevocably lost to the environment. Various concepts for making the walls of the steam generator impermeable, e.g., vapor deposition of refractory metal or use of duplex piping, have been considered. We have been studying the possibility of utilizing the oxide formed in situ by steam oxidation of the base alloy to retard permeation rates. Earlier work¹⁻³ with sub-atmospheric steam showed that, for selected alloys, tritium permeation rates were reduced several orders of magnitude by the oxide formed from reaction with the steam. None of the past work was done at the high steam pressures and temperatures encountered in an actual steam generator.

During this report period, we have designed and constructed an apparatus that will permit measurement of tritium permeation rates through candidate steam generator materials which are undergoing oxidation by high-pressure steam (up to 10 MPa) at temperatures up to 1000 K. The apparatus consists essentially of two sub-systems. In one, which is a closed loop, steam is generated, flows through the test specimen, is condensed, and the condensate is returned to the generator. Tritium from the other sub-system, an Ar-4% H₂ feed gas supply containing tritium at the ppm level, permeates the test specimen and is trapped by the condensate. Analyses of the condensate for tritium, along with other required input, allows calculation of the tritium permeation rate.

In our initial step in the shake-down of the apparatus, the permeability of nickel was

determined in the absence of steam. The permeabilities measured over the temperature range 460-975 K were in excellent agreement with those of Bell and Redman⁴ determined previously. The same specimen in the presence of 931 kPa (135 psi) steam gave a steady-state permeation rate of 1.8×10^{-7} cc(T₂)·mm/min·cm²·torr^{1/2} at 465 ± 5 K. This value is not markedly different from the value 4×10^{-7} obtained under nonoxidizing conditions, a result expected from similar work with iron. Once the apparatus is completely operational, the permeation behavior of Incoloy 800 and similar steam generator materials will be determined.

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5.3 Study of the Iron-Chromium Sigma Phase

(J. Brynstad, H. L. Yake¹)

The iron-chromium sigma (σ) phase plays an important and undesired role in stainless and other chromium-containing steels because of its brittleness.² We have continued the study of this phase using conventional x-ray diffraction as well as synchrotron radiation.

Extensive (4000-8500 observations) single-crystal Mo Kα Bragg diffraction data sets were collected and analyzed for phases with compositions near Cr₄₈Fe₅₂ that had been heat-treated at three temperatures (790, 740, and 650°C) within the region of σ phase stability. Precisions of measurement varied from <1% for the relatively few intense diffraction maxima to ~5-10% for the more numerous weak reflections. No clear indication of the absence of a center of symmetry was found in any data set, or in any of the results obtained by least-squares refinements in S.G. P4₂/mm. Average occupation parameters of limited precision (±5-8%) were

derived for the five independent lattice sites of the σ structure in the course of the refinement of each data set. The crystal from the alloy equilibrated at 740°C was also studied using synchrotron radiation (SR) Bragg diffraction at photon energies just below the Fe and Cr K absorption edges where differences (Δf) in the atomic scattering factors of Fe and Cr approach 25-35%. (For Mo K α radiation, Δf is only 8-11%.) Site-occupation parameters derived from the SR diffraction data show greater precision (± 1 -2%) than the conventional data results, but do not differ from them significantly. Variations in site-occupation parameters with equilibration temperature are small ($< 2\sigma$) but physically sensible for the three temperatures studied. The distributions are in reasonably good agreement with results of neutron powder diffraction experiments on comparable materials. A marked preference for Fe atoms to occupy the two 12-fold coordination sites is found, with Cr atoms distributed about equally among the one 15-fold and two 14-fold sites. Vector maps and difference vector maps computed from $[F_{\text{obs}}^2 - F_{\text{calc}}^2]$ (average occupation of all sites) give useful indications of the actual atom distributions.

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5.4 Study of the τ -phase $\text{Fe}_x\text{Cr}_{23-x}\text{C}_6$

(J. Brynstad, H. L. Yakel,¹ J. F. Land)

The Fe-Cr-C τ -phase plays a very important role in all chromium-containing steels because it affects the properties of these steels. However, nothing has been known until now about preferred site occupation of the metal atoms or the solubility of iron as a function of temperature in this phase. In the evaluation of the thermodynamic functions for this phase, it invariably has been assumed in the literature that iron and chromium distribute randomly over the metal sites.

The study of this phase has continued,² with emphasis on the determination of preferred site

occupation of the metal atoms in the structure. Tau phase carbides of composition $\text{Fe}_x\text{Cr}_{23-x}\text{C}_6$, with $x \sim 7, 4$ and 1.7 have been prepared in Fe-Cr-C alloys by heat-treatments at 1200°C for about 170 hr. The carbide phase was isolated by electrolytic dissolution of the matrix in 10% HCl/methanol solutions and analyzed for chemical compositions and homogeneity by classical methods. It was found that the Me/C ratio for the pure Cr_{23}C_6 was 23/6 within experimental error; this ratio decreased with increasing Fe content in the carbide. No obvious explanation for this result has yet been found.

Single crystals of each composition were studied by Mo K α ($\lambda_1 = 0.7093 \text{ \AA}$) x-ray diffraction methods to try to determine the distributions of Fe and Cr atoms on the four independent lattice sites of the well-known τ structure (S.G. $Fm\bar{3}m$, $a_0 \sim 10.59 - 10.65 \text{ \AA}$). Least-squares analyses of extensive (2000 - 3000 observations at $3^\circ < 2\theta < 130^\circ$), precise [average $\sigma(I)/I < 3\%$] data sets demonstrated that site-occupation parameters could be measured even at the lowest Fe content studied. Precisions of the estimates of these parameters ranged from $< \pm 2\%$ at the higher Fe contents to $\sim \pm 5\%$ at the lower. Site-occupation is far from random, with Fe atoms preferentially occupying $4a$ sites (cubo-octahedral geometrically close-packed coordination) and Cr atoms preferentially occupying $32f$ sites (faces of Friauf polyhedra). The so-called τ -stabilizer sites ($8c$) can be occupied by no more than one Fe atom for every 2 Cr atoms. The eventual instability of the τ phase ($\text{Fe}_x\text{Cr}_{23-x}\text{C}_6$) in the Fe-Cr-C system (which occurs for $x > \sim 8$) appears to be related to the necessity of placing more Fe atoms on the energetically unfavorable $48h$ and $32f$ sites.

The results demonstrate that this phase cannot be well described in terms of "classical" models; i.e., as ideal, regular or subregular solid solutions of Fe and Cr in the lattice as has been the approach in all published (model) calculations until now.

1. Metals and Ceramics Division.
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5.5 Preparation of Metal Phosphates by Metathesis Reactions with BPO_4

(C. E. Bamberger)

The chemical properties of the compound BPO_4 ($= \text{B}_2\text{O}_3 \cdot \text{P}_2\text{O}_5$), often called boron phosphate, are essentially unknown. We have recently found that BPO_4 (prepared by igniting mixtures of H_3BO_3 and H_3PO_4) can be reacted with metal oxides (and should do likewise with salts) at temperatures above 600°C to produce metal phosphates. Although no thermodynamic data are available, our results lead us to conclude that such metathesis reactions occur because the stability of the metal phosphate formed is significantly higher than that of BPO_4 . Furthermore, since the stability of the metal phosphate depends on the oxidation state of the metal ion, at the temperature range studied (600 – 1200°C), these metathesis reactions also involve thermal reduction of the metal ion to a lower valence with attendant O_2 evolution. This has been demonstrated by heating ground mixtures of BPO_4 with different oxides under a flow of inert gas and determining the relative rate and amount of O_2 evolved. The solid products were characterized by x-ray powder diffraction, chemical analysis, Raman spectroscopy and, in some cases, by microspectrophotometry (Pu, Np phosphates) and Mössbauer spectroscopy (Np phosphates). Examples of the reactions studied are:

Additionally, when BPO_4 was reacted with either Fe_3O_4 or Fe_2O_3 , O_2 evolution occurred. Although the reactions were not allowed to run to completion, we reduced 2/3 of the Fe(III) present initially in each oxide to Fe(II). Results from Mössbauer spectroscopy agreed very well with the O_2 measured. A reaction of PuO_2 with BPO_4 also evolved O_2 yielding a blue product; while its visible absorption microspectrum does not indi-

cate the presence of Pu^{4+} , the x-ray diffraction pattern can be interpreted as a mixture of PuPO_4 and PuP_2O_7 . A reaction of PuO_2 with $(\text{NH}_4)_2\text{HPO}_4$ gave similar overall results which at this stage are not fully understood; thus, the behavior of plutonium will be studied further.

In order to find a reagent for dissolving unreacted BPO_4 , solubility tests were conducted first with only BPO_4 and later with mixtures of BPO_4 and CePO_4 . Although boiling concentrated acids such as HNO_3 , HCl and aqua regia had no effect on BPO_4 , warm $0.5 \text{ } N$ NaOH dissolved it completely without affecting the CePO_4 .

The use of BPO_4 for the preparation of metal phosphates thus provides an attractive novel synthetic method for micro and possibly macro crystals because noxious gases are not evolved and refractory oxides can be converted to phosphates at only moderately high temperatures. Excess reagent and/or byproduct B_2O_3 can be easily removed. Studies are currently underway to determine thermodynamic data for BPO_4 .

5.6 Calculations of Thermodynamic Properties of Multicomponent Solution Systems Based on Information from Binary Systems: A Study of the Merits of Various Approaches

(J. Brynestad, R. O. Williams¹)

There is presently considerable interest and activity in developing analytical expressions for representing the thermodynamic functions of solutions. However, only in relatively few cases are experimental data available for binary and higher systems over adequate composition ranges. When no data on multicomponent systems are available, a common approach is to use experimental data from the respective binary systems and extrapolate into the multicomponent range. In so doing, there are several problems that must be addressed, the three more important being:

1. To find adequate analytical formulisms for representing the binary data to be used for the extrapolations.
2. To find adequate approaches to extrapolation into the multicomponent region.

3. To find reliable experimental and theoretical criteria by which the merits of different approaches may be evaluated.

To date no truly satisfactory answers have been found for any of these problems. As a consequence, there are many different approaches and "schools" to be found in the literature. It is obvious, however, that one criterion for an acceptable approach must be that the formalism does not introduce self-contradictions or violations of basic thermodynamic principles. Another criterion must be that the formalism is in accordance with general experimentally verified and/or accepted theoretically derived properties of multicomponent systems.

During a search for adequate methods for describing dilute solutions (alloys) it was observed that certain combinations of formalisms may give rise to inconsistencies, such that if a given formalism for describing the binary systems is employed together with a given method of extrapolation into the multicomponent system, the predicted (calculated) behavior violates basic thermodynamics. As an example, one generally accepted formalism for describing binary systems is the so-called "subregular model" (see, for example, ref. 2). This model has been extensively used in the literature for extrapolating into ternary alloy systems by the so-called Kohler method.³ However, we have demonstrated that this combination gives rise to self-contradictory results.⁴ The same applies if the subregular model is used in conjunction with the so-called Toop method.⁵

Another more elusive criterion is that an analytical representation must be in reasonable accordance with the measured behavior of solution systems. Darken⁶ concluded, on the basis of experimental data on liquid binary metallic systems, that the "excess stability," defined as the second derivative of the excess free energy with respect to atom (mole) fraction, approaches a constant in each terminal region. This observation has received little attention, not even opposition, in spite of the fact that practically all published analytical formalisms for binary systems violate Darken's criterion.

We have analyzed this problem at some length. It seems that although Darken's criterion may be too rigid, insofar as the accuracy of the experimental data he used does not seem to justify such a rigid conclusion, it is nevertheless almost valid. This implies, that although one may allow for some deviation from this criterion, within experimental uncertainty, it puts a severe restriction as to the types of analytical expressions that should be used for an adequate representation. We propose a new analytical series for representing the free energy of mixing of binary systems.⁷ This series obeys a slightly modified Darken criterion. We also show how these "models" are to be treated when they are used for extrapolations into multicomponent systems. We demonstrate that this new approach gives rise to predicted properties in the terminal regions that are significantly different from those predicted by the most commonly used approaches.

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5.7 Redox Measurements in Molten Urania

(A. T. Chapman,¹ J. Brynestad, G. W. Clark²)

The following is an extract of our recently published paper:³ Numerous investigators have studied the stoichiometry changes in solid UO_{2+x} . However, no attempt had been made to investigate experimentally stoichiometry changes in molten urania. We have studied the stoichiometry changes of molten urania by means of the direct internal-zone melting of urania pellets in $\text{H}_2\text{O}/\text{H}_2$ and CO_2/CO gas mixtures. It was possible to vary the oxygen-to-uranium (O/U) ratio of the molten oxide between 1.90 and 2.06.

The oxygen pressures in the controlled gas mixtures were calculated for the temperature extremes of the samples (surface temperature of 2200 K and interior temperature of ~ 3150 K) for comparison with the literature information on solid $\text{UO}_{2\pm x}$. Excellent agreement was found between the molten urania oxygen pressures calculated for the interior temperature (~ 3150 K) and the extrapolated oxygen isobars for solid UO_{2+x} ; from this a phase diagram has been proposed for the hyperstoichiometric oxide up to the liquidus curve. However, no such agreement with literature data for UO_{2-x} was found, and we have suggested reasons for this discrepancy.

The internal-molten-zone technique is used to measure redox equilibria in refractory molten oxides at temperatures above 2300 K where heating and containment problems are severe. We retain

some reservation about the ability to obtain true equilibrium thermodynamic data for the molten phase because of the unavoidable steep temperature gradient required to contain the molten zone. Nevertheless, the internal-zone technique measurements of molten urania provide future investigators with the parameters necessary to vary the stoichiometry of molten urania in a controlled manner. It is a useful technique for similar studies when no other experimental techniques are available.

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1. School of Ceramic Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332.
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6. CHEMISTRY OF TRANSURANIUM ELEMENTS AND COMPOUNDS

6.1 Preparation and Properties of Transplutonium Metals

(R. G. Haire)

The first five transplutonium elements are available in multi-microgram or larger quantities which are sufficient for preparing samples of their metals. The supply of either the ^{241}Am or the ^{243}Am isotope is sufficient so that the limits for preparation of americium metal are established by the equipment's capacity and the radiation levels encountered. In our case, the preparation of americium metal has been on the 100 mg or less scale. Basic studies on curium are carried out using the ^{248}Cm isotope whose availability is more comparable to the supply of the ^{249}Bk and ^{249}Cf isotopes. Thus, the preparation of curium, berkelium and californium metals is currently carried out on the 5-10 mg scale. The situation changes drastically with einsteinium, due both to the limited quantity (<1 mg) and the radiation characteristics of the most available isotope, ^{253}Es . The half-lives of ^{249}Bk ($t_{1/2} = 314$ days) and ^{253}Es ($t_{1/2} = 20$ days) also preclude preparation of metal for future use, as the in-growth of their daughters becomes a limiting factor. Because of the limited quantities of the metals often becomes an integral part on an experiment and either the major portion or the entire preparation is used in the experiment. Ideally, a preparation would be used for a number of different non-destructive measurements, but many of the experiments being carried out on the metals completely consume them (heat of solution, heat of vaporization, etc.).

These metals are prepared by two different syntheses, the particular method chosen being based mainly on the volatility of the actinide product.¹ Currently, americium, californium and einsteinium metals are prepared by distillation from an actinide oxide-lanthanum or thorium metal mixture. Berkelium and curium metals are prepared by lithium metal reduction of the actinide tetrafluoride. During this report period approximately 10 mg of ^{248}Cm metal, 15 mg of ^{249}Bk metal, 40 μg of ^{253}Es metal and 150 μg of ^{253}Es metal in the form of an alloy were prepared. The

purity of these metals ranged from 70-300 ppm cation impurities (excluding oxygen, nitrogen and hydrogen which cannot be determined for these small sample sizes).

The main uses for the ^{248}Cm metal was for magnetic work (see Section 6.9) and high-pressure x-ray diffraction. The curium metal exhibited the double-hexagonal close packed structure. High pressure x-ray diffraction studies of this material are in progress as part of a collaborative program with Los Alamos National Laboratory. Pressures up to 60 kbar have not altered the dhcp structure. The curium study is an extension of previous work² on ^{243}Am metal where the americium metal changed from dhcp to fcc to monoclinic to orthorhombic (α -uranium structure-type) with pressure. The latter structural form is viewed as representing a bonding change in the metal at the high pressures (150 kbar), where some 5-f electron involvement produces the α -uranium structure-type. Since the density of the 5f electron distribution near the bonding orbitals rapidly diminishes above plutonium (5f electrons become more localized), it may be more difficult to force curium metal to undergo a similar change with pressure. Such a transformation would be expected to occur in curium at even higher pressures than observed for americium metal.

The 15 mg of ^{249}Bk metal was produced in two different preparations: one preparation was essentially used for measuring the heat of solution of the metal (see Section 6.2); and the second product was employed for determining the heat of vaporization of the metal (see Section 6.3). Small portions of these preparations were taken for magnetic studies (see Section 6.9), the preparation of other compounds, and for an attempt to re-determine the melting point of the metal. The melting point measurements were only partially successful, indicating the melting point of berkelium metal may be up to 100°C higher than the reported value of 986°C.³

The preparation of pure einsteinium metal free of any supporting substrate has not been reported. Crystallographic data on einsteinium metal have been obtained by electron diffraction using thin-film deposits on electron microscopy grids.⁴

Multi-microgram deposits (5-30 μg) of einsteinium have also been prepared on tantalum and platinum discs for magnetic measurements at ORNL. The scarcity of einsteinium, together with the very high specific heat and alpha activity of the available ^{253}Es isotope, do not offer much promise of being able to prepare a multi-microgram, bulk form of einsteinium metal that is free of a support material. In a collaborative effort to obtain vapor pressure data for einsteinium metal (see Section 6.3), two einsteinium-lanthanide metal alloys (1 mole % einsteinium) were prepared. Europium and ytterbium were chosen for the alloys based on their metallic properties and their vapor pressures. Each metal alloy was prepared by simultaneously reducing a mixed oxide $[(\text{Eu},\text{Es})_2\text{O}_3 \text{ and } (\text{Yb},\text{Es})_2\text{O}_3]$ with lanthanum metal, and subsequently co-distilling/co-condensing the europium-einsteinium and the ytterbium-einsteinium metal vapor. Each alloy was obtained from a tantalum collection plate in the form of soft, bright, metallic-looking chips. The self-heating of the ^{253}Es isotope (1 milliwatt/ μg) was sufficient to give rise to some sublimation of the product when it was isolated in high vacuum.

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6.2 Enthalpy of Solution of Berkelium Metal¹

(J. Fuger,² R. G. Haire, J. R. Peterson³)

The solution microcalorimeter, which was designed for use with the transplutonium elements, has been previously used to determine the heat of solution of ^{243}Am metal, ^{248}Cm metal, and ^{249}Cf metal.⁴ A description of the calorimeter and the initial measurements on ^{248}Cm metal have been published.⁵ The data for ^{249}Cf metal have also been reported.⁶

The first data on the enthalpy of solution of berkelium metal were reported in 1975,⁷ with a value of $-576 \pm 25 \text{ kJ mol}^{-1}$ being given for dissolution of the metal in 1 M HCl. With the availability of milligram quantities of well-characterized (<100 ppm impurities by mass spectrometry, dhcp crystal form) berkelium metal (see Section 6.1), the heat of solution of berkelium metal was remeasured.⁸ Six determinations of the heat of solution of berkelium metal gave an average value of $-600.2 \pm 4.8 \text{ kJ mol}^{-1}$. The samples ranged in size from 212 to 308 μg . The presence of the ^{249}Cf daughter in ^{249}Bk metal is unavoidable, as it grows in at the rate of $\sim 0.2\%$ per day. The samples used for this recent determination contained $\sim 5\%$ of the daughter at the time of dissolution. However, the enthalpy of solution of californium metal is very similar to that of berkelium metal and the uncertainty limits of $\pm 4.8 \text{ kJ mol}^{-1}$ are large enough to neglect the substitution of this amount of californium for berkelium in the samples. The recent value for berkelium metal agrees with our 1975 reported number⁷ but it is considerably more precise and believed to be more accurate.

The enthalpy of solution of americium metal has been shown to vary only slightly as a function of HCl concentration.⁹ Assuming the same level of variation for berkelium metal, the $\Delta H_f^\circ (\text{Bk}^{3+}, \text{aq})$ can be set equal to $-601 \pm 5 \text{ kJ mol}^{-1}$. Then the standard enthalpy of formation of trivalent berkelium is distinctly less negative than the corresponding values for americium, curium, and californium (-616.7 ± 1.2 ,¹⁰ -615.0 ± 0.5 ,¹⁰ and -617 ± 11 ,⁶ kJ mol^{-1} , respectively). The standard, room-temperature crystal forms of all four metals (double hexagonal closest packed, α phase) were used for the measurements. In the series of lanthanide metals, the $\Delta H_f^\circ (\text{M}^{3+}, \text{aq})$ is significantly more positive for the two divalent metals, europium and ytterbium, but there is no reason nor evidence to suggest that the more positive value found for berkelium metal implies some divalency.

Using the estimated values $S^\circ(\text{Bk}, \text{C}, \alpha) = 76 \pm 1 \text{ J mol}^{-1} \text{ K}^{-1}$,^{11,12} and $S^\circ(\text{Bk}^{3+}, \text{aq}) = -188 \pm 17 \text{ J mol}^{-1} \text{ K}^{-1}$,¹⁰ in combination with the

ΔH_f° (Bk^{3+} , aq) above, we obtained ΔG_f° (Bk^{3+} , aq) = $581 \pm 7 \text{ kJ mol}^{-1}$ and E° ($\text{Bk}^{3+}/\text{Bk}^\circ$) = $-2.01 \pm 0.03 \text{ volt}$.

1. Research sponsored in part by DOE contract DE-AS05-76ER04447 with the University of Tennessee, Knoxville, TN.

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6.3 Enthalpies of Vaporization and Vapor Pressures of Actinide Metals¹

(J. W. Ward,² R. G. Haire, P. D. Kleinschmidt²)

A collaborative program for measuring the vapor pressures and the heats of vaporization of actinide metals exists between ORNL and the Los Alamos National Laboratory. The Knudsen effusion technique is used to obtain vapor pressures of the metals as a function of temperature, and the

heat of vaporization can be calculated using this data. A mass spectrometer system identifies the volatile species to confirm that the vapor consists only of monomeric metal atoms. The vapor pressures are determined either with the mass spectrometer in conjunction with calibrating targets or from target data alone.

Previous experiments on ^{243}Am metal,^{3,4} ^{249}Cf metal^{3,5} and preliminary data for ^{249}Bk metal^{3,6} have been reported. The measurements made on americium metal were extended to the liquid state, and also examined the use of americium alloys to ascertain their value for determining vapor pressure data. Experiments with californium were made both on the pure metal and on californium-lanthanide alloys.

The initial vapor pressure measurements on ^{249}Bk metal gave lower pressures and a higher heat of vaporization than were expected from actinide systematics. Recently new measurements were carried out using a larger quantity ($\sim 7 \text{ mg}$) of freshly prepared berkelium metal in a single crystal tungsten crucible.⁷ These new data are considered to be more reliable. Two experimental problems associated with the earlier berkelium experiment were the small amount of berkelium metal available and the tendency for the berkelium metal to alloy with the tantalum crucible at higher temperatures. In this recent work, the vapor pressure of the berkelium metal was measured over the temperature range of 1100-1500 K. The vapor pressure data have been combined with appropriate estimates for solid free-energy functions and the crystal entropy (S°_{298}) to calculate enthalpies, entropies and heat capacities from 298 to 3000 K. Vapor pressure data were collected randomly at different temperatures during the experiment and showed no scatter or residual cell effects. Six liquid data points and ten solid data points were collected before the sample was exhausted. The vapor pressure of berkelium metal can be described by the following equations:

$$\text{Solid state: } \log P (\text{atm}) = 5.84 \pm 0.22 - (15,730 + 264)/T$$

liquid state: $\log P \text{ (atm)} = 5.27 \pm 0.14 - (15,047 \pm 203)/T$

Figure 6.1 shows the vapor pressure as a function of temperature, and lists the heat of vaporization as $74.1 \pm 0.9 \text{ kcal mol}^{-1}$ based on an average of second and third law data. This value compares to empirical predictions of $70\text{--}76 \text{ kcal mol}^{-1}$ based on spectroscopic and calorimetric data.^{8,9}

Alloys of ^{253}Es with two lanthanide metals ([Es, Eu] and [Es, Yb], 1 mole % Es) were employed in an effort to obtain vapor pressure data for einsteinium metal. Several experimental difficulties were encountered in these measurements which did not allow an accurate description of the einsteinium metal system to be constructed. The limited amount of data did establish that the heat of vaporization of einsteinium metal was between -30 to $-40 \text{ kcal mol}^{-1}$. This compares to the value of $-45.3 \text{ kcal mol}^{-1}$ for the heat of vaporization of californium metal,⁵ whose vapor

pressure is greater than samarium metal (trivalent metal) but less than that of europium metal (divalent metal). Thus, these preliminary data for einsteinium suggest that this metal is probably divalent. An empirical prediction for the heat of vaporization of einsteinium metal has been given as $-38 \text{ kcal mol}^{-1}$,¹⁰ which is identical to the value for divalent ytterbium metal. The vapor pressures of the first five transplutonium metals and some selected lanthanide metals are compared in Fig. 6.2.

Fig. 6.1. Relationship of the vapor pressure of berkelium metal with temperature.

1. Work supported in part by DOE, Office of Basic Energy Sciences, Chemical Sciences Division contract with Los Alamos National Laboratory.

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6.4 Studies of Lanthanide and Transplutonium Oxide Systems¹

(R. G. Haire, J. P. Young,² J. R. Peterson,³ J. Y. Bourges⁴)

Studies of the transplutonium oxides can be classified into two areas of interest: (1) stabilization of higher oxidation states; and (2) use as an alternate medium to halides for determining the structural and chemical effects of radioactive decay. This second area concen-

Fig. 6.2. Comparison of the vapor pressures of the first five transplutonium metals with some selected lanthanide metals.

trates on the state of the progeny, or the products, but it also includes changes that occur to the original material. The results of all these studies not only provide a basic understanding of these materials but also have relevance to environmental concerns about them.

Several different approaches have been taken to obtain and stabilize the higher oxidation states of the first five transplutonium elements in the solid state. One of the goals has been to determine if einsteinium can be obtained in the tetravalent (or higher) oxidation state. An oxidation state above three has not been reported for a bulk form of an einsteinium compound. One approach to try to achieve this goal has been the preparation of alkali metal or alkaline earth-actinide oxide compounds followed by treatment of them with atomic or molecular oxygen at elevated temperatures. Our most complete investigation has been done with the preparation and examination of BaAnO_3 -type

compounds (An = tetravalent actinide or lanthanide),⁵ where x-ray diffraction and absorption spectrophotometry have been used for analyses of the products. Although the desired einsteinium compound was not obtained [the product contained only einsteinium(III)], the americium, curium, berkelium, californium, cerium, praseodymium and terbium compounds were prepared on the micro-scale. A summary of the x-ray data for these products and literature values for some of the lighter actinide compounds is presented in Fig. 6.3. The deviation of uranium, neptunium and plutonium lattice parameters from the actinide curve probably represents partial oxidation above their tetravalent state.

The structural and chemical effects of radioactive decay in oxide matrices are referred to in Section 6.7. Presented here are the results of companion studies on oxides to confirm that absorption spectrophotometric analyses can be used to follow the structural consequences of

radioactive decay. Both solid-state absorption spectra and x-ray powder diffraction have been employed to study the transplutonium elements in several oxidation states.⁶ During the course of these studies it has been found that a compound's structure, or its local environment, can be deduced from its solid-state spectrum, once the spectrum has been correlated with a particular structure.^{7,8} The work described here determined that room-temperature absorption spectral data could be used to determine the structural environment of lanthanide and transplutonium sesquioxides. Three structural forms of these sesquioxides are known (designated classically as A, B, or C forms), the particular form the sesquioxide will possess being dependent on the cation size, its thermal history and other factors. The structural environment of the metal ions is different in the three sesquioxide forms, and hence, there are differences in their absorption spectra.

Some of these sesquioxides can be prepared in all three forms while others essentially crystallize in only one or two of the structural types. To generate the desired structural environment a metal ion would have in each sesquioxide structure-type, it was necessary in some instances to use mixtures of sesquioxides in which the metal

ion of interest was a minor constituent. Neodymium sesquioxide can be used as an example, and absorption spectra of neodymium in the three structural environments are shown in Fig. 6.4.⁹ The spectrum of pure Nd₂O₃ (A-form, hexagonal) can be compared to the spectra of neodymium in the monoclinic (B-form) Eu₂O₃ host and in the cubic (C-form) Eu₂O₃ host. The contribution of europium to the absorption spectra is not significant here. The most striking differences in

these spectra occur between that for the cubic form and the spectra for the other two structures. The differences in the absorption peaks can be classified into two categories: (1) the degree of splitting; and (2) the relative intensities. The spectrum for the cubic (Nd, Eu)₂O₃ exhibits a high-degree of splitting whereas the spectra for the hexagonal and monoclinic forms show unsplit absorption envelopes likely due to unresolved transitions. Only the relative intensity (not absolute) of the peaks can be compared since our microscope spectrophotometer is a single beam instrument. The most obvious changes in the relative intensity of the neodymium absorption peaks occur in the four bands between 680 and 1000 nm.

For our purposes, the important aspect is that reproducible spectra obtained at room temperature can be recognized as originating from a M(III) species in a particular sesquioxide polymorph. Several other lanthanide and transplutonium ions have been investigated in a similar manner in an effort to characterize their spectra with their sesquioxide environment. These data can then be used to help follow the ingrowth of progeny metal ions in a decay sequence, such as the ingrowth of berkelium and californium oxides in Es₂O₃. A number of absorption spectra have been obtained from Es₂O₃ samples at different intervals during their radioactive decay sequence and the particular structural environment in which the daughter and granddaughter exist is being elucidated.

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6.5 Studies of the Anhydrous Halides of the Transplutonium Elements¹

(D. D. Ensor,² R. G. Haire, J. R. Peterson,³ J. P. Young⁴)

The anhydrous halides of the first five transplutonium elements have been the subjects of a number of studies. One of the main objectives of these studies was to establish the trends and differences in the chemical and physical properties for the 5f compounds as compared to the 4f materials. The anhydrous halides are especially useful in this regard in that each of the transplutonium elements can be obtained in at least two, and in some cases three, different oxidation states (II, III or IV) in these compounds. These halides have been used for systematic studies of the transplutonium elements using absorption spectrophotometry and x-ray diffraction.⁵⁻⁸ They have also been employed for assessing the chemical and structural consequences of radioactive decay (see Sections 6.7 and 6.8), and for magnetic studies (see Section 6.9).

6.5.1 Dihalides

The dihalides of californium^{5,8} and einsteinium^{5,6} have been prepared and the products characterized by absorption spectrophotometry, and also by x-ray diffraction in the case of californium. The preparation of americium dihalides had been reported earlier.⁹ The ease or difficulty of preparing a transplutonium dihalide can be summarized in the tabulation below:

Relative Stabilities of Divalent State of the
Transplutonium Elements

II/III couple ¹⁰	Method of Preparation	Element
below -1.6 V	$\text{MX}_3 + \text{H}_2$ or MX_3 heated in vacuum	Cf, Es
-1.6 to -2.7 V	$\text{MX}_3 + \text{M}$ or $\text{M} + \text{HgX}_2$	Am
above -2.7 V	MX_2 unstable or not salt-like	Bk, Cm

The difficulty in preparing dihalides of curium and berkelium is obvious from these data.

Absorption spectra of divalent berkelium halides are critically needed to fully interpret existing data on progeny growth in studies of the chemical consequences of radioactive decay (see Section 6.9). In the latter studies, einsteinium dihalides have been found to decay into californium dihalides (granddaughter product), which implies an intermediate berkelium dihalide (daughter product). Conclusive spectral evidence for such an intermediate has not been obtained in these decay studies, due in part to a lack of knowledge about a berkelium dihalide spectrum.

A few attempts had previously been made to prepare berkelium dibromide by reacting the tribromide with berkelium metal.⁵ The result of that work was that only the californium daughter (~5% due to ingrowth) was reduced to the divalent state. Experimentally, it is very difficult to assure an exact stoichiometry of the reactants on the microgram scale. The recent attempts have been aimed at maintaining an excess of berkelium tribromide so that the final products after reduction with berkelium metal would be the dibromide and some residual tribromide. Additional reductions of berkelium tribromide were also made using lanthanum metal as a reductant, as a lanthanum tribromide product would not interfere with the absorption spectra of berkelium compounds. Since berkelium dibromide is expected to be a very reactive material, the experimental technique has been to quickly melt the tribromide-metal mixture to quench-in the

desired dibromide product in a tribromide melt before it could react with the container. The different "zones" of the resulting product were then analyzed with the microscope spectrometer. The area of the sample farthest from the initial site of the metal reductant produced only absorption peaks for berkelium and californium tribromide. In the region where the metal had reacted with the tribromides, the product was very dark in color (nearly opaque) and only limited absorption peaks could be obtained from this area. One such absorption peak could not be assigned to either Bk(III), Cf(III) or Cf(II), suggesting that it might be due to a Bk(II) absorption. X-ray diffraction data on these products did not provide evidence for the presence of BkBr_2 . Additional efforts to prepare a well-characterized dihalide of berkelium are planned.

6.5.2 Trihalides

The continuing interest in the trihalides of the transplutonium elements fall into one of four categories: (1) their use for other syntheses; (2) as sample material for consequences of radioactive decay studies (see Section 6.7); (3) as standards for magnetic studies (see Section 6.9); and (4) for elucidation of their phase behavior. The first three aspects are discussed in other sections and only the last topic will be briefly discussed here.

As a first approximation, the phase behavior of the transplutonium trihalides should be similar to the behavior of comparable (similar ionic radii and halide ion) lanthanide trihalides. Studies of berkelium trifluoride⁷ have shown that two polymorphs can be prepared; one form has the LaF_3 -type trigonal structure and the second exhibits the YF_3 -type orthorhombic structure. It has been possible to distinguish between these two forms of BkF_3 by absorption spectrophotometry even though the coordination number (nine) of berkelium is the same in each form.⁷ Absorption spectrophotometry has also been used to study $^{253}\text{EsF}_3$ and its decay products.¹¹ The difficulty in obtaining x-ray data from einsteinium com-

pounds precludes a direct determination of the structure of EsF_3 . However, absorption spectra and x-ray data obtained for the daughter (BkF_3) and granddaughter (CfF_3) in aged samples of EsF_3 suggested that the original EsF_3 samples crystallized in the LaF_3 -type trigonal (high-temperature) structure. This conclusion is in accord with the prediction of the structure based on the ionic radius of Es(III) and the phase behavior of the lanthanide fluorides.

Recently, absorption spectra for the two crystal modifications of californium trichloride were obtained. The UCl_3 -type (hexagonal) and the PuBr_3 -type (orthorhombic) structures had been crystallographically confirmed earlier. The absorption spectrum for each polymorphic form is shown in Fig. 6.5. Each form can be distinguished by differences in the absorption bands (symmetric versus asymmetric, split versus unsplit, and the relative intensities of the peaks) at 16.2 , 13 and $11.4 \times 10^5 \text{ m}^{-1}$. Spectra were also obtained for both structural types of BkCl_3 ; the PuBr_3 -type (orthorhombic) form of BkCl_3 has not been reported previously.

Another approach to resolve phase behavior, and identify the form of trihalides encountered in radioactive decay sequences (see Section 6.7), is using lanthanide hosts to provide the desired environment for the transplutonium element. We are currently establishing such standard spectra for the transplutonium elements. An example of

Fig. 6.5. Absorption spectra of californium trichloride in its two crystal modifications.

this work is shown in Fig. 6.6 where four absorption spectra of einsteinium-lanthanide tribromides are reproduced. These spectra represent three different crystal environments for einsteinium (the terbium and lutetium bromide hosts have the same crystal form). Such spectra can be useful in interpreting other

Fig. 6.6. Absorption spectra of einsteinium in lanthanide tribromide hosts (LuBr_3 and TbBr_3 - rhombohedral; SmBr_3 - orthorhombic, and LaBr_3 - hexagonal).

spectra of einsteinium tribromides. To date only one crystalline form (AlCl_3 -type monoclinic) has been observed with pure EsBr_3 .

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6.6 Microscale Preparation and Characterization of Selected Lanthanide and Actinide Phosphates¹

(S. A. Morris,² D. E. Hobart,² G. M. Begun, J. R. Peterson²)

In order to properly evaluate the use of "monazite-like" materials as a primary containment for nuclear waste,^{3,4} the basic physical and chemical properties of pure actinide phosphates must be understood. To achieve this aim, we have begun to investigate the microscale preparation and characterization of lanthanide and actinide orthophosphates. Characterization of the orthophosphates included x-ray powder diffraction, laser Raman and absorption spectrophotometric analyses.

The technique used for the microscale preparation of rare-earth orthophosphates involves the dissolution and reaction of rare-earth oxides in

a flux material at elevated temperature. The flux is suspended in a single loop of annealed platinum wire, forming a "bead". The flux material is prepared by heating lead diorthophosphate,

The rare-earth oxide is introduced and the following reaction takes place,

This technique has been used to prepare La, Ce, Pr, Nd, Tb, and Lu phosphates from the corresponding oxides. The technique has been successfully applied in an glove-box facility to prepare U, Np, Pu, and Am phosphates.⁵

X-ray diffraction analyses of crystalline orthophosphates of La, Pr, and Nd confirmed their structures as the monoclinic "monazite" form with formulas LaPO_4 , PrPO_4 , and NdPO_4 . These results were substantiated by laser Raman spectroscopy of LaPO_4 and NdPO_4 . The Raman scattering spectra compared quite well to those of the same phosphates prepared previously by another method.⁴ Terbium and lutetium orthophosphates prepared by the presently described method were found to exhibit the tetragonal "xenotime" structure, as determined by x-ray diffraction analysis.

It was not possible to prepare a trivalent cerium orthophosphate since the product was entirely Ce(IV) (as an oxide or phosphate). The fact that cerium was not reduced to the trivalent state under the conditions of the experiment was attributed to the relatively low value of the Ce(IV)/Ce(III) standard reduction potential of about 1.7 V vs NHE.⁶ By correlation of the results with the standard reduction potential of the actinide M(IV)/M(III) redox couples, a prediction was made concerning which of the actinides would form trivalent phosphates under the conditions of the experiment: all transplutonium elements, with the exception of Bk, should form trivalent phosphates from M(IV) starting materials, while U, Np and Pu should remain in the tetravalent state.

Uranium(VI) oxide (UO_3), uranium(IV) oxide (UO_2), neptunium(IV) oxide (NpO_2), and plutonium

oxide (PuO_2) were applied separately to previously prepared beads of flux material on a single loop of annealed platinum wire. The beads were then heated to about 1300°C via electrical resistance. Both yellow UO_3 and dark green UO_2 reacted with the flux and, upon cooling, turned green. When the reaction of NpO_2 with $\text{Pb}_2\text{P}_2\text{O}_7$ was completed, the bead was light green. The Pu product was dark brown.

Absorption spectrophotometric analysis confirmed the presence of U(IV), Np(IV) and Pu(IV) in the final products. X-ray powder diffraction analysis indicated that the product for uranium was UP_2O_7 , exhibiting a cubic structure. The neptunium and plutonium x-ray films were not of sufficient quality to identify an orthophosphate product.

When light brown AmO_2 was reacted with the $\text{Pb}_2\text{P}_2\text{O}_7$ flux, the resultant product was pink in color and the absorption spectrum was that of Am(III). The monoclinic "monazite" pattern was observed via x-ray diffraction analysis. This result confirms the earlier prediction that all transplutonium elements, aside from Bk, form M(III) orthophosphates when starting with M(IV) reactant material.

It should be noted that, in the present work, all preparations were performed in air and thus oxygen is present as an oxidizing agent. Additionally, the flux bead technique exposes a large surface of the reaction mixture to the surrounding atmosphere.

Future goals of this work include the use of the microscale flux "bead" method for the preparation and characterization of transplutonium element phosphates including Bk, Cf, and Es.

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6.7 Chemical and Structural Consequences of Radioactive Decay Processes¹

(J. P. Young,² R. G. Haire, J. R. Peterson,³ D. D. Ensor⁴)

Studies of the chemical and structural consequences of radioactive decay were continued from the last report.⁵ These studies have relied on absorption spectrophotometry and x-ray diffraction to determine not only the stability of the parent compound to radiation but to also ascertain the effects of the radioactive decay processes on the oxidation state and structure of the progeny.⁶ This work initially investigated the anhydrous halides of the transplutonium elements in oxidation states of II, III, and IV, but recent work has included studies of the oxides as well. Several decay chains are available for such studies, but the ^{253}Es sequence outlined below is especially attractive.

The half-lives in this scheme are short enough to generate both daughter and granddaughter products in reasonable periods of time. In addition, parallel studies starting with ^{249}Bk compounds can be carried out and compared to the results found for the above system.

From the data collected to date, two conclusions have been reached:⁷ One of these is that the oxidation state of the parent is retained by the progeny; and, secondly, that the progeny probably retains the structural environment of the parent. In effect, the thermalization of the recoil species resulting from α or β^- decay in the solid state is a process of charge-

compensated ion implantation. Thus, except for the charged species that escape the bulk phase, natural radioactive decay can maintain a charge balance as shown for the following cases. For α decay:

followed by neutralization of the He^{2+} to yield ultimately ${}_{Z-2} A^{n+}$ and He. Likewise for β^- decay:

followed by reaction of the free electron to yield ultimately ${}_{Z+1} A^{n+}$. Radioactive decay is also a single atom event; i.e., in each decay event in the solid state the recoiling ion can find itself in a matrix of 10^n host species. Therefore, it seems reasonable that a recoiling ion would adopt the structure of its host (which may be its parent if the parent was the pure bulk-phase starting material).

In most cases, it has not been possible to obtain x-ray data for einsteinium or einsteinium containing compounds;⁸ when they can be obtained it is only over a limited time span. In contrast, absorption spectra can be readily obtained from such samples over long periods of time. It has been found that a compound's structure, or its local environment, can be deduced from its solid-state absorption spectrum once the spectrum has been correlated with a particular structure (see, for example, Section 6.4). In order to further elucidate the mechanisms and changes accompanying the radioactive decay processes, a set of standard absorption spectra are being collected for the trivalent transplutonium ions in different lanthanide hosts.

It has been established from our studies that Es(II) halides eventually produce a Cf(II) granddaughter, which implies that a Bk(II) daughter was formed as an intermediate. Efforts to prepare pure Bk(II) compounds (see Section 6.5.1) have not been successful, and the lack of standard absorption spectra for Bk(II) have precluded the positive identification of such a species in the aging Es(II) samples. Additional

studies have been done with mixtures (<10 mole % ^{253}Es) that have been prepared. In one set of experiments, Es(II) was placed in lanthanide(III) halide hosts to ascertain the effect of the solid matrix on the oxidation state of the progeny. Preliminary results from these experiments indicate that a Cf(II) granddaughter is being generated in accord with the thought that the oxidation state of the parent is maintained by the progeny. With Es(III) in lanthanide(III) hosts, the initial data support the contention that both the parent and the recoiling ions [Bk(III), Cf(III)] accept the structural environment of the lanthanide hosts.

It is intended that these progeny growth studies be expanded to other decay systems and that other anions or compounds also be considered. The tentative conclusions that have been reached about the retention of oxidation state and structure by the pure transplutonium compounds would be expected to be limited to reasonable situations. In the cases cited for the transplutonium ions, there are no severe chemical or physical instabilities imposed by the maintenance of oxidation state or structure. In contrast, severe chemical instabilities could arise in other α or β^- decay schemes, such as $\text{Pa(V)} \xrightarrow{\alpha} \text{Ac}$, $\text{Th(IV)} \xrightarrow{\alpha} \text{Ra}$, $\text{Br}^{1-} \xrightarrow{\beta^-} \text{Kr}$, etc. In the latter cases, the maintenance of oxidation state and/or structure does not seem probable. Thus, the present work has the aim of establishing the limits for the maintenance of oxidation state and/or structure and elucidating the accompanying mechanisms and consequences of radioactive decay in the solid state. An application of such studies, especially in the oxide systems, would be to provide data to yield a better understanding of the processes taking place in stored nuclear materials.

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6.8 Studies of Material Balance in the Decay of Es and Bk Halides¹

(R. L. Hahn, A. L. Paige,² D. Garrett,² J. P. Young,³ R. G. Haire, J. R. Peterson²)

As part of the on-going study of the chemical effects associated with radioactive decay in bulk compounds of ²⁵³Es and ²⁴⁹Bk,⁴ we have been examining in detail the question, "What are the quantitative limits for the data obtained for solid samples from the single beam, microscope spectrophotometer?" The aims of this work have been 1) to determine the statistical errors of the method, and 2) to verify that peaks observed in the absorption spectrum indeed follow a time dependence consistent with that expected for radioactive growth and decay.

The problems inherent in the use of a single-beam instrument for quantitatively analyzing microgram amounts of solid compounds are twofold: 1) an average background, determined prior to or after the measurement of the solid sample's absorption, must be used to subtract effects, such as scattering from the quartz capillary containing the sample, etc; and 2) the path length of the light beam traversing the sample cannot be reproduced because of changes in the orientation of the solid each time that it is placed in the spectrophotometer. Thus, it is not obvious that the Beer-Lambert law for absorbance,

$$A = \log(I/I_0) = \ell \epsilon c, \quad (1)$$

is applicable to these samples (ℓ is the path length in the sample; ϵ , the absorptivity; and c , the concentration of the absorbing species).

To address these problems, a computer code was written to evaluate the absorbance for a given peak in the spectrum as the net area under the peak. By using a non-radioactive sample, NdF₃, we were then able to demonstrate that the two problems cited above were not serious ones when the data were treated on a *relative basis*. That is, from Eq. (1), one expects that the relative absorbances of two peaks in a spectrum of a homogeneous sample are given by

$$\frac{A_1}{A_2} = \frac{\epsilon_1}{\epsilon_2}, \text{ since } \ell \text{ and } c \text{ are constant.}$$

For two spectra of the same sample taken at two different times, I and II, with different sample orientations, ℓ_I and ℓ_{II} ,

$$\frac{(A_1)_I}{(A_1)_{II}} = \frac{\ell_I}{\ell_{II}}, \quad (2)$$

since ϵ_1 and c are constant, and so

$$\frac{(A_1)_I/(A_2)_I}{(A_1)_{II}/(A_2)_{II}} = 1. \quad (3)$$

For nine spectra taken of the NdF₃ sample at random orientations, we found that Eq. (3) is obeyed to better than 5% for five different peaks. Thus, we demonstrated that the single beam spectrophotometer can provide quantitative data, when the Beer-Lambert law is used in a relative manner.

For radioactive samples, as, e.g., ²⁴⁹BkCl₃ in which ²⁴⁹Bk decays to ²⁴⁹Cf, the situation is complicated by the facts that the ²⁴⁹Bk and ²⁴⁹Cf concentrations vary with time, and that radiation damage in the solid may have deleterious effects on the measured absorption spectra. If the radiation effects are not serious, we would expect, from Eqs. (1-3), that spectral peaks of an initially pure (at time t_0) sample of ²⁴⁹BkCl₃ would be altered at later times t_i , so that

$$\frac{A_{B1}(t_i)}{A_{B1}(t_0)} = \frac{\ell(t_i) c_B(t_i)}{\ell(t_0) c_B(t_0)} = \frac{\ell(t_i)}{\ell(t_0)} F_B(t_i - t_0) \quad (4)$$

where A_{B1} is the absorption of a particular peak, B_1 , in the Bk(III) spectrum, and from the

radioactive decay laws,

$$C_B(t_i) = C_B(t_0)e^{-\lambda_B(t_i-t_0)} = C_B(t_0) F_B(t_i-t_0). \quad (5)$$

The problem, of course, is that $l(t_i)/l(t_0)$ is not measured, so that $C_B(t)$ apparently cannot be determined in Eq. (4). However, if we choose peak B1 as an internal standard by requiring it to obey Eqs. (4-5), we can then derive values of $l(t_i)/l(t_0) = L(t_i)$ for each spectrum from the measured values of $A_{B1}(t_i)$ and $A_{B1}(t_0)$ and the calculated values of $F_B(t_i-t_0)$. Then it should follow, if $L(t_i)$ is characteristic for a given spectrum, that for any other Bk(III) peak, B_2 , in that spectrum

$$\frac{A_{B2}(t_i)}{A_{B1}(t_0)} = \frac{\epsilon_{B2} L(t_i) F_B(t_i-t_0)}{\epsilon_{B1}}$$

or $\frac{A_{B2}(t_i)}{L(t_i)} = \text{const } F_B(t_i-t_0); \quad (6)$

and for any peak, C_1 , in the spectrum due to daughter $^{249}\text{Cf(III)}$,

$$\frac{A_{C1}(t_i)}{A_{B1}(t_0)} = \frac{k\epsilon_{C1} L(t_i) F_C(t_i-t_0)}{\epsilon_{B1}}$$

where

$$F_C(t_i-t_0) = \frac{\lambda_C}{(\lambda_C - \lambda_B)} [e^{-\lambda_B(t_i-t_0)} - e^{-\lambda_C(t_i-t_0)}],$$

$$\text{or } \frac{A_{C1}(t_i)}{L(t_i)} = \text{const } F_C(t_i-t_0) \quad (7)$$

Here, k is the fraction of Cf(III) that arises from Bk(III); its value, ≤ 1 , tells us if a material balance of a particular oxidation state is found for the sample. These equations indicate that applying the $L(t_i)$ values (already determined for reference peak B1) to any other peaks, such as B2 or C1, in the spectra should ensure that the absorbance values for these peaks exhibit the proper variation with time as mandated by the laws of radioactive growth and decay. Fig. 6.7 illustrates that this result is indeed obtained, at least for well-defined peaks

Fig. 6.7. Plot of the normalized absorbance values, $A(t_i)/L(t_i)$, for selected peaks observed in $^{249}\text{BkCl}_3$ as a function of time. F_B and F_C are curves calculated from the radioactive decay laws.

in the $^{249}\text{BkCl}_3$ spectrum; in the figure, the ratio $A(t_i)/L(t_i)$ is plotted vs (t_i-t_0) for selected peaks. The values of $L(t_i)$ were obtained for the chosen standard peak, at 1050 nm, of ^{249}Bk . The curves drawn through the measured points are the calculated functions F_B and F_C . It is seen that the 860 and 760 nm peaks follow the behavior expected for the ingrowth of ^{249}Cf , and that the doublet at 620 and 640 nm is due to both ^{249}Bk and ^{249}Cf . In general, the agreement of the experimental data with the decay laws is better than 15%.

Further aims of this work are to derive relative values of the absorptivities, ϵ , of the

different spectral peaks of ^{249}Cf , ^{249}Bk and ^{253}Es ions. Knowing these values should allow us to make quantitative statements about the value of k , the fraction of daughter in a particular oxidation state that arises from the decay of its parent in a given valence state.

1. Research partially sponsored by Division of Nuclear Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under contracts with the University of Tennessee (Knoxville).

2. University of Tennessee, Knoxville.

3. Analytical Chemistry Division.

4. See Section 6.7.

6.9 Magnetic Characterization of Localized Actinide Ions¹

(S. E. Nave,² P. G. Huray,² R. G. Haire)

For the purpose of identifying magnetic moments of relatively isolated actinide ions, we have chosen to study the compounds with the most electronegative anions, namely the fluorides. In most of the actinide fluorides, the preparation of more than one actinide charge state is possible. Comparisons between such compounds are important as they reveal the magnetic changes brought about by removal of the 5f electrons. That the ions are relatively isolated is demonstrated by the small paramagnetic Curie-Weiss constant, θ_p , found for each system.

Americium has been prepared both as the trifluoride and as the tetrafluoride. The Hund's rule, LS coupling scheme would predict a magnetic moment of $\mu=0$ for Am^{3+} and $\mu=0.84 \mu_B$ for Am^{4+} . A 1.113-mg sample of AmF_3 at 1600 G has shown a large temperature independent part to its magnetic susceptibility $\chi_m = 710.6 \times 10^{-6}$ e.m.u./mole (in substantial agreement with a previous study)³ and a temperature dependent part with $\mu_{\text{eff}} = 0.63 \mu_B$ and $\theta_p = 1.8$ K. This latter value for μ_{eff} , although not zero, is smaller than that reported previously. Our AmF_4 sample was not well characterized in the x-ray analysis, but gave $\mu_{\text{eff}} = 0.59 \mu_B$ and $\theta_p = 1.5$ K. This result suggests a large fraction of the sample was still trifluoride.

Curium trifluoride and tetrafluoride were produced and checked by x-ray analysis and optical absorption. Both techniques agreed with the 3+ and 4+ state, respectively, for most (perhaps 97%) of the samples. This element represents a rigorous test of simple LS, Hund's rule predictions as the theoretical values of magnetic moment are $\mu = 7.94 \mu_B$ for Cm^{3+} and $\mu = 0$ for Cm^{4+} . The 203.1- μg CmF_3 sample at 1206.7 G yields $\mu_{\text{eff}} = 7.66 \mu_B$ and $\theta_p = 7$ K. The 224.6- μg CmF_4 sample is considerably more complicated to analyze as seen in Fig. 6.8, a plot of χ^{-1} versus temperature. Rather than the normal straight line indicative of Curie-Weiss behavior, we obtain a curved line. If we ignore the curvature in χ^{-1} at high temperature and take only its asymptotic slope at low temperatures, we obtain $\mu_{\text{eff}} = 5.05 \mu_B$ and $\theta_p = 8$ K. If we treat the curvature as due to a temperature independent part, then $\chi_m = 0.0336$ e.m.u./mole, and the temperature dependent part requires $\mu_{\text{eff}} = 3.75 \mu_B$ with $\theta_p = 0$ K. In either case, the deviation from the theoretical value is extremely large. A theoretical evaluation of the next excited state (above the $^8S_{7/2}$ ground state) is underway to see if this state is low enough in energy to be thermally populated in this temperature range, so as to lead to such a temperature-independent term.

Berkelium dihydride, trifluoride, tetrafluoride, and dioxide compounds have also been produced. Theoretically, Bk^{2+} should have $\mu = 10.65 \mu_B$; Bk^{3+} , $\mu = 9.72 \mu_B$; and Bk^{4+} , $\mu = 7.94 \mu_B$.

The BkH_2 sample (with a 6.8% Cf ingrowth) was not clearly identified by x-ray analysis; an observed maximum in χ between 28 K and 34 K indicates some of the Bk metal may not have reacted to form pure dihydride. The 46.1- μg sample at 1603.4 G yields a $\mu_{\text{eff}} = 7.92$ and a $\theta_p = -43$ K. Experimentally, a 143.5- μg BkF_3 sample at 1603 G (with 3% of Cf ingrowth) has given $\mu_{\text{eff}} = 9.23 \mu_B$ and $\theta_p = 77.9$ K. The BkF_4 sample (44.2 μg with a 2% Cf ingrowth) yielded a classic Curie-Weiss χ^{-1} vs T curve and $\mu_{\text{eff}} = 7.80 \mu_B$ with $\theta_p = -8$ K. Our BkO_2 (56.6 μg with 3% Cf ingrowth) sample surprised us by also yielding very little curvature in its χ^{-1} vs T

Fig. 6.8. Inverse susceptibility versus temperature for curium tetrafluoride.

curve. Its slope was consistent with $\mu_{\text{eff}} = 7.92 \mu_B$ and $\theta_p = 250$ K. We have been informed that CmO_2 has been measured and, in contrast to BkO_2 , the curvature of its χ^{-1} vs T curve was substantial. We intend to corroborate this result.

1. Research partially sponsored by Division of Nuclear Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under contracts with the University of Tennessee (Knoxville).

2. University of Tennessee and Transuranium Research Laboratory.

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6.10 Nonlocalization in Compounds of Actinide Elements¹

(S. E. Nave,² P. G. Huray,² R. G. Haire, J. R. Peterson²)

Delocalization and interatomic Coulomb correlations are of considerable consequence in determining the magnetic properties of the 5f

electrons. In the lighter actinides (Th through Pu), the overlap of the 5f electrons produces a significant bandwidth and hybridization with the 6d-7s-7p bands, requiring an itinerant or delocalized electron description. In the transplutonium actinides, increasing spatial localization produces smaller overlap.

The degree of the 5f overlap is assumed to depend upon the An-An internuclear separation, which may be systematically varied by the use of a series of binary compounds. One such series is the actinide mononictides (N, P, As, Sb and Bi), which exhibit^{3,4} fcc (NaCl-type) structures in which the An-An distance increases as the atomic number of the pnictogen increases. Uranium and neptunium mononictides have been found to exhibit magnetic transitions with transition temperatures which increase monotonically with An-An distance. This tendency is contrary to the expected behavior for a direct dipole-dipole or overlap exchange mechanism, and suggests an RKKY or superexchange interaction via the pnictogen. The plutonium mononictides exhibit magnetic transitions, the temperatures of which increase

at first with the An-An separation, reach a maximum near 4 Å, and then decrease. Americium nominally has a 5f electronic structure which is non-magnetic based on the LS coupling and Hund's rule. Measurements of the magnetic susceptibility of the metal, AmN and AmAs have shown⁵ little temperature dependence and are consistent with an electronic arrangement exhibiting only a small Curie-Weiss magnetic moment. Kanellakopoulos⁵ has measured the magnetic properties of ²⁴⁴CmN and ²⁴⁴CmAs and has found $T_C = 109$ K with $\mu_{\text{eff}} = 7.02 \mu_B$ for the nitride, and $T = 88$ K with $\mu_{\text{eff}} = 6.58 \mu_B$ for the arsenide. Our study⁶ of dhcp curium metal using the longer-lived ²⁴⁸Cm has shown that it exhibits an antiferromagnetic transition with $T_N = 65$ K. The fcc metallic phase⁶ of ²⁴⁸Cm exhibited a ferrimagnetic transition at $T_N = 205$ K with two apparent moment sites having $\mu_{\text{eff}} = 5.73 \mu_B$ and $\mu_{\text{eff}} = 6.53 \mu_B$.

We have more recently used our SQUID micromagnetic susceptometer⁷ to determine the temperature dependence of ²⁴⁸CmP and ²⁴⁸CmSb. Both are found to exhibit a high temperature Curie-Weiss behavior with a magnetic transition at low temperature. The results are shown in Fig. 6.9 for an applied field of 1601 G. Here the square of the magnetic

Fig. 6.9. Square of the specific magnetization (normalized to the extrapolated 0 K value) versus temperature for Cm pnictides.

moment (normalized to the extrapolated 0 K value) is plotted as a function of temperature to identify more clearly the Curie temperature T_C . It may be seen from this figure that, for CmP, $T_C = 73$ K and that for CmSb, $T_C = 162$ K. These results combined with values⁵ for CmN and CmAs are plotted as a function of An-An separation in Fig. 6.10. Closed symbols are used for ferromagnetic transition temperatures, T_C , and open symbols are used for antiferromagnetic transition temperatures, T_N .

Fig. 6.10. Magnetic transition temperatures of actinide pnictides versus An-An separation (ferromagnetic-closed symbols, antiferromagnetic-open symbols).

It may be seen from this figure that, in contrast to the lighter actinides, the Cm transition temperatures yield a minimum within the range of An-An spacings provided by the mononictide compounds. The more tightly bound, localized, 5f wave function of the heavier Cm will thus likely require extended exchange mechanisms like the RKKY type or superexchange with the pnictogen to explain this observation. Even though the RKKY interactions must take into account modified Fermi surfaces for the specific compounds, it is difficult to see how such a picture can be consistent with this experimental trend without a change of magnetic type. It is interesting to note, for example, that the lanthanide 4f homologue of Cm, which is Gd, forms a series of mononictides which have transition temperatures of 72 K, 15 K, 25 K, and 28 K for the compounds N, P, As and Sb, respectively. However, in the Gd series the first compound is ferromagnetic and the others are antiferromagnetic.

A plot of $[\sigma(T)/\sigma(T \rightarrow 0)]^2$ versus T for a BkN sample, where σ is the specific magnetization, is shown in Fig. 6.11. Two samples were measured, and both exhibited a transition to an ordered state at a T_C of 87.7 K as determined by a straight line fit to the linear region. It is not possible to determine if the transition is ferromagnetic or ferrimagnetic from these

measurements since the ordered moment is only $0.29 \mu_B$. Close agreement between the ordered moment and μ_{eff} would verify ferromagnetism, but disagreement between the values does not rule it out unless the effect persists to higher magnetic fields. Above this transition temperature the BkN samples also exhibited a Curie-Weiss behavior. However, the measured moment of the BkN with its less electronegative nitride anion would indicate a valence of +4 for the Bk ion in this picture. Obviously, the nitride is a more complicated system than the others and probably is in fact a semimetal. This is indicated by its physical appearance (metallic) and the fact that it orders magnetically, indicating some contribution to coupling of the Bk moments from conduction electrons as Bk occurs in metal.

1. Research partially sponsored by Division of Nuclear Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under contracts with the University of Tennessee (Knoxville).

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Fig. 6.11. Square of the specific magnetization (normalized to the extrapolated 0K value) versus temperature for BkN.

6.11 Raman Spectra of the Uranyl Ion

(G. M. Begun, L. M. Toth¹)

Understanding the aqueous chemistry of the uranyl ion is important to extraction and waste studies of systems containing uranium. The infrared and Raman spectra of uranyl ion have received considerable attention in the past; consequently, there are many reports that describe shifts in the position and intensity of the active vibrational modes. We have studied the changes that occur in the uranyl ion spectrum when hydrolysis is followed by aggregation of the

mononuclear species.² Raman spectra were recorded with a Ramanor HG-2S spectrophotometer of aqueous $\text{UO}_2(\text{NO}_3)_2$ solutions with a series of different pH values. Figure 6.12 shows the Raman spectrum of a 0.1 M uranyl nitrate solution at pH 1.3. At this pH all the uranyl is present in the unhydrolyzed form. The bands at 869

Fig. 6.12. Raman spectrum of aqueous 0.1 M $\text{UO}_2(\text{NO}_3)_2$ at pH = 1.3: excitation 514.5 nm. Slits, 6 cm^{-1} .

(polarized) and 177 cm^{-1} are due to the symmetrical stretching and bending modes, respectively, of the UO_2^{2+} ion, while the bands at 1046 (p), 725, and 1408 cm^{-1} are nitrate ion vibrational modes.

The Raman spectrum changes in the 800-900 cm^{-1} region as the pH of the solution is increased as shown by the A-F sequence of Fig. 6.13. The growth of a band at 851 cm^{-1} (p) accompanied by a decrease of the 869 cm^{-1} band first occurs and is followed by the appearance of yet another band at 836 cm^{-1} (p) (cf. curve F, Fig. 6.13). The appearance of the 851 cm^{-1} band had previously been identified as the $\text{U}_2\text{O}_5^{2+}$ species in which two UO_2^{2+} ions are bridged by an O^{2-} , but more recent data³ indicate that the species should be characterized instead as the related dihydroxy-bridged aggregate, $(\text{UO}_2)_2(\text{OH})_2^{2+}$.

The equilibria between UO_2^{2+} and its hydrolysis products are

Fig. 6.13. Raman spectra of 0.01 M $\text{UO}_2(\text{NO}_3)_2$ solution at pH = (A) 1.3, (B) 3.07, (C) 3.45, (D) 3.55, (E) 3.88, (F) 4.02. Excitation either 514.5 or 633.1 nm.

From the data given,³ we have calculated values for the respective equilibrium quotients, $\log Q_{22} = -5.90$ and $\log Q_{35} = -16.39$, and used them to determine the equilibrium distribution of dinuclear and trinuclear hydrolysis products as a function of pH. Figure 6.14 shows the calculated equilibrium distribution of the uranyl ion and its hydrolysis products as a function of pH

Fig. 6.14. Equilibrium distribution of the uranyl ion and its hydrolysis products as a function of pH for 0.1 M $\text{UO}_2(\text{NO}_3)_2$ (ionic strength = 0.3) with: 1,0 = UO_2^{2+} ; 2,2 = $(\text{UO}_2)_2(\text{OH})_2^{2+}$ and 3,5 = $(\text{UO}_2)_3(\text{OH})_5^+$. Positions marked A-F correspond to pH values at which similarly identified curves of Fig. 6.13 were obtained.

at 0.1 M UO_2^{2+} . From this graph, it is apparent that, at pH 3.8, the 2,2 species is dominant (60%) and is accompanied by approximately 20% of the total U(VI) in each of the 1,0 and 3,5 species, respectively. The close correspondence between the equilibrium distribution of U(VI) species at pH 3.8 and the relative intensities of the bands in Fig. 6.13, curve F, led to the assignment of the shoulder at 836 cm^{-1} as due to the symmetric stretching mode of the U(VI) in the trinuclear cluster, $(\text{UO}_2)_3(\text{OH})_5^+$. One further striking aspect is that the intensity changes of the bands at 836, 851, and 869 cm^{-1} (sequence A-F of Fig. 6.13) follow the equilibrium distribution shown in Fig. 6.14 for the 3,5, 2,2 and 1,0 species, respectively. (The pH values at which A-F of Fig. 6.13 were measured are indicated on Fig. 6.14). Heretofore, no discussion of Raman spectra for uranyl clusters larger than the dinuclear species has been reported.

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6.12 Cation-Cation Complexes of Pentavalent Actinides

The initial report about the existence of complexes of pentavalent actinides, AnO_2^+ , with other multiply charged cations (cation-cation complexes) was made by Sullivan et al.¹ in 1961. Several different techniques have been used to study these complexes,¹⁻⁹ such as proton spin relaxation and potentiometric titrations,¹ electron paramagnetic resonance,⁸ infrared spectroscopy,⁴ and Mössbauer spectroscopy.⁹ To a large extent, absorption spectrophotometry has been used to measure the strengths of the complexes, with shifts in the wavelengths of electronic transitions taken to be evidence for complexation.^{1-3,8} The detailed nature of these complexes, however, is still not clear.^{5-7,10}

The following sections discuss studies done using a variety of experimental techniques on complexes of NpO_2^+ with NpO_2^{2+} and UO_2^{2+} , and of AmO_2^+ with UO_2^{2+} and NpO_2^{2+} .

6.12.1 Raman Spectrometric Evidence for a Dimer of NpO_2^+ and for a Complex of NpO_2^+ with UO_2^{2+} in Aqueous Perchlorate Solutions

(B. Guillaume,¹¹ G. M. Begun, R. L. Hahn)

Raman spectrometry can often be used to detect the formation of complexes in solution from changes in vibrational spectra. Although the Raman scattering of actinides (in oxidation states V, VI, and VII) in solution has been reported, no Raman studies have previously been made of cation-cation complexes. We have used this technique to study the formation of such complexes of NpO_2^+ in acidic aqueous solutions.¹²

To obtain quantitative Raman analyses, the non-complexing perchlorate ion was used as an internal standard in our solutions, with the ν_4 band at 627 cm^{-1} being chosen as the reference. In a given series of spectral determinations, the perchlorate ion was maintained at constant concentration. The acid concentration and ionic strength were also kept constant. By normalizing the neptunyl bands to this internal standard, the effects of such experimental factors as sample cell variations, cell position, laser power

fluctuations, and absorptivity of the sample were eliminated.

As seen in Fig. 6.15, in dilute solutions containing neptunium, ≤ 0.2 M in NpO_2^+ , only the symmetrical stretching vibration, ν_1 , of NpO_2^+ at 767 cm^{-1} is Raman active. At higher NpO_2^+ concentrations, from 0.3 M to 1.2 M, two new bands appear at 180 and 738 cm^{-1} . The band at 180 cm^{-1} can be assigned to ν_2 , the bending vibration of the linear triatomic $(\text{O}=\text{Np}=\text{O})^+$ ion. We attribute the band at 738 cm^{-1} to an associated neptunyl-neptunyl species. A further increase in neptunium concentration, above 1.5 M, leads to a fairly complicated spectrum in the range $650\text{--}850\text{ cm}^{-1}$. At least six overlapping peaks can be distinguished, approximately centered at 685 , 712 , 738 , 767 , 783 and 820 cm^{-1} .

Fig. 6.15. Raman spectra of different concentrations of neptunyl(V) in perchlorate solution, at constant $\text{HClO}_4 = 1.33$ M and constant total $\text{ClO}_4^- = 4.26$ M ($\mu = 4.26$). Respective neptunium concentrations are shown on the curves.

If the peak at 738 cm^{-1} is indeed due to the association of two or more NpO_2^+ ions, analysis of this peak compared to the peak at 767 cm^{-1} will yield information on the self-association of Np(V) . A least-squares fit of the data to the equation

$$I_{738}/I_{627} = A(I_{767}/I_{627})^B$$

in the neptunium concentration range from 0.1 to 0.9 M (Fig. 6.16), gave the results: $A = 0.342 \pm 0.017$ and $B = 2.02 \pm 0.096$. This value of B , so close to 2 , is strong evidence that a

Fig. 6.16. Dependence of the relative intensity of the band at 738 cm^{-1} on the relative intensity of the band at 767 cm^{-1} . The curve is the least-squares fit to the data, Eq. (7), $I_{738}/I_{627} = 0.342 (I_{767}/I_{627})^{2.02}$, for Np concentrations ≤ 1 M.

neptunium dimer is indeed formed. We interpret the systematic deviation of points above the line in Fig. 6.16 as evidence that even higher polymers are formed at NpO_2^+ concentrations above 1 M. This conclusion is consistent with the observation (Fig. 6.15) that, above 1.0 M concen-

tration, additional peaks appear in the vicinity of the ν_1 band of NpO_2^+ . From these data, we obtain a value of the dimer formation constant,

$$\frac{K_2}{\Gamma} = \frac{[\text{Np} \cdot \text{dimer}]}{[\text{NpO}_2^+]^2} = 0.82 \pm 0.05,$$

where Γ is the activity coefficient ratio.

The effect of acidity on the neptunyl dimerization was also studied. At most, there is a variation of $\sim 20\%$ in the intensity ratio of the dimer to monomer peaks for a change in acidity from 0.1 M to 2.65 M, indicating that protons are not strongly involved in this association reaction. This result is markedly different from that found for polymerization of Pu^{4+} and UO_2^{2+} at higher pH values, where polymerization proceeds by hydrolysis and so depends sensitively on $[\text{H}^+]$.

The Raman spectra of dilute neptunium(V) perchlorate solutions are also markedly modified by the addition of uranium(VI) at Np(V) concentrations below those where dimerization is observed. Upon addition of 2 M UO_2^{2+} , the ν_1 band of NpO_2^+ at 767 cm^{-1} decreases in intensity and a new band centered at 741 cm^{-1} appears. This result is strong confirmatory evidence for the claimed formation^{1,8} of a complex of $\text{Np(V)}\text{-U(VI)}$. The values of K/Γ obtained for this complex, by taking either the Raman data or absorption spectrophotometric data for the same solutions, are in excellent agreement with each other. The K/Γ values increase with uranyl ion concentration, a trend that we attribute to changes in the activity coefficient of UO_2^{2+} . Below 1 M U(VI) , K/Γ is fairly constant, with a value of 2.5 ± 0.5 .

While the present Raman data have supplied strong confirmatory evidence for the existence of actinyl-cation complexes, the question of their structure in solution is still open. Raman spectroscopy has the potential of resolving this question, since it supplies information about changes in vibrational modes and symmetries of the molecular species present in solution. For example, while the ν_3 antisymmetric stretching vibration and the ν_2 bending mode are Raman inactive in the linear, symmetric O=M=O

structure, we note their appearance in some of our Raman spectra as the actinyl ion (either NpO_2^+ or UO_2^{2+}) concentration changes, indicating perturbations of the simple linear structure. Also, depolarization data are indicative of the symmetries of vibrational transitions in a particular structure. More experiments investigating these effects are in progress.

6.12.2 Investigation of Cation-Cation Complexes by Large-Angle X-Ray Scattering

(D. Guillaume,¹¹ A. H. Narten, R. L. Hahn)

As part of the study of cation-cation complexes of neptunium(V), NpO_2^+ , we have used the technique of wide-angle x-ray scattering¹³ to determine the pair distribution functions of the ions in solution. Our aim in this work was to learn if a well defined distance could be found for nearest neighbor actinide atoms in the solution. Finding such a characteristic distance would provide strong evidence for a chemical association between the actinide ions, and serve as verification of the existence of cation-cation complexes of NpO_2^+ .

Five different solutions containing either NpO_2ClO_4 or $\text{UO}_2(\text{ClO}_4)_2$, or both of these compounds, were prepared. ClO_4^- ion was used because of its weak complexing ability. All of the solutions were acidic, with HClO_4 concentrations varying from 0.07 to 0.2 M. A special sample holder was constructed so that a minimum volume of solution, $\sim 1 \text{ ml}$, could be used (to minimize the hazard of radioactive contamination) while exposing a flat surface area $> 2 \text{ cm}^2$ to the Mo K-x radiation.

Details of the x-ray scattering apparatus and data analysis are given in Ref. 14. The angular distributions of the scattered radiation were analyzed to give structure factors, $S(k)$, where $k = 4\pi \sin \theta / \lambda$. These were then Fourier transformed to give the radial pair distribution functions, $G(r)$, where $G(r)$ is related to the probability that if one atom is at $r=0$, a second atom will be found at a distance between r and $r+dr$.

The resulting radial distributions so obtained were found to contain several peaks, including those that were attributable to the Cl-O (1.5 Å) and O-O (2.3 Å) distances in the ClO_4^- ion.¹⁵ It was also noted that the usual structure¹⁶ found for liquid water, with a peak at 2.8 Å, was severely perturbed by the presence of the large actinyl and ClO_4^- ions. The radial distributions, (for the five different solutions), from which the known contributions due to ClO_4^- have been subtracted, are shown in Fig. 6.17. The peak at 1.8 Å is the actinyl-oxygen distance in the linear NpO_2^+ and UO_2^{2+} ions; this value agrees with the distances determined for solid neptunyl

Fig. 6.17. Radial distribution functions for solutions of actinyl perchlorates. The effects of ClO_4^- ion have been subtracted.

(V) compounds¹⁷ and for solids and solutions containing the uranyl(VI) ion.¹⁸

The feature in the radial distributions that we wish to draw attention to is the peak at 4.2 Å that is found for solutions 1 to 3, which contain either concentrated Np(V) or both Np(V) and U(VI). Solution 4, which contains 0.5 M

NpO_2^+ , has a small peak at this distance, while solution 5, containing UO_2^{2+} only, does not. There is some indication, for solutions 1 to 3, that the intensity of the peak at 4.2 Å increases with increasing actinide ion concentration. However, the intensities of these peaks are so low that a quantitative dependence upon concentration cannot be established.

We interpret the peak at 4.2 Å as representing the nearest neighbor distance between actinide atoms in the cation-cation complexes. The fact that the peak also appears in the 1.7 M solution of Np(V), in the absence of U(VI), indicates that self-association of NpO_2^+ ions occurs at high concentrations. This result supports the conclusion derived independently from Raman scattering¹⁹ that a dimer of Np(V) is formed in such solutions.

It is noteworthy that the actinide-actinide distance that we find, 4.2 Å, is comparable to the value of 3.9 Å reported as the U-U distance for solutions containing polymers of hydrolyzed uranyl(VI) species.^{18,20} A point of distinction between the two sets of results is that the uranium atoms in the polymers are joined by OH^- bridges, while the cation-cation complexes are formed in strongly acidic media, where hydrolysis is not possible.

6.12.3 Spectrophotometric Study of Complexes of AmO_2^+ with UO_2^{2+} and NpO_2^{2+} in Aqueous Perchlorate Solutions²¹

(B. Guillaume,¹¹ D. E. Hobart,²² J. Y. Bourges¹¹)

The aim of the present work²³ was the study of the cation-cation complexes, $\text{Am(V)}-\text{U(VI)}$ and $\text{Am(V)}-\text{Np(VI)}$. The isotopes neptunium-237 and americium-243 were used. Solutions of exclusively Np(VI) were prepared by controlled potential electrolysis of a mixture of Np(V) and Np(VI). Am(V) was produced by peroxodisulfate/Ag(I) oxidation of Am(III) in 2 M Na_2CO_3 . The resultant Am(VI) solution was then heated to prepare the americium(V) double carbonate solid which was dissolved in perchloric acid. Stock solutions of Am(V) without the complexing actinide cation were prepared with $\text{Ca}(\text{ClO}_4)_2$.

All spectrophotometric measurements were performed in 1-cm micro quartz cells with a Cary Model 14-H spectrophotometer.

As previously described,⁷ solutions of Am(V) in the presence of U(VI) exhibit new absorption bands at 520, 732, and 765 nm, in addition to the usual bands. The formation of Am(III) and Am(VI), due to the disproportionation of Am(V), was spectrophotometrically monitored and the final Am(V) concentration was corrected. The formation constant of the Am(V)-U(VI) complex was calculated by the formula,

$$K/\Gamma = [\text{AmO}_2\text{UO}_2^{3+}] \times [\text{AmO}_2^{+}]^{-1} \times [\text{UO}_2^{2+}]^{-1}$$

where Γ is the ratio of the activity coefficients. The concentration of the complex was determined by taking the difference between the total AmO_2^{+} concentration and that of the noncomplexed AmO_2^{+} . As shown in Fig. 6.18, the values of K/Γ increase with increasing U(VI) concentration. However,

Fig. 6.18. Values of K/Γ as a function of the concentration of M(VI) for cation-cation complexes of Am(V) with UO_2^{2+} and NpO_2^{2+} .

the mean value, $K/\Gamma = 0.35$, has a moderate standard deviation ($\sigma_{K/\Gamma} = 18\%$). The molar absorptivity coefficients for the 520, 732, and 765 nm bands were 29 ($\sigma=21\%$), 42 ($\sigma=13\%$), and 27 ($\sigma=24\%$), respectively.

The single value obtained for the Am(V)-Np(VI) complex, via the same procedure as described

above, was $K/\Gamma = 0.095 \pm 0.030$. For the absorption peaks of the Am(V)-Np(VI) complex observed at 733 and 765 nm, the molar absorptivity coefficients were estimated to be 37 ± 8 and 11 ± 5 , respectively.

Thus, the americyl(V)-uranyl(VI) and americyl(V)-neptunyl(VI) complexes are much weaker than the corresponding neptunyl-M(VI) complexes. For the actinyl(V)-actinyl(VI) complexes, $\text{MO}_2^{+}\text{-M}'\text{O}_2^{2+}$, the variation of the strength of complexation follows the general tendency:

for both M or M'. Further work in the elucidation of the exact nature of the formation of the complexes is required to fully understand the behavior of cation-cation complexes of the actinide elements.

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6.13 Studies of the Less Stable, Higher Oxidation States of Selected Actinides

As part of the studies of the less stable, higher oxidation states (above 3+) of the actinides, investigations have been carried out to find those complexing media that would stabilize these unusual oxidation states in solution. Reports on studies carried out in concentrated carbonate and fluoride solutions follow.

6.13.1 Spectroelectrochemistry of Aqueous Carbonate Solutions¹

(D. E. Hobart,² K. Samhoun,³ R. G. Haire, J. Y. Bourges,⁴ B. Guillaume,⁴ J. R. Peterson²)

Spectroelectrochemistry at optically transparent electrodes (OTE) in conjunction with cyclic voltammetry has been applied to the study of the Np(VII)/Np(VI) and Am(IV)/Am(III) redox couples in aqueous alkali-metal carbonate solutions. The strong complexation provided by carbonate ions affects the formal reduction potentials of these redox couples and stabilizes the higher oxidation states. The absorption spectra and redox potentials of the Np(VII)/Np(VI) couple in Na₂CO₃ solution and the Am(IV)/Am(III) couple in (NH₄)₂CO₃, Na₂CO₃-NaHCO₃, K₂CO₃ and Cs₂CO₃ media were measured.

Heptavalent neptunium can be prepared by electrolytic oxidation of Np(VI) in 0.25-1.5 M

Na₂CO₃-0.2 M NaOH.⁵ The stability of Np(VII) in carbonate solution makes the Np(VII)/Np(VI) redox couple amenable to spectroelectrochemical investigation.

A concentrated solution (> 1 M) of ²³⁷Np(VI) was prepared in 1 M HClO₄ and an aliquot introduced into 2 M Na₂CO₃. This 10⁻² M Np(VI) solution was adjusted to pH 13 by addition of NaOH, and cyclic voltammetry was then performed at a platinum wire microelectrode. The cyclic voltammogram displayed a reversible wave for the Np(VII)/Np(VI) redox couple, and the formal reduction potential (E°') was found to be 0.46 ± 0.01 V in this medium. [All potentials given here are referenced to the normal hydrogen electrode (NHE)]. This Np(VI)-Na₂CO₃ solution was subsequently placed in a platinum screen OTE in the light beam of a spectrophotometer. An absorption spectrum of the yellow-green Np(VI) solution was recorded prior to electrolytic oxidation, and spectra were then recorded as a function of time during the potential-step electrolysis. Np(VII) appears dark green in Na₂CO₃ solution. The E°' for the Np(VII)/Np(VI) redox couple in this medium is presently being determined spectroelectrochemically to provide a more accurate value than that obtained via cyclic voltammetry.

Tetravalent americium is unstable with respect to disproportionation in most mineral acid solutions, because of the high value, about 2.4 V, of the Am(IV)/Am(III) potential.⁶ It is possible to prepare stable Am(IV) in strongly complexing aqueous solutions such as concentrated alkali metal fluorides,⁷ concentrated phosphoric acid,^{8,9} and acidic sodium pyrophosphate solutions.⁸ Our recent work stabilizing Pr(IV) and Tb(IV) in concentrated aqueous alkali metal carbonate solutions suggested the possibility of stabilizing Am(IV) in this same medium.¹⁰

Solutions of from 10⁻¹ to 10⁻² M ²⁴³Am(III) were prepared in various carbonate solutions (2 M (NH₄)₂CO₃, 2 M Na₂CO₃-NaHCO₃, 5.5 M K₂CO₃, and 5 M Cs₂CO₃) by dissolving freshly precipitated Am(OH)₃ into these carbonate solutions. Cyclic voltammograms of Am(III) in Na₂CO₃ solution were recorded at a platinum microelec-

trode as a function of pH (see Fig. 6.19). The pH was adjusted by bubbling CO_2 through the solution. At pH 9.7, a reversible voltammogram of the Am(IV)/Am(III) redox couple was obtained from which an E° value of 0.92 ± 0.01 V was determined. The same solution was placed in an OTE of reticulated vitreous carbon (RVC). An absorption spectrum of the Am(III) solution was recorded prior to electrolysis (Fig. 6.20). A potential of 0.60 V was applied to the cell and increased to more positive values until a change

Fig. 6.19. Cyclic voltammograms of Am(III) in $2\text{ M Na}_2\text{CO}_3$ at various pH values. (Pt electrode, sweep rate: 50 mV/s , $[\text{Am(III)}] = 1.0 \times 10^{-3}\text{ M}$).

Fig. 6.20. Solution absorption spectra of Am(III) and Am(IV) in $2\text{ M Na}_2\text{CO}_3$ solution.

in the spectrum was noted. The solution first turned golden-yellow and then red-brown. The absorption spectrum of the product, Am(IV) , is shown in Fig. 6.20.

The assignment of oxidation state IV to the oxidized americium species was based on electrochemical and spectroscopic evidence and determination that only a one-electron transfer was involved, as shown by spectrophotometric and potentiometric titrations with $\text{K}_4\text{Fe(CN)}_6$ in $2\text{ M Na}_2\text{CO}_3$ solution.

Assuming the shift in reduction potential provided by complexation with carbonate ions is 1.7 V less positive than that in non-complexing solution,^{6,10} the standard reduction potential for the Am(IV)/Am(III) couple can be calculated. This value is 2.62 ± 0.01 V which agrees well with that recently reported by Morss and Fuger.¹¹

Recent attempts were made to oxidize electrolytically Cm(III) to Cm(IV) in Na_2CO_3 solution. These attempts were unsuccessful even with the use of ozone oxidation and by varying both the concentration and pH of the carbonate solutions. We therefore conclude that the standard reduction potential for the Cm(IV)/Cm(III) redox

couple is greater than the accepted value of +3.2 V/NHE.⁶

It is expected that concentrated alkali metal carbonate media may be exploited as a means to generate and stabilize other, less-stable higher oxidation state actinides such as Cf(IV) and Es(IV), and that spectroelectrochemical techniques will be increasingly utilized as a method to study actinide redox couples.

6.13.2 Aqueous and Nonaqueous Solutions of HF-CsF¹

(M. Hara,¹² D. E. Hobart,² R. G. Haire, G. M. Begun, J. R. Peterson²)

In order to investigate the possibility of producing Cm(V) using electrochemical and spectroscopic techniques, studies on electrolytic oxidation of selected tetravalent actinides were performed in concentrated fluoride solutions. Concentrated HF(48%) solution and anhydrous HF, both saturated with CsF, were chosen as solvents because of a high concentration of fluoride ion and a smaller water content than that in 15 M CsF, (in which Cm(IV) was first observed¹³). A series of electrolytic oxidation experiments with U(IV), Np(IV), and Am(IV) using several types of electrodes was carried out in order to find a suitable procedure for electrolytic oxidation of Cm(IV).

Platinum was found to be superior as a working electrode to the other electrodes examined (reticulated vitreous carbon (RVC)¹⁴ and Ni) because of minimal reactivity in the concentrated fluoride solution. A saturated calomel electrode (SCE), connected via a salt bridge, was used as the reference electrode in the concentrated HF, saturated with CsF; the Cu/CuF₂ reference electrode was used in the anhydrous HF, saturated with CsF. Teflon tubes fitted with Teflon filter membranes were used as containers for the salt bridge, Cu/CuF₂ electrode, and counter electrode.¹⁵ For most experiments using cyclic voltammetric measurements and controlled-potential electrolyses, 0.5 - 1.0 mL of sample solution was placed in a 1-cm path-length plastic cuvette in which two Pt electrodes

and the reference electrode (or the salt bridge) were immersed.

It was found that M(IV) fluorides were rather soluble in the concentrated HF, saturated with CsF, but that M(III) and M(V) fluorides were insoluble; M(VI) fluorides were sparingly soluble in this medium (12 M HF and 15 M CsF).

Anodic current waves due to oxidation of U(IV) to U(V) and successive oxidation of U(V) to U(VI) were observed by cyclic voltammetric measurements with a Pt working electrode in the concentrated HF, saturated with CsF. Soluble U(IV) and Np(IV) fluorides were electrolytically oxidized to the hexavalent state at more positive potentials than +0.2 and +1.4 V vs SCE at a Pt working electrode, respectively. But, Am(IV) was reduced to Am(III) even at +1.6 V vs SCE, which was the anodic potential limit for water at a working electrode in this medium.

In order to solve the problem of limited anodic potential range for water, the anhydrous HF, saturated with CsF, was then used as a solvent for M(IV) fluorides, and an extended anodic potential limit over that for water (+2.4 V vs Cu/CuF₂ or +2.2 V vs SCE at a Pt working electrode) was obtained in this medium (31 M HF and 13 M CsF). It was found that M(IV) and M(VI) fluorides were rather soluble, but that M(III) fluorides were insoluble in this medium; soluble U(V) (identified as UF₆⁻) was generated upon heating the solution of UF₄ dissolved in the anhydrous HF nearly saturated with CsF.

Cyclic voltammograms of U(IV) at a Pt electrode in the anhydrous HF, saturated with CsF, indicated that the U(V)/U(IV) redox couple was almost reversible in this medium, and the value of E°' was measured to be +0.7 V vs Cu/CuF₂; the reversibility was reduced in the anhydrous HF, nearly saturated with CsF. Soluble fluoride species showed electrochemical activity at a Pt working electrode. Redox systems U(IV) ⇌ U(V), U(IV) + U(IV), and Np(IV) ⇌ Np(VI) were studied by means of controlled-potential electrolyses. Np(V) was not observed in the course of electrolyses probably because of rapid disproportionation of Np(V) fluoride species (NpF₆⁻).¹⁶ On the other hand, no change in the concentration of

Am(IV) was observed after the electrolysis, even at +2.4 V vs Cu/CuF₂ at a Pt working electrode.

Preparation of anhydrous curium fluoride and dissolution in HF-CsF medium will be the next procedure attempted. Although Am(IV) could not be oxidized in HF-CsF, the stabilization of U(V) in this medium is a notable accomplishment.

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6.14 Thermodynamics of the Complexation Reactions of Americium(III) and Curium(III) with Aminopolycarboxylate Ligands¹

(D. D. Ensor,² A. H. Shah²)

The stability constants for the complexation reactions of trivalent actinides with various aminopolycarboxylate ligands have been measured at 25°C.³ The thermodynamic data (ΔH , ΔS)

available for these reactions are sparse and contain large uncertainties. Because of the importance of these very strong complexing agents in various separation processes for the trivalent actinides from the chemically similar trivalent lanthanides, a systematic study of the thermodynamic parameters which control these reactions has been undertaken.

The aminopolycarboxylate ligands used for the study were iminodiacetic acid, nitrilotriacetic acid, ethylenediaminetetraacetic acid and diethylenetriaminepentaacetic acid. The stability of the first complex

of each of the ligands with Am(III) and Cm(III) was measured using a solvent extraction technique. The organic phase utilized dinonylnaphthalenesulfonic acid as the cation exchanger. All aqueous phases were maintained at 0.5 M ionic strength by the addition of NaClO₄.

The enthalpies of formation for each reaction were derived from the variation of the stability constants over the temperature range of 5° - 50°C. These data were fitted by a method of least-squares analysis to the van't Hoff isochore. Previous determinations of enthalpy changes for the actinides have been done by this method.⁴

The thermodynamic parameters measured for Am(III) and Cm(III) are contained in Table 6.1. The results show that strong complexes are formed with each ligand studied. As expected, Cm(III) shows a slightly more negative ΔG due to its higher ratio of charge to radius. The reactions are entropy controlled since both Am(III) and Cm(III) have endothermic enthalpy changes coupled with large positive entropy changes. Data for Nd(III)^{5,6} are included in Table 6.1 for comparison. The trivalent actinides form slightly stronger complexes than the lanthanides because Am(III) and Cm(III) exhibit a more negative ΔG . The nature of the interaction between these ligands and the actinides is essentially ionic, as evidenced by the linear dependence of the ligand basicity upon the log K_1 . This dependence is shown in Fig. 6.21 for Am(III). Similar behavior was

Table 6.1 Thermodynamic Parameters
(25°C; $\mu = 0.5 \text{ M NaClO}_4$)

	Am(III)	Cm(III)	Nd(III) ^a
Ionic Radius (Å)	1.01	0.980	0.995
IDA			
ΔG (kJ/mol)	-44.9 ± 0.3	-45.0 ± 0.5	
ΔH (kJ/mol)	$+17 \pm 1$	$+21 \pm 1$	
ΔS (J/mol·K)	208 ± 5	220 ± 7	
NTA			
ΔG (kJ/mol)	-63.9 ± 0.3	-64.4 ± 0.4	-61.1 ± 0.5
ΔH (kJ/mol)	$+15.6 \pm 0.9$	$+21 \pm 2$	-6.4 ± 0.4
ΔS (J/mol·K)	267 ± 4	288 ± 7	184 ± 2
EDTA			
ΔG (kJ/mol)	-95.7 ± 0.6	-96.2 ± 0.5	-89.87 ± 0.3
ΔH (kJ/mol)	$+19.5 \pm 1.5$	$+23 \pm 2$	-27.5 ± 0.3
ΔS (J/mol·K)	387 ± 7	400 ± 8	209 ± 2
DTPA			
ΔG (kJ/mol)	-120.6 ± 0.6	-121.3 ± 0.6	-114.6 ± 0.04
ΔH (kJ/mol)	$+40 \pm 2$	$+42 \pm 2$	-38.4 ± 0.5
ΔS (J/mol·K)	539 ± 9	548 ± 9	256 ± 2

^aRefs. 5 and 6.

Fig. 6.21. Variation of basicity with $\log K_1$ for different complexing ligands and Am^{3+} .

obtained for the trivalent lanthanides.^{5,6}

The enthalpy changes are more positive than the corresponding lanthanide data. This trend has been observed previously⁴ and has been interpreted to mean an increased dehydration of the actinide ions compared to the lanthanide ions.

The large positive entropy changes for the actinides also support this interpretation. Fig. 6.22 shows the correlation of entropy change with the number of carboxylate groups. The linear dependence indicates that all the carboxylate groups on a particular ligand are participating in the interactions with the metal ion. The slope of the line for Am(III) shows a 100 J/K·mol gain in entropy per carboxylate group. Similar data for Nd(III) yielded a value of 60 J/K·mol. The differences in these values can be attributed to the loss of one additional water molecule per carboxylate group by the actinides during the complexation reaction.

The results of this study demonstrate the importance of the thermodynamic parameters to the understanding of the complexation reactions of the actinides and lanthanides. The free energy change only provides information concerning the strength of the interaction and exhibits only small variations between these families. The enthalpy and entropy changes show considerable differences in magnitude and sign between the actinides and lanthanides.

Fig. 6.22. Correlation of the change of entropy vs number of carboxylate groups.

These variations in the aminopolycarboxylate system can be interpreted as evidence of an enhanced dehydration of the actinide ion during the formation of a complex. The extent of this increased dehydration is approximately one additional water molecule lost per carboxylate group when compared to lanthanide ions.

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6.15 The Collaborative U.S. - German Effort to Synthesize Superheavy Elements by the Irradiation of ^{248}Cm with ^{238}U Ions

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During the past few years, a group from the Gesellschaft für Schwerionenforschung (GSI) and the University of Mainz has been studying the possibility of using damped heavy-ion collisions to produce superheavy elements (SHE) in reactions of the very heavy ions from the UNILAC with ^{238}U targets.⁶ In reactions of the ^{238}U beam with ^{238}U , cross section upper limits of 10^{-32} cm^2 to 10^{-35} cm^2 were obtained for half-lives between 1 ms and 1 y.

These experiments also gave the interesting result that the yields of heavier actinides, of ^{96}Cm , ^{98}Cf , ^{99}Es and ^{100}Fm , were substantially enhanced by more than an order of magnitude when ^{238}U was the projectile as compared to ^{136}Xe . An analysis of the $^{238}\text{U}+^{238}\text{U}$ cross sections indicated that most of the heavy products that survived fission were formed in the low energy tails of the energy-loss distributions. It was found that as many as 3-4 neutrons were emitted from the primary fragments, implying average excitation energies of 30-40 MeV in the heavy fragments that survived in the $^{238}\text{U}+^{238}\text{U}$ collisions; in the $^{136}\text{Xe}+^{238}\text{U}$ reaction, similar mass transfers should occur at considerably lower excitation energies, resulting in much larger survivabilities of the heavy actinide products. Thus, the large increase in actinide production with ^{238}U ions, relative to ^{136}Xe , has to be considered as evidence for a much larger primary yield of heavy reaction products prior to deexcitation by fission. Based on such arguments, a theoretical analysis of the

$^{238}\text{U} + ^{238}\text{U}$ data predicted⁷ that, if a thick ^{248}Cm target were used in place of the ^{238}U , the production cross section for superheavy element $Z = 114$, with low excitation energy ≤ 30 MeV, would be increased by a factor of ~ 100 .

Accordingly, a collaboration was established between U.S. scientists at Lawrence Livermore National Laboratory, Lawrence Berkeley Laboratory, ORNL and the scientists from GSI and the University of Mainz. The U.S. scientists supplied the targets of ^{248}Cm , obtained from the U.S. production program of transplutonium elements, and the chamber in which reaction products that recoiled out of the metallic Cm targets could be collected for analysis. Many days of running time on UNILAC with the 10 MeV/amu ^{238}U beam were provided by GSI. To isolate the superheavy elements and various heavy actinide chemical fractions, radiochemical separations were done similar to those used in the U+U experiments.

The first irradiations were performed in October, 1979. Several ^{248}Cm metal targets, containing either 3.2 or 7.27 mg/cm² ^{248}Cm (97% isotopic purity), had been produced by evaporation onto molybdenum foils. Before the beam entered the ^{248}Cm target, it passed through Mo windows and cooling gas, reducing the energy to 7.4 MeV/amu. The two target thicknesses were sufficient to further degrade the beam energy, E , to near or below the Coulomb barrier, B ($1.8 \geq E/B \geq 1.09$ or 0.96). Any reaction products emitted within laboratory angles of $\leq \pm 55^\circ$ were stopped in a copper catcher. Chemical fractions of ^{84}Po , ^{85}At and ^{96}Cm through ^{102}No were separated by high temperature gas phase, or by high pressure ion exchange, chromatography, utilizing anionic bromide complexes of the products,⁶ within ~ 1 h after irradiation. The gas-phase chemistry also should have separated elements 112 through 118, based on their predicted volatility in the elemental state, while the solution chemistry should have been effective for elements 108 through 116. In most cases, the different fractions, which were deposited on thin foils, were counted between two large-area surface barrier detectors for spontaneous fission events and α -particles, over

a period of several months. In some experiments, two of these counter pairs were positioned inside a neutron multiplicity counter, so that neutrons emitted in coincidence with fission fragments could be recorded. This counter, equipped with 30 ^3He tubes, had an efficiency of 32% for detection of a single neutron.

In these initial irradiations, difficulties were encountered because of premature failure, by formation of pin holes and cracks, of the ^{248}Cm targets in the ^{238}U beam. The integrated number of beam particles incident upon several different targets, varied from 1.7×10^{14} to 2.9×10^{15} , a factor of 5 to 10 less than the value needed to set a sensitive limit on SHE production in the $^{238}\text{U} + ^{248}\text{Cm}$ reaction. The limits obtained from these first experiments are shown in Fig. 6.23. It is seen that no superheavy elements were seen with cross sections as low as 10^{-31} to 10^{-34} cm².

Fig. 6.23. Preliminary upper limits for the production cross sections of spontaneously fissioning superheavy elements in the $^{238}\text{U} + ^{248}\text{Cm}$ reaction at 7.4 MeV/amu incident energy.

The measured formation cross sections for transcurium isotopes in the $^{238}\text{U} + ^{248}\text{Cm}$ reaction are shown in Fig. 6.24. Note that the cross sections for ^{100}Fm , ^{99}Es and ^{98}Cf are three to four orders of magnitude higher than in the $^{238}\text{U} + ^{238}\text{U}$ reaction. These increases are larger than the theoretically estimated values. In addition, isotopes of ^{101}Md were observed with

Fig. 6.24. Mass distributions of radioactive nuclides of Cf, Es, Fm, and Md produced in the reactions of $\leq 7.4 \text{ MeV/amu}$ ^{238}U with ^{248}Cm . Similar yields from the reactions of $^{48}\text{Ca} + ^{248}\text{Cm}$ are also shown.

the ^{248}Cm target, whereas they were not produced when the target was ^{238}U . For ^{259}No , which was not observed, we found an upper cross section limit of 30 nb. The cross sections for the much less fissile projectile-like fragments ^{84}Po and ^{85}At are the same, within the error limits, in the $^{238}\text{U} + ^{248}\text{Cm}$ and $^{238}\text{U} + ^{238}\text{U}$ reactions, indicating that the integral primary yield distribution, before fission can take place, is nearly the same in both reactions. These results are of interest because they indicate that analogous reaction mechanisms (i.e., similar energy and angular momentum distributions) are occurring in the transfers of nucleons from projectile to target nucleus in the U+U and U+Cm reactions, with the differences in observed cross sections being due to differences in the fissilities of the various excited intermediate nuclides. A detailed analysis of these reaction data, and comparisons with those obtained by bombarding very heavy targets with other beams,

such as ^{48}Ca and ^{136}Xe , is in progress, and should shed light on the mechanisms, and the influence of the nuclear potential energy surfaces involved in these reactions.⁸

Finally, it should be noted that many of the target lifetime problems noted above have been solved, and that a long production run for SHE was done recently at GSI.⁹ A total integrated flux of 1.9×10^{16} ^{238}U particles was obtained, about 6 times the total fluence in the 1979 runs. Data are still being obtained from this experiment, but it is clear that the results will be comparable in quality to those obtained in the earlier U+U runs. Thus, one will be able to make a definite statement concerning the probability of producing superheavy elements in deep inelastic collisions between heavy projectiles and targets.

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6.16 Search for a Spontaneous Fission Emitter in Atlantis-II Hot Brines¹

(J. Halperin, R. W. Stoughton, B. H. Ketelle, T. Lund,² R. Brandt²)

From studies of hot brines originating off the Cheleken Peninsula on the eastern coast of the Caspian Sea, Flerov and co-workers³ have reported observations of spontaneous fission activities. From these observations they conclude that they have observed one or more naturally occurring superheavy elements (SHE). This claim has stimulated investigations into other hot brines that may have a similar geologic origin. These brines presumably contact the upper mantle and are relatively rich in some of the more volatile heavy elements. Using a neutron multiplicity counter, we have examined several kilograms of precipitate, largely ferric sulfide, collected from the Atlantis-II deep (some 2500 meters below the surface of the Red Sea). Since decay by spontaneous fission is expected from superheavy elements or alternatively from their daughters, this provides the means for both a very sensitive and a highly discriminating detection technique. The observation of the characteristic bursts of neutrons emitted in spontaneous fission and the evaluation of the number of neutrons associated with this fission event, ν , provide evidence bearing on the possible existence of SHE. Since the fast neutrons emitted in fission are highly penetrating, multikilogram samples can be investigated

non-destructively in neutron multiplicity counters. The emitted bursts of multiple neutrons are thermalized and detected in ^3He proportional counters to provide a characteristic signature which serves to discriminate fission from most other sources of neutron background. Only highly energetic cosmic rays which can be attenuated by operating at depths below grade and with anticoincidence shielding provide the principal background for this system. The neutron multiplicity counter used here has been described previously.⁴ It provides an output of the number of detected events for a range of neutron multiplicities. From this measured spectrum of ν and other counter parameters we can construct the intrinsic spectrum characteristic of the sample. In nature, ^{238}U is the only known nuclide of significance exhibiting spontaneous fission decay [$T_{1/2}(\text{S.F.}) = 8.2 \times 10^{15} \text{ yr}$, $\bar{\nu} = 2.0$]; theoretical predictions of $\bar{\nu}$ (SHE) range as high as ~ 10 . Thus the observation of spontaneous fission in the absence of uranium or for samples corrected for their uranium content would support the inference of SHE decay (provided of course that the sample not be contaminated with transuranium sources). The observation of high values of $\bar{\nu}$ would strengthen the inference since the largest value of $\bar{\nu}$ for known nuclides at most only slightly exceeds 4.

The results of the neutron measurements on a 2.36 kg sample of dry precipitate from the Atlantis-II deep are summarized in Table 6.2. The sample was counted for 29.8 live days and was compared with interspersed empty counter backgrounds of 15.8 live days. The uncertainties arise principally from counting statistics and are given as standard errors (1σ). The natural uranium content of the samples was evaluated by making use of an activation analysis technique involving the measurement of delayed neutrons. The technique⁵ has been demonstrated to be capable of an accuracy of $\pm 2\%$ for samples in the 10 ppm concentration range. The uranium content was determined here as $8.8 \pm 0.2 \text{ ppm}$. Its contribution to background is listed in column 4. Since the counter system is located some 18 m below grade and benefits from a minimum of 20 m

Table 6.2 Neutron multiplicity measurements for 2.36 kg sample of Atlantis II.
The uncertainties listed represent standard errors (1σ).

Neutron Multiplicity	Atlantis II Sample (c/day)	Empty Counter Bgd (c/day)	Uranium Bgd (c/day)	Substrate Bgd (c/day)	Net Activity (c/day)
2	20.80 ± 0.84	17.10 ± 1.0	2.36 ± 0.05	1.8 ± 0.9	-0.5 ± 1.6
3	1.68 ± 0.24	0.95 ± 0.24	0.49 ± 0.02	0.3 ± 0.15	-0.06 ± 0.37
4	$0.24 \pm 0.09_1$	$0.13 \pm 0.09_2$	0.049 ± 0.003	0.08 ± 0.04	-0.02 ± 0.14
≥ 5	0.13 ± 0.065	0.06 ± 0.06	0.0033 ± 0.0003	0.05 ± 0.025	$+0.017 \pm 0.092$

water equivalent shielding, the nucleonic component of the cosmic ray flux has been well filtered and the muon interactions with sample and counter provide the principal part of our nonuranium background. This contribution to background has been evaluated for the Atlantis-II sample and they are listed in column 5. The last column lists the net activity found. In every case this is small compared to the estimated uncertainties, and we conclude that we have detected no evidence for spontaneous fission in the sample.

In order to calculate the limits of the spontaneous fission rate implied from the observed limits of the neutron multiplicity distribution, it is necessary to specify the form of the distribution in ν . We make use of the Gaussian approximation⁶ to that spectrum characterized by the width parameter, σ_ν , as well as $\bar{\nu}$. In order to interpret the calculated spontaneous fission rates in terms of possible superheavy element concentrations, we take the dominant decay mode to be spontaneous fission and make the conventional assumption of $A = 300$ a.m.u. and $T_{1/2} = 10^9$ yr in order to express the data in concentration units, $C(\text{g/g})$. Since the net observed count rates for each multiplicity are small compared to the estimated uncertainties, we have based the SHE concentration limits on these uncertainties (last column of Table 6.2). Figure 6.25 summarizes the results of these estimates as a function of $\bar{\nu}$. The experimental limit for each multiplicity value is

Fig. 6.25. Upper limits for SHE concentrations, $C(\text{g/g})$, observed in Atlantis-II based upon neutron multiplicity measurements (for assumed S.F. decay, $A = 300$ amu and $T_{1/2} = 10^9$ yr).

interpreted as an independent measure of the concentration limit. Our sensitivity limits are appreciably greater for higher assumed values of $\bar{\nu}$ than is the case for lower values. For example, the sensitivity improves approximately one order of magnitude going from $\bar{\nu}=3$ to $\bar{\nu}=8$. This reflects the higher efficiency of the counter system for detecting higher multiplicity events. These results support the conclusions reached by T. Lund et al.⁷ in their parallel chemical investigations of the Atlantis-II samples. Of course since no chemistry has been

performed on this sample in our measurements, no losses should have been sustained.

The results reported by Flerov et al.³ and our results reported here do not readily lend themselves to a direct comparison. Whereas we examined the predominantly sulfide precipitate collected at the Atlantis-II site, they investigated the waters from the Cheleken hot springs by first passing that concentrated salt solution through an ion exchange column followed by an elution procedure designed to collect the largest part of the heavier elements in the brine. This was followed by a step involving the precipitation of insoluble hydroxides. If we associate their reported results for the hydroxide insoluble fraction ($C \approx 4.5 \times 10^{-13}$ g/g of superheavy elements) with our sulfide insoluble precipitate, we may contrast that result with the data reported here. In that case, our limit for $\bar{v}=3$ of $C \leq 3.9 \times 10^{-13}$ g/g is only slightly but not significantly less than their measurement; whereas at $\bar{v}=4$, our limit of $C \leq 2.3 \times 10^{-13}$ g/g may be interpreted as being significantly lower than theirs. Of course for higher assumed values of $\bar{v}$, the upper limits set here fall progressively lower than their reported value.

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6.17 Applications of Heavy-Ion Induced X-Ray Emission to Chemical Analysis and to Studies of Chemical Bonding

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As part of a program to identify and pursue the most promising applications of heavy ions from the Holifield Heavy-Ion Research Facility (HHIRF), a study is being conducted on the possible use of the HHIRF in obtaining chemical information on complex materials such as coal and its products of combustion through measurements of x-rays emitted under heavy-ion impact. Because of the short ranges of heavy ions in matter and the high cross sections for production of x-rays, heavy-ion induced x-ray emission can be a highly sensitive method of microanalysis, with excellent spatial resolution.⁷ Of greater interest is the potential for study of oxidation states and bonding of elements in chemical compounds. Heavy projectiles are very effective in producing multiple ionization, which in turn yields satellite lines at energies higher than the normal x-ray lines. The relative intensities of these satellite lines have been shown⁸ to correlate with the chemical form of certain target elements. Thus, heavy-ion induced x-ray fluorescence analysis with emphasis on the satellite lines was considered a possible method for identifying the chemical forms of, for example, sulfur in coal.

Experiments were carried out in July 1980 at the Oak Ridge Isochronous Cyclotron (ORIC) to evaluate the utility of ion-induced x-ray spectroscopy. Targets of elemental V, Cu, Nb, Ta, and Pt were bombarded with ⁴⁰Ar ions of energies 36.0, 56.4, 76.6, and 103 MeV to determine x-ray yields as a function of target atomic number and projectile energy. A Si(Li) x-ray spectrometer was employed. K-series x-rays were observed from the ⁴⁰Ar projectiles

and from V, Cu, and Nb targets; L-series radiations were seen for Nb, Ta, and Pt; and M-series radiations were detected for Ta and Pt.

The yields obtained encouraged us to implement a wavelength-dispersive spectrometer capable of resolving some of the important features of the K_{α} -satellite line structure. In May 1981 a computer-controlled, curved-crystal spectrometer of moderate resolution (~ 7 eV at 2000 eV) was employed in measurements of x-ray spectra from bombardment of 15 different targets with 36-MeV ^{40}Ar ions at ORIC. Although data analysis is not complete, qualitative spectral variations due to differences in chemical environment are apparent. The individual peaks denoted $K_{\alpha}L^n$ arise from sulfur K_{α} x-ray emission from an atom with an additional number of L-electron vacancies n , created during the violent heavy-ion collision. The targets studied showed wide variations in their respective K_{α} -satellite line structures. Detailed interpretation of the spectra in terms of the effective charge of the sulfur atoms or

the effective valence electron density is incomplete. One interesting artifact of these experiments, also noted previously,⁹ is that the yield of $K_{\alpha}L^0$ x-rays from some targets is anomalously high, even after correction for fluorescence by projectile and target x-rays.

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7. SEPARATIONS CHEMISTRY

7.1 Solvent-Extraction Complexes of the Uranyl Ions

ORNL-DWG. 81-3813

(J. H. Burns)

It has long been recognized that molecular structure is among the important variables that must be considered in obtaining effective solvent-extraction reagents, but in uranium extraction, very little direct study of relevant structures has occurred. Analyses have now been made of the molecular structures of some complexes of the uranyl ion with organophosphorus reagents which are known to be powerful extractants. From the configurations of these molecules we can obtain some clarification of the role played by structure in complex formation, in stoichiometry of complexes, and possibly in synergism.

Uranyl complexes with acidic and neutral extractants as well as with (synergistic) combinations of these have been prepared as crystals and studied by X-ray diffraction. The structures of two of these have been elucidated in detail; a third is in progress. The results obtained suggest the presence of some structural constraints on composition and connectivity which may be of general applicability to solvent-extraction systems and need to be considered in the design of more effective extraction reagents. The two structures are described in the following.

7.1.1 Crystal and Molecular Structure of Dinitratobis(tri-*n*-butylphosphine oxide)dioxouranium(VI)

By melting together at 65°C a 1:2 molar ratio of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and tri-*n*-butylphosphine oxide (TBPO) this complex was obtained, and crystals were grown from the melt. They are monoclinic, $C2/c$, and have unit cell dimensions of $a = 8.496(2)\text{\AA}$, $b = 29.630(7)\text{\AA}$, $c = 14.063(3)\text{\AA}$, and $\beta = 94.92(2)^\circ$ at 23°C. In this cell are four molecules of $\text{UO}_2(\text{NO}_3)_2(\text{TBPO})_2$, one of which is pictured in Fig. 7.1. In the molecule the linear uranyl ion is coordinated about its equator by

Fig. 7.1. A molecule of $\text{UO}_2(\text{NO}_3)_3(\text{TBPO})_2$ with atoms represented by their thermal ellipsoids.

a plane of six O atoms supplied by two bidentate NO_3^- ions and two neutral TBPO molecules. This same equatorial arrangement is found in $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ and $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, except that in these there are water molecules (at 2.40-2.46 Å) in the sites occupied by TBPO molecules (at 2.35 Å) in the complex. The shorter (and stronger) bond to the TBPO reflects the ability of this more basic substance to displace H_2O from the uranyl coordination. The stoichiometry of this complex results from requirements of electroneutrality as well as the need for enough O atoms to fill the space around the equator (six is the usual number when some of the ligands are bidentate). The butyl groups, oriented towards the exterior of the complex, make it hydrophobic.

7.1.2 Crystal and Molecular Structure of Di- μ -dibutylphosphatobis [nitrato(tri-*n*-butylphosphine oxide)dioxouranium(VI)]

This complex was prepared, as representative of a synergistic mixture, by melting together $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, TBPO, and di-*n*-butylphosphoric acid (HDBP). The crystals are triclinic, $P\bar{1}$,

and contain one dinuclear molecule of $[\text{UO}_2(\text{NO}_3)(\text{DBP})(\text{TBPO})]_2$ per unit cell whose dimensions are $a = 13.510(6)\text{\AA}$, $b = 13.741(5)\text{\AA}$, $c = 10.054(4)\text{\AA}$, $\alpha = 121.32(2)^\circ$, $\beta = 100.28(3)^\circ$, and $\gamma = 79.99(3)^\circ$ at 23°C . The molecule, shown in Fig. 7.2, contains two uranyl ions doubly bridged by dibutylphosphato ions plus one bidentate NO_3^- ion and one TBPO molecule completing the equatorial 5-coordination about each uranyl ion.

Fig. 7.2. The dimeric molecule of $[\text{UO}_2(\text{NO}_3)(\text{TBPO})(\text{DBP})]_2$. Carbon and oxygen atoms are not labelled.

Several factors related to structure seem to be operative in the formation of this complex. As in the complex described above, water is absent from the coordination, and the molecule formed results from satisfying the need for electro-neutrality and for completing the equatorial coordination of the uranyl ion. The fact that the phosphato ligand is bridging rather than bidentate is important to this complex; however, knowing whether this also occurs in the complex with dibutylphosphoric acid alone is needed for comparison and awaits our completion of its structure analysis. It is significant that the donor O atom of the neutral TBPO is bonded directly to the U atom and is not held by hydrogen bonds as has been proposed. This suggests that the optimal amount of neutral additive for synergism to occur may be dictated by the requirements of the uranium coordination. Whether these are met

entirely by the neutral molecules or partly by additional anions depends, of course, on what the anion is and on its charge.

7.2 Short-Range Order in Hydrocarbon Mixtures

(F. Dowell, S. J. J. Watowich¹)

Precise measurements of the densities of binary liquid mixtures of a series of normal alkanes (*n*-pentane through *n*-octadecane) in a branched alkane, squalane (2,6,10,15,19,23-hexamethyltetracosane), were made at 25°C . These studies were performed to test the theory of one² of us that there is short-range order (orientational alignment) between the straight chain portions of neighboring molecules in such mixtures as well as odd-even effects (alternation of the magnitudes of physical properties as the carbon number in a chain varies from odd to even) and that these two phenomena are related. (It should be noted that this alignment need not involve only all-trans sequences in the chains). This theory was motivated by a consideration of the following experimental data:

Comparisons of excess enthalpies, excess entropies, and excess heat capacities for binary liquid mixtures of straight chain alkanes and very highly branched alkanes or cyclic alkanes and for binary liquid mixtures of straight chain alkanes with other straight chain alkanes of different length to provide³⁻⁵ evidence that short-range order or alignment occurs between neighboring chains in liquid *n*-alkanes. Depolarized Rayleigh scattering,^{4,6} x-ray diffraction,⁷ and magnetic birefringence⁶ experiments have also been cited as evidence for the existence of short-range order in *n*-alkanes; however, the interpretation of this non-thermodynamic data is presently the subject of considerable controversy—much more so than in the case of the bulk thermodynamic data cited earlier.

It has been noted by one⁸ of us that the following effects observed experimentally are probably related to short-range order in *n*-alkanes: the odd-even alternation^{9,10} in nematic-isotropic transition temperature, entropy change, nematic order parameter, and fractional volume change

as a function of tail carbon number in pure liquid crystals with alkyl tail chains, and the odd-even alternation¹¹ in nematic-isotropic transition temperature as a function of solute carbon number in binary mixtures of n-alkane solutes in liquid crystal solvents with alkyl tail chains. This latter study with mixtures also suggested that an n-alkane molecule is sensitive to the exact number of carbon atoms in the alkyl tail chain of a liquid crystal solvent and can distinguish between odd and even numbers of carbon atoms in such a tail chain, even at very small concentrations of the n-alkane solute in the liquid crystal solvent.

In addition, there is some unexplained preliminary data (activity coefficients¹² and heats of mixing⁵) in some binary mixtures of n-alkanes in squalane that suggest that the n-alkane chains may be sensitive to the location of the methyl branches in the squalane molecules.

Understanding short-range order is a vital part of understanding the organization of chain molecules in condensed phases, organization that is important in a number of basic and applied research areas: polymer structure and crystallization; plastics applications; biomembrane structure; soaps and micelles; coal structures; chromatography, solvent extraction, surfactant system processes (as in enhanced oil recovery), and other separation methods in various processes pertinent to many industrial, biological, and energy applications.

The relative orientations of n-alkane chains one with respect to the other in liquid mixtures are difficult to probe. However, by attaching one of several kinds of structures to a normal alkane chain, one can gain more information about the relative orientations of neighboring chains. Through packing effects as a function of changing the density or by means of an electric or magnetic field, the long molecular axes of the rigid cores of liquid crystal molecules can be made to order parallel to a preferred axis, thus providing some information about the relative orientations, one with respect to the other, of the n-alkyl chains attached to these cores. Similarly, the methyl branches in the squalane molecules in this study here were used

as markers (or brackets) on the straight chain backbone of the molecule to mark off straight chain sections of the molecule that could align with portions of neighboring straight chain solutes in the mixture. If sections of neighboring chains align somewhat, then they can pack more efficiently and the density of the mixture is greater than if there were no alignment.

In this study here, the densities of approximately equimolar mixtures of squalane and the n-alkanes mentioned previously were measured at 25°C by an oscillating tube density measurement system and were normalized to values for exactly equimolar mixtures. These normalized measured densities were compared with the calculated ideal mixture densities (in which there is zero volume change on mixing). Deviations of the measured densities from the calculated ideal densities revealed (1) less compact packing with increasing solute n-alkane carbon number; (2) an odd-even alternation for the n-alkanes between n-decane and n-heptadecane, with the even-numbered alkanes packing more compactly than the odd-numbered in the mixtures; and (3) more compact packing with n-tetradecane and n-hexadecane (compared with n-pentadecane). (See Fig. 7.3). Result (1) would seem to indicate, not surprisingly, that shorter n-alkane chains seem to pack more efficiently between the squalane methyl branches than do the longer n-alkanes. Results (2) and (3) are consistent with the theoretical model developed by one² of us for short-range order and odd-even effects.

Result (3) also seems to indicate the following: an efficient packing occurs when the number of carbon atoms in the n-alkane solute chain is equal to the number of carbon atoms in two sequences of solvent carbon atoms, with each sequence defined by a set of nearest-neighbor methyl branches in a squalane molecule. (These sequences of solvent carbon atoms include those in the methyl branches as well as those in the chain backbone between the branches.) For squalane, the number of carbon atoms in these sequences is either 7 or 8; and the solute n-alkanes having more compact packing in squalane have 14 and 16 carbon atoms each. The fact that two sequences of solvent carbon atoms are important would seem

Fig. 7.3. Plot of reduced density deviation; $\Delta \rho_r = \{[(\text{normalized measured density})/(\text{ideal density})] - 1\}$ vs. solute *n*-alkane carbon number for exactly equimolar binary mixtures of *n*-alkanes in squalane at 25°C.

to suggest that one section of an *n*-alkane chain aligns with one sequence in one squalane molecule while another section of the *n*-alkane chain aligns with a sequence in a second squalane molecule; geometrical models confirm that this type of packing is reasonable.

These experimental density measurements should be considered as somewhat preliminary results.

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7.3 Statistical Mechanics of Chain Molecule Systems (Liquids, Liquid Crystals, Micelles, Polymers): Chain Flexibility

7.3.1 Lattice Theory

(F. Dowell)

A theoretical lattice model for (1) semiflexible chain molecules, for (2) rigid cores having semiflexible tail chains, and for (3) head groups having semiflexible tail chains was developed¹⁻⁴ in part in preceding reporting periods and was improved and extended in this reporting period.⁴⁻⁵ Type (1) molecules include straight chain molecules, from *n*-alkanes to polyethylene. Type (2) molecules include simple liquid crystals. Type (3) molecules include soaps, micelles, and alkyl chains with functional head groups. This model is the first model to actually treat type (2) molecules and the first to explicitly treat type (3) molecules in a simple, highly tractable way.

This lattice model has been applied in three dimensions (simple cubic geometry)¹⁻⁵ and in two dimensions (square planar geometry).⁵ The hard core of each molecular segment occupies one lattice site; there are also unoccupied sites in the lattice. The model includes segmental Lennard-Jones (LJ) intermolecular interactions for both core and tail segments.

In this theoretical model, combinatorial lattice statistics are used to derive an explicit form for the configurational partition function of the system. From this partition function are derived explicit equations for all of the thermodynamic properties of the system at any given pressure and temperature.

This theoretical model is the first model to reproduce (and in some cases, to predict) and to explain in structural terms all of the features and trends in molecular ordering and thermodynamic properties observed in the nematic (N) and isotropic (I) phases in type (2) molecule systems, in particular, in homologous series of pure liquid crystals and in mixtures of *n*-alkane solutes in liquid crystal solvents. (In the nematic liquid crystal phase, the long molecular axes of the molecules tend to orient parallel to a preferred axis.)

This theoretical model is also the first model to reproduce, predict, and explain in structural terms the features and trends in molecular ordering and thermodynamic properties observed in type (2) molecule systems in smectic A (SA) and re-entrant nematic liquid crystalline phases. [In the SA phase, the molecules stack in layers such that the planes of the layers are perpendicular to the preferred axis of orientation for the long axes of the molecules. The molecules in one layer are not in register with the molecules in another layer; within each layer, there is liquid-like disorder in two dimensions for a three-dimensional (3d) system (that is, a bulk system) and liquid-like disorder in one dimension for a 2d system (that is, a surface or film). The ordinary nematic phase is stable at temperatures higher than those at which the smectic A phase is stable. The nematic phase stable at temperatures lower than those at which the smectic A phase is stable is called the re-entrant nematic phase.]

In certain ranges of temperature and density, the rigid core portions and the semiflexible tail portions of the oriented molecules tend to segregate, with the rigid portions preferring to pack with the rigid portions in other molecules and the semiflexible portions with the semiflexible portions in other molecules, thus forming

the layered smectic A phase. However, at lower temperatures, it becomes increasingly difficult to make a trans-gauche rotation in the tail chains, and the tails become rather rigid; the difference then between packing tails and cores becomes small enough such that the SA phase is no longer stable, and the re-entrant nematic phase is then the stable phase.

Properties studied with this model for the isotropic, nematic, and smectic A phases and at transitions between these phases include: tail chain flexibility, densities, entropies, core and tail orientational order parameters, smectic A ("layering") order parameter. (For example, see Table 7.1). The features and trends observed experimentally in these systems are reproduced qualitatively by this lattice model with only hard (steric) repulsions. Furthermore, this model with the attractions and soft repulsions gives better quantitative agreement with experiment than does any other model. (See also Table 7.2 in the next section.)

In this model,¹⁻⁵ the N-I transition is weakly first order in 3d and second order in 2d. Also, the SA-I transition is very weakly first order in 2d and 3d, and the N-SA transitions are second order in 2d and 3d, in accord with experiment. The range of temperature over which the SA phase is stable is greater at the high temperature end in 2d than in 3d, also in accord with experiment.

Most of the general principles applicable to simple liquid crystal structures are also applicable, with little or no modification, to some type (3) molecules, such as soaps and micelles. It is also interesting to note that it is a trivial exercise to add electrostatic, dipole-dipole, and dipole-induced dipole interactions to this lattice model using the generalized form that was developed¹⁻⁵ for intermolecular interactions [a specific case of this generalized form was the use of only London dispersion forces (treated via Lennard-Jones potentials)].

1. F. Dowell, J. Chem. Phys. **69**, 4012(1978).
2. F. Dowell, J. Chem. Phys. **70**, 5494(1979).
3. F. Dowell, Bull. Am. Phys. Soc. **25**, 213 (1980).

Table 7.1 Transition thermodynamic properties and molecular order parameters for a system of molecules for which $r = 4$, $f = 8$, $E_b/(Pv_0) = 0.833$ as calculated by the lattice model with only hard repulsions

	N $\leftrightarrow$ SA		N $\leftrightarrow$ I		SA $\leftrightarrow$ I	
	2d	3d	2d	3d	2d	3d
$\frac{kT}{Pv_0}$	0.588	0.737	0.882*	1.05*	166	60.2
ρ	0.951	0.920	0.887	0.849 _N	0.0598 _{SA}	0.125 _{SA}
θ	0	0	0	0	1	1
η	0.985	0.977	0	0.629	0.0316	0.0162
$2u$	0.326	0.392	0.437	0.474	0.665	0.663
$\frac{\Delta\rho}{\rho_{\text{more order}}}$	0	0	0	0.00829	0.0110	0.00315
$\frac{\Delta S_c}{N_S k}$	0	0	0	0.452	0.0134	0.00492

r : number of rigid core segments in a molecule.

f : number of semiflexible tail segments in a molecule.

E_b : tail bond bending energy.

P : pressure.

v_0 : hard core volume of a molecular segment.

k : Boltzmann constant.

T : absolute temperature.

ρ : density; fraction of total volume occupied by segment hard core volumes.

θ : smectic A order parameter; $0 \leq \theta \leq 1$.

η : core orientational order parameter; $0 \leq \eta \leq 1$.

$2u$: fraction of tail bonds that are flexed (bent).

S_c : configurational entropy.

N_S : number of molecules in system.

$\tau = \eta(1-3u)$: tail orientational order parameter; $0 \leq \tau \leq 1$.

*: transition between metastable phases.

4. F. Dowell, Phys. Rev. A., submitted for publication.

5. F. Dowell, to be published.

7.3.2 Variable Hole Theory

(F. Dowell)

A new theory, which will here be called a variable hole (VH) theory, was begun in a previous reporting period and has been considerably

extended¹ in this reporting period. This VH theory is intended to replace the preceding lattice theory for the three types of molecular systems discussed in the preceding section. In contrast to the lattice model, the VH model has no division of the system volume into discrete lattice sites; no restriction of the long molecular axes and the intramolecular bonds to a limited number of system axes or to an oversimplified geometry; and no restriction of

Table 7.2 N $\leftrightarrow$ I transition thermodynamic properties and molecular order parameters for various systems at P = 1 atm as calculated by the VH model and the lattice model

r	f	$\frac{E_b}{k}$ (K)	$\frac{\epsilon_{cc}}{k}$ (K)	$\frac{\epsilon_{tt}}{k}$ (K)	$v_0 \times 10^{-22}$ (cm ³)	T_{NI} (K)	η_N	V_N (cm ³ /mole)	$\frac{\Delta\rho}{\rho_N}$ (%)	$\frac{\Delta S_c}{N_S k}$
VH model:										
4	0	-	600	600	0.5643	388.4	0.5422	481.2	18.01	1.300
4	0	-	600	600	0.4514	388.1	0.5445	384.5	18.09	1.310
5	0	-	600	600	0.4514	401.5	0.2616	537.9	9.09	0.508
5	0	-	900	300	0.4514	384.6	0.2554	541.4	8.85	0.490
Lattice model with only hard repulsions:										
4	0	-	0	0	0.5643	0.3	0.7612	150.8	2.50	0.156
5	0	-	0	0	0.4514	0.7	0.7988	191.2	8.10	0.301
Lattice model with LJ (12,6) interactions:										
4	0	-	503.7	503.7	0.5643	409.0	0.6613	325.7	0.18	0.254
5	0	-	322.2	322.2	0.4514	409.0	0.6468	348.4	0.48	0.200
PAA (exper.) $mv_0 = 2.257 \times 10^{-22} \text{ cm}^3$										
						409.0	0.36- 0.42	225	0.35	0.169- 0.224

See also symbol key with Table 7.1 in the preceding section.

ϵ_{cc} : magnitude of the minimum in the LJ potential energy curve for the intermolecular interaction between two non-end core segments.

ϵ_{tt} : defined similarly to ϵ_{cc} , except is for two tail or end core segments.

$\epsilon_{ct} = (\epsilon_{cc} \times \epsilon_{tt})^{1/2}$

V : volume of the system.

$m = r + f$.

PAA: *p*-azoxyanisole.

See Ref. 4 of the preceding section for references to PAA experimental data.

segment hard core volumes to one size and shape for core and tail segments, or even to one size and shape for all core or for all tail segments. The "variable hole" in the model is the average volume around each molecule, including the hard core volume of the molecule. This hole varies in size and shape as the density of the system and the arrangement of neighboring molecules in the system varies as a function of temperature and pressure.

The hard repulsions in this model are calculated using a method somewhat similar in some respects to a van der Waals or free-volume approach for simple spherical molecules. However, each molecule in the VH model can be composed of

many molecular segments, connected by bonds (some of which can be rigid and others of which can be semiflexible); and this VH model explicitly treats the actual shape of the molecule when calculating interactions. Attractions and soft repulsions are taken into account by Lennard-Jones interactions between intermolecular segments; again, there are different interactions for different types of segments.

To test the variable hole concept, results for this VH model with a simple cubic geometry and with the hard core volumes of all of the molecular segments set equal were compared¹ with the results for the simple cubic lattice model of the preceding section. (See Table 7.2) The

Table 7.3 $N \leftrightarrow I$, $SA \leftrightarrow I$, and $N \leftrightarrow SA$ transition thermodynamic properties and molecular ordering parameters for various systems at $P = 1$ atm as calculated by the VH model

$N \leftrightarrow I$												
#	r	f	$\frac{E_b}{k}$ (K)	$\frac{\epsilon_{cc}}{k}$ (K)	$\frac{\epsilon_{tt}}{k}$ (K)	$v_0 \times 10^{-22}$ (cm ³)	T_{NI} (K)	η_N	V_N (cm ³ /mole)	$\frac{\Delta\rho}{\rho_N}$ (%)	$\frac{\Delta S_c}{N_s k}$	2u
1	5	1	250	900	300	0.4514	357.4*	0.3036	646.7	8.644	0.6879	0.4984
2	5	2	250	900	300	0.4514	341.2*	0.3063	761.1	7.500	0.7638	0.4901
3	5	2	800	900	300	0.4514	369.8*	0.0752	820.9	2.456	0.1035	0.1870

$SA \leftrightarrow I$								
#	T_{SAI} (K)	η_{SA}	V_{SA} (cm ³ /mole)	$\frac{\Delta\rho}{\rho_{SA}}$ (%)	$\frac{\Delta S_c}{N_s k}$	2u	θ	
1	358.0	0.2993	647.3	0.086	0.6730	0.4987	0.0140	
2	382.5	0.0163	819.1	0.479	0.0159	0.5099	0.0273	
3	370.8	0.0699	822.3	2.285	0.0941	0.1878	0.0037	

$N \leftrightarrow SA$									
#	T_{NSA} (K)	η_{SA}	η_N	V_{SA} (cm ³ /mole)	$\frac{\Delta\rho}{\rho_{SA}}$ (%)	$\frac{\Delta S_c}{N_s k}$	2u	θ	
1	38	1	1	471.6	0	0	0.0028	0	
2	39	1	1	555.2	0	0	0.0033	0	
3	115	0.9983	0.9983	556.8	0	0	0.0019	0	

See symbol keys with Tables 7.1 and 7.2.

results for molecular ordering and thermodynamic properties for type (2) molecule systems in the isotropic, nematic, smectic A, and re-entrant nematic phases and in transitions between these phases are somewhat similar for both models, giving one confidence in the VH approach. (See Table 7.3 for more results with this VH model.) This VH model and the lattice model in the preceding section are thus far the only theoretical models to actually treat type (2) molecules in the above mentioned phases.

This VH model has been extended¹ to include (1) short-range order (that is, order of ≤ 15 Å,

as compared to the long-range order of >100 Å defining liquid crystalline phases) in straight chain systems and (2) odd-even effects seen in molecular ordering and thermodynamic properties as the number of carbon atoms in a chain varies from odd to even. This VH model has also been extended¹ to treat more ordered liquid crystal phases and crystalline solids, as well as branched chain alkanes. The model is being extended to include a continuum of molecular orientations.

1. F. Dowell, to be published.

7.4 Recovery of Uranium for Wet-Process Phosphoric Acid

(F. J. Hurst)

Approximately one-half of the U.S. phosphoric acid production capacity is presently being treated in six phosphate plants to recover about 3.6 million lb of U_3O_8 per year using the ORNL DEPA-TOPO Process.^{1,2} This process uses a synergistic combination of reagents, di-2-ethyl-hexyl phosphoric acid (DEPA) and trioctyl phosphine oxide (TOPO) for the difficult extraction of the uranium after oxidation to its hexavalent state. An important part of the process is the reductive strip step, in which the uranium is reduced to the tetravalent state to facilitate its recovery from the organic extractant before conversion to a high-grade U_3O_8 product in a second cycle using the same reagent.

Half of the uranium currently unrecovered is contained in phosphoric acid produced in 15 plants which are relatively small (<400,000 tons of P_2O_5 per year) or which process phosphate rock that is relatively low in uranium (<0.01%), and where the economics of uranium recovery have been marginal. Declining uranium prices (from a high of ~\$45 in 1976 to \$24 /lb of U_3O_8 today) coupled with constantly rising operating costs (estimated to have increased from \$10-\$15 initially to ~\$30/lb U_3O_8 today) are jeopardizing phosphates as a source of uranium, a source which could be 20% of our annual U.S. production. More important, uranium not recovered when the rock is processed for fertilizers is lost forever. The purpose of our current research program is to improve efficiency of the process in order to make uranium recovery more cost effective and thereby conserve this resource.

Uranium Dissolution and Distribution. When phosphate rock is acidulated to produce wet-process phosphoric acid, the uranium present in the rock distributes between the acid and the precipitated calcium sulfate. In a review³ of this problem we found that depending on operating conditions, up to 40% of the uranium can be lost to the precipitate in dihydrate processes (most common in this country), while up to 80% may be

lost in hemihydrate precipitation processes. The major variable that affects this distribution is the redox potential of the slurry during acidulation, i.e., oxidizing conditions favor distribution to the acid while reducing conditions favor distribution to the calcium sulfate. In the case of hemihydrate processes, which produces a more concentrated acid (40-50% P_2O_5 compared to 28-30% for dihydrate processes), and for which uranium recovery is much more difficult and uneconomical with our current generation of extractants, an alternate uranium recovery route is suggested; that is, diversion to and subsequent recovery of uranium from the calcium sulfate residue.

Phase Separation. The efficient design of mixer-settlers is of great importance in mixing efficiency, settler capacity, and solvent losses. Recent discussions with operating personnel in the uranium recovery operations leads us to believe that many of the mixer-settler units in the current generation of plants have been over-designed. As a result, we measured (by techniques in Ref. 4) the dispersion band thickness in mixing for the DEPA-TOPO-wet-process phosphoric acid system, and found some surprising results. For example, as shown in Fig. 7.4, when the logarithm of the band width was plotted as a function of the logarithm of the flow rate of the aqueous phase, the increase (slope of 3) in thickness was essentially the same whether the system was operated aqueous-continuous at an aqueous/organic ratio of 2/1 or organic-continuous at a ratio of 1/1. This means that the same size equipment can be used with either mode of operation. Currently, most operators prefer to disperse the organic phase (the one with the lower flow rate) because they can simply mix the two phases at an aqueous/organic ratio of 2/1 and can supposedly use smaller equipment. However, when using this mode of operation there is a greater risk of forming stabilized emulsions from solids that may be present, and of encountering significantly higher entrainment of solvent in the acid raffinate. For decreasing solvent entrainment in the acid phase, the organic-continuous mode is preferred. However, in this

Fig. 7.4. Effect of aqueous throughput on phase separation.

mode, organic phase must be recycled within each stage to maintain at least a 1:1 phase ratio in the mixer and this increases the volumetric load on the mixer. The new data indicated that this would not add to the settler area requirement. The data also show that the nominal aqueous feed capacity for clean acid is about $6 \text{ mL min}^{-1} \text{cm}^{-2}$ ($1.6 \text{ gal min}^{-1} \text{ft}^{-2}$) or at least a factor of 3 times greater than the design value used in many of the current generation of uranium recovery plants.

The Effect of Dissolved Oxygen. We discovered that the presence of dissolved oxygen in the DEPA-TOPO extract results in excessive oxidation and consumption of ferrous iron during the reductive strip step.⁵ For example, our measurements, summarized in Table 7.4, show that in a typical batch shakeout in which DEPA-TOPO extract containing U(VI) was contacted with a 6 M H_3PO_4 strip solution containing a large excess of Fe(II) (deemed necessary from past experience) for 15 min, the mole ratio of Fe(II) oxidized to uranium stripped was 19/1 (sample 2). However, when the test was repeated in the absence of air and after sparging the extract with nitrogen to remove dissolved oxygen, the mole ratio was only 2/1

(sample 1), the stoichiometric ratio expected from the equation

In another test in which oxygen removal was incomplete and the contact time was increased to 60 min, very large amounts of Fe(II) were oxidized (samples 3 and 4). Sample 5 represents an extreme example of improved stripping and consumption efficiency that can be achieved by elimination of oxygen from all sources. In this case, the initial mole ratio Fe(II)/U(VI) was only 2.2/1 (10% excess) and the organic/aqueous ratio was 10/1. These conditions make stripping very difficult because only about 1% of the hexavalent uranium distributes to the aqueous phase where it is available for reduction to its almost inextractable tetravalent state. The rate determining step is the reduction of U(VI) by Fe(II) rather than the distribution of U(VI) from the solvent to the acid, which is relatively fast. After mixing overnight, 45% of the uranium was stripped by a stoichiometric amount of ferrous iron. In a duplicate test (sample 6) without oxygen removal, only 10% of the uranium was stripped and the mole ratio of Fe(II) consumed to uranium stripped was a factor of ten greater.

A series of tests were made without uranium present to determine the ferrous iron consumption when a typical reductive strip solution ($\sim 6 \text{ M H}_3\text{PO}_4$ plus 10 mg Fe(II)/ml) was contacted for 15 min with DEPA-TOPO solvent containing varying amounts of oxygen (Table 7.5). In test 7, in which the solvent was saturated with oxygen before mixing, 15.6% of the Fe(II) was oxidized. This is equivalent to 0.23 mg of O_2 per ml of solvent and is in excellent agreement with the value of 0.24 mg of O_2 per ml that we measured for the dissolved oxygen in the solvent by the method of partial pressures.* Without sparging, the solvent would normally be saturated with air rather than oxygen. Consistent with this, sample 8 gave a lower oxygen equivalent

*Determined by Gilbert M. Brown, Electrochemistry group, using a technique of partial pressures based on Henry's Law.

Table 7.4 The effect of oxygen on the reductive stripping of hexavalent uranium with ferrous iron

Conditions: a typical 0.5 m DEPA--0.125 M TOPO-NDD extract containing hexavalent uranium mixed in sealed vessels with 6 m H_3PO_4 plus ferrous iron (added as $FeSO_4$) at $\sim 25^\circ C$ under the conditions shown.

Sample No.	Treatment	Phase Ratio org/Aq	Contact Time min	mmoles		Initial mole ratio Fe(II)/U(VI)	Uranium Stripped, %	Mole Ratio of Fe(II) oxidized to U stripped*
				U	Fe(II)			
1	N_2 sparge	2/1	15	0.0067	1.84	275	57	2/1
2	none	2/1	15	0.0067	1.84	275	49	19/1
3	N_2 sparge	1/1	60	0.0034	1.82	535	94	22/1
4	none	1/1	60	0.0034	1.82	535	93	66/1
5	Argon sparge	10/1	~ 16 hr	0.025	0.054	2.2	45	2/1
6	none	10/1	~ 16 hr	0.025	0.054	2.2	10	20/1

*The stoichiometric ration of Fe(II)/U(VI) is 2/1 based on equation 1 in the text.

Table 7.5 The consumption of oxygen by ferrous iron during reductive strip; uranium not present

Conditions: Pure 0.5 M DEPA-0.125 m TOPO-NDD (no uranium present) mixed in sealed vessels at an organic/aqueous phase ratio of 2/1 with 6 M H_3PO_4 containing ferrous iron (added as $FeSO_4$) for 15 min at $\sim 25^\circ C$ under the conditions shown.

Test No.	Treatment	mmoles of Fe(II)		Oxygen Equivalent mg O_2 per ml of solvent *	Fe(II) oxidized, %
		Initial	Oxidized		
7	O_2 sparge	1.84	0.287	0.23	15.6
8	none	1.84	0.120	0.095	6.5
9	Argon sparge	1.84	<0.002	<0.001	<0.1

*Based on 0.25 mole of oxygen consumed per mole of Fe(II) oxidized.

(0.095 mg O_2 per ml of solvent), though not as low as expected. Oxidation was nearly eliminated (test 9) by carefully flushing the mixing vessel and sparging the solvent and aqueous phase with argon (which is much heavier than air). In this case less than 0.1% of the Fe(II) was oxidized.

An excessive oxidation of Fe(II) can lead to a large buildup of Fe(III) in the stripping circuit. As the Fe(III) concentration increases the Fe(II) concentration must be increased in order to reduce the U(VI) effectively.⁶ If the Fe(III) concentration gets high enough (as has happened in some operating plants), a complex ferric potassium phosphate compound may precipitate in the stripping

units. Formation of such a precipitate can, and has, led to periodic shutdown to clean out the solids. Also, the presence of solids is a major cause of inordinate solvent losses. In addition, high ferric iron concentrations can result in a less pure U_3O_8 product, and this has led to some problems in the second cycle. For example, several operating plants have modified our second cycle with more costly techniques in order to minimize iron contamination of their U_3O_8 product.⁷

Solvent Losses and Continuous Testing. Another way to significantly reduce costs is by minimizing losses of the relatively expensive ($\sim \$8/\text{gal}$) sol-

vent. Current losses are estimated to be from two to four times greater than predicted from our laboratory tests and amounts to \$2 to \$4 per lb of U_3O_8 . We are setting up a five stage (3 extraction, 2 stripping) continuous countercurrent solvent extraction system to determine how these losses may occur. The proposed tests call for the use of radioactive tracers in order to better determine the losses.

We also plan to install a sparger for continuous removal of dissolved oxygen from the extract and to use intrastage electrolysis units to minimize the formation of ferric iron during stripping. Incorporation of these innovations should decrease the consumption of Fe(II) significantly and result in the production of a very pure (almost iron free) product solution.

7.4.1 Recovery of Uranium from Lignites

There is a renewed interest in lignites as a source of fuel and for the possible by-product recovery of uranium. For this reason, we reviewed and published⁸ a summary of the experimental work carried out at ORNL during 1952 to 1954 that deals with the sulfuric acid leaching of lignite ash for uranium recovery. A discussion of the possible utilization of sulfur dioxides in flue gases is included.

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7.5 Flow Through Porous Bodies

7.5.1 Adsorptive Properties of Hydrous Zr(IV) Oxide

(D. A. Palmer, R. E. Meyer, J. S. Johnson, Jr.)

Hydrous zirconium oxide, in common with other hydrous oxides, behaves as a cation exchanger at high pH and an anion exchanger at low pH. This change of sorptive properties with pH is generally associated with acid and base equilibria between the oxide and the solution. Thus at low pH, the oxide will tend to pick up hydrogen ions which are not readily exchangeable. The excess positive charge associated with the proton is balanced by anions which are readily exchangeable. Similarly, at high pH the oxide tends to pick up non-exchangeable negative charges, presumably hydroxide groups, and exchangeable cations balance this negative charge.

In order to characterize these observations, we have found it useful to study cation and anion uptake as a function of pH and concentration of the ions. For example, we have measured the uptakes of Na^+ and Br^- on alumina and have correlated these uptakes with measurements of sorption of trace ions on alumina (cf. Section 9.2 of this report). Most of the sorption behavior of alumina is understandable on the basis of general equilibrium equations which relate the activities of the electrolytes in the aqueous solutions to the corresponding activities in the adsorbent. However, there are some significant departures from behavior derived from these equations.^{1,2} Some of these deviations might be due to the relatively high solubility of alumina especially when the pH departs significantly from neutral. Hydrous zirconium oxide is highly insoluble over a wide pH range and thus eliminates this complication from studies which compare experiment to theory.

Measurements were therefore made of Na^+ and Br^- ion uptake on hydrous zirconium oxide over a wide range of pH and from 0.001 M to 0.1 M NaBr. Results are shown in Fig. 7.5. In general, results are similar to results obtained in the same experiment for alumina (Section 9.2), but

Fig. 7.5. Uptake of Br^- and Na^+ on hydrous zirconium oxide. Solid symbols, Br^- ; open symbols, Na^+ . Circles, 0.1 M; triangles, 0.01 M; squares, 0.001 M; hexagons, 0.0001 M.

a noticeable exception is that the uptakes on ZrO_2 tend to level off at low pH. Also, although in some pH regions the slopes of log uptake vs pH are about the same for both Al_2O_3 and ZrO_2 , the uptake lines for ZrO_2 do not have the same parallel behavior which we observed for Al_2O_3 . Analysis of these data for ZrO_2 is not yet complete, but preliminary indications are that these data are more consistent with general ion exchange behavior than those for alumina.

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7.5.2 Modification of Ion-Exchange Properties of Activated Charcoal by Nitric Acid Treatment

(J. S. Johnson, Jr., F. H. Sweeton, C. G. Westmoreland, K. A. Kraus)

Activated charcoals are usually thought of as adsorbents for organic compounds. However, they

also have ion-exchange properties for inorganic ions^{1,2} and these properties sometimes surprisingly parallel those of organic resins.³ Because these materials are likely to have greater stability than commercial organic exchangers under exposures to radiation, high temperature, and aggressive chemical conditions, they are of considerable interest in a number of applications.

Treatment of activated carbons with nitric acid has been shown by Puri, et al.,⁴ and others⁵ to increase exchange capacity of charcoals substantially. We have tested Puri's recipe on high-surface-area carbons (of the order of $1000 \text{ m}^2/\text{gm}$) and found that the materials were essentially disintegrated by it. The effects of milder exposures are the subject of this section.

Charcoals from two suppliers, Barnebey Cheney and Nucon, were investigated. Although the adsorptive properties of the as-received materials were substantially different--from 0.05 to 0.35 moles of sodium ion uptake/kg solid from solutions of pH from 10 to 11--and were generally substantially less after an outgassing procedure used in some cases, all had similar properties after nitric acid treatment under the same conditions, the spread of sodium uptakes being within 30%.

Figure 7.6 illustrates the effect of oxidation conditions on monovalent ion uptake, measured by isotope dilution. It can be seen that this index of ion-exchange capacity can be increased dramatically, by an order of magnitude or more, by exposure to fuming HNO_3 or to lower concentrations at elevated temperature for a few hours. As one might expect, the increase is greater for higher acid concentrations, for higher temperatures, and for longer times of exposure. The increase is somewhat more rapid for smaller particle sizes. Tests by W. P. Eathery and coworkers of the Metals and Ceramics Division indicated some degradation by oxidation of particle size and of particle strength (from crushing measurements), but the effects were not great enough to preclude usefulness in columns subjecting the particles to moderate stresses.

Uptake increases substantially with pH, other conditions such as electrolyte concentration being the same. Figure 7.7 summarizes some results for three ions adsorbed on a large-

Fig. 7.6. Effect of oxidation conditions on monovalent ion uptake by charcoals (measured from 0.01 M Na_2CO_3 , pH 10.5).

Fig. 7.7. Uptake of monovalent and divalent ions on charcoal (Nucon, -6, +14 mesh).

particle-size Nucon. The relative variation is much less for the oxidized than for the non-oxidized material, and the differences between the uptakes of the various ions is also much less. The behavior of both, however, is that typical of weak-acid ion exchangers, with the pK for proton dissociation from ion-exchange groups of the oxidized adsorbents being lower. The most obvious interpretation is that nitric acid treatment has increased carboxylic relative to less acidic groups, such as phenolic. Support for this interpretation was obtained by C^{13} NMR measurements by E. W. Hagaman on as-received and oxidized samples, in which the peak attributable to carboxylic groups was much more prominent on the oxidized. Capacity increase was in any case not the result of increase in surface area; nitric acid treatment had little effect (Table 7.6).

Nitric acid treatment also modifies selectivities. Figure 7.8 summarizes distribution coefficients (amount per kg of charcoal/amount per liter of solution) for trace Co(II) in exchange

Table 7.6 Surface areas and helium densities of Nucon charcoal samples* (-100, +200 mesh)

	Sample wt	Helium Density	Surface Area
As-received	0.0507 g	2.013 g/cm^3	1020 m^2/g
After HNO_3 treatment (90% HNO_3 for 35 min @ 70°C)	0.0509	2.062	970

* J. D. Kintigh, Metals and Ceramics Division.

with NH_4^+ . The variations of D with electrolyte concentration is approximated very roughly by ideal ion exchange equations, which predict a slope of -2 in the function plotted.

Both treated and untreated charcoals can be loaded considerably beyond trace levels before exchange isotherms become non-linear (values of D decrease with loading), although loading effects are encountered at smaller fractions of uptake than ideal equations would predict.

Figure 7.9 presents loading curves for as-received small-mesh Barnehey Cheney charcoal and

Fig. 7.8. Adsorption of Co(II) on activated charcoal.

Fig. 7.9. Effect of loading of divalent ions on their distribution coefficients (0.2 M Na(I)).

for the same material exposed to 90% HNO_3 at 70°C for 35 minutes. Distribution coefficients decline significantly at loadings of the divalent ions above a percent of their uptakes.

In summary, nitric acid treatment can increase ion-exchange capacities of charcoals into a range typical of organic resins.

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7.5.3 Preparation of Activated Carbons Filled With Hydrus Zr(IV) Oxide

(S.-Y. Shiao, J. S. Johnson, Jr.)

Inorganic adsorbents can be expected to be more stable than organic materials to radiation, to elevated temperatures, and to many aggressive chemical environments. Many hydrous oxides have extremely interesting ion-exchange capacities and selectivities.¹ Although they have been the subject of voluminous research, they have not been used to a great extent in practical situations to which they would appear to be particularly applicable. Probably the main reason is the difficulty of preparing them in forms suitable for use in chromatographic columns. In addition to the problem of attainment of desirable particle sizes and distribution of sizes for good flow rate; low channeling, and favorable exchange kinetics, there are problems in some media of dispersion or peptization of the solids.

One approach which has shown promise as a remedy is incorporation of adsorbents in the pores of activated carbon. The excellent chromatographic properties of the carbons are in this manner combined with the specific adsorptive properties of the inorganics. This approach has been used with hydrous Fe(III) oxide,² hydrous

Sn(VI) oxide,³ zinc sulfide,⁴ and AgCl,⁵ the last to remove iodide by metathesis. However earlier attempts to fill carbons with hydrous Zr(VI) oxide have not been very successful, in that the amount of the oxide it has been possible to incorporate in pores has been low in comparison to the 2-3 moles per kg charcoal attained with Fe(III) and Sn(IV). Hydrous Zr(IV) oxide is, however of particular interest because of its low solubility; isoelectric point in the neutral pH region: high anion-exchange capacities in acidic solution and cation-exchange capacities in basic media; its high selectivity for many anions (for example, for anions of Cr(VI), Mo(VI), W(VI), etc.) which might be useful in ore processing; and its ability to form mixed oxides with such acidic oxides as those of P(V), Mo(VI), and W(VI) which have remarkable separation properties for cations.¹ We have consequently attempted to increase the loading of charcoal with this oxide.

Incorporation of Fe(III) and Sn(IV) oxides in carbon is effected by different mechanisms. With Fe(III), advantage is taken of the high distribution of this ion on the solid from several molar HCl solutions, a parallel to the adsorptive properties of organic ions exchange resins.² With Sn(IV), the high solubility of SnCl_4 allows high loading simply from filling the pores with an aqueous solution.³ In either case, the hydrous oxide is precipitated by exposing the carbon after loading with Fe(III) or Sn(IV) to ammonia gas. The relatively limited solubility of Zr(IV) compounds under conditions of interest plus the fact much of the oxide tended to precipitate on the surface when we tried preparation by the method used with tin led us to investigate systematically adsorption of Zr(IV) on activated carbon over a wide range of aqueous compositions.

In general, values of D at trace levels of Zr(IV) tend to increase with decreasing acidity. However, the highest loading of Zr(IV) which can be attained does not always correspond to the highest value of trace-level D . Loading curves from nitric acid solutions illustrate this point (Fig. 7.10). A plausible explanation

Fig. 7.10. Effect of loading on distribution coefficients of Zr(IV) on oxidized charcoal (oxidation conditions: 90% HNO_3 , 70°C, 35 min).

is that hydrolytic polymers become too large for pores if pH is too high.

The hydrolysis of Zr(IV) is complex and is known to vary with anions present.⁶ Loading was consequently also investigated in chloride, sulfate, and fluoride systems. On the basis of these results, nitrate systems were selected for emphasis in attempts to fill charcoals. By successive treatments with 0.05 M zirconyl chloride in 1 M HNO_3 (with a solution volume to solid weight ratio about 100) alternated with NH_3 exposure, about 0.6 moles of hydrous Zr(IV) oxide was incorporated in a kilogram of as-received Barnebey Cheney charcoal and about 0.8 moles Zr(IV)/kg of this material treated with HNO_3 ("oxidized" in figures; see Section 7.5.2). Although these loadings are not as high as with Fe(III) and Sn(IV), they are enough to be useful.

It should be emphasized that the objective here is not necessarily to increase ion-exchange capacity of the charcoal, but rather to change its properties to those of the oxide. In fact, the capacity of an oxidized charcoal as indicated by

Na(I) uptake, is lowered by filling with hydrous Zr(IV) oxide (Fig. 7.11). Uptakes of oxidized charcoals filled with Zr(IV) oxides are higher than those of as-received, a trend expected from the higher Zr(IV) loadings attainable. In general the increase in cation uptake with pH is what would be expected of this hydrous oxide.

Fig. 7.11. Sodium ion uptake on charcoal filled with hydrous Zr(IV) oxide (from 0.1 M NaCl; charcoal oxidation conditions: 70% HNO_3 , 60°C, 2 hrs).

Investigation of the ion-exchange and chromatographic properties of these filled carbons has only begun. We have attempted to fill with mixed Zr(IV)/P(V) oxide by equilibrating charcoal with 0.05 M zirconyl chloride in 1 M HNO_3 and then passing 1 M H_3PO_4 through a column of it. Preliminary results of sodium uptake indicate considerably higher capacities than with the hydrous oxide alone and rather surprising dependence on the NaCl concentration of the solution phase (Fig. 7.12).

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Fig. 7.12. Uptake of sodium ions on charcoal filled with Zr(IV)-P(V) hydrous oxides (oxidation conditions: 70% HNO_3 , 60°C, 2 hrs).

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7.5.4 Adsorption of Tc(VII) on Inorganic Solids

(D. A. Palmer, R. E. Meyer)

Technetium 99 is a fission product with a long half-life of 2.12×10^5 years, and, as a result, would be one of the more active nuclides after 10,000 years of nuclear waste storage. Consequently, this isotope represents a potential hazard to the environment should it escape the containment of the repository. The removal of technetium by sorption is therefore of considerable interest both from the standpoints of geo-

logic isolation and of separation from process streams. For this reason, we have carried out systematic studies of sorption on a variety of inorganic adsorbers and on minerals which are likely to be present in host geological formations for nuclear waste repositories. Both oxygenated and deoxygenated solutions are of interest; for oxic solutions, technetium is most likely present as TcO_4^- , and for anoxic conditions, the possibility of reduction to lower oxidation states which may be insoluble under some solution conditions must be considered. Here we summarize work under oxic conditions, which has been published.¹ Work under anoxic conditions is in progress.

In order to investigate sorption from solutions of very low concentration, Tc95m ($t_{1/2}=61\text{d}$, $E_Y=0.204\text{ MeV}$) was used, generally at a solution concentration of about 10^{-12} molar. In order to insure that the technetium was present as an anion, sorption experiments were conducted with strong acid, strong base, and weakly basic organic ion exchangers; and behavior typical of anions was found.

A large number of minerals were investigated over the pH range ca. 4-9. For most of these, distribution coefficients less than 5 liters/kilogram were found. (Distribution coefficients are here defined as amount per kilogram of solid divided by amount per liter of solution.) For some clay minerals, slightly larger values ranging up to about 25 were found. In many cases, the distribution coefficient decreased with pH, behavior which is typical of anion exchange.

Hydrous oxides of aluminum and zirconium were also studied. Because this class of adsorbers generally has cation exchange properties at high pH and anion exchange properties at low pH, a decrease of distribution coefficient with pH is expected. As shown in Fig. 7.13 such a decrease is observed, especially in the more dilute solutions. A significant salt effect is also observed. Similar observations were noted for adsorption of TcO_4^- on hydrous aluminum oxide.

A unique inorganic ion-exchange substance with the general formula, $[(\text{CH}_3\text{O})\text{X}]_n$, where X is an exchangeable anion, has been described by Weiss.²

Fig. 7.13. Plot of adsorption versus pH on ZrO_2 in NaCl solutions: $\bullet$ 0.01 M; $\circ$ 0.1 M; $\blacktriangle$ 0.25 M. The $\blacktriangle$ points were obtained by the circulating column method, and the remainder are from the batch method.

The adsorption-pH profile of this polymer proved to be quite unusual as shown in Fig. 7.14. Both batch and circulating column methods were used. In the latter method, solution was circulated through a loop which contained a column of the material. For this material, adsorption is

Fig. 7.14. Plot of adsorption versus pH for TcO_4^- on $[(\text{CH}_3\text{O})\text{Cl}]_n$ in 0.1 M NaCl ($\bullet$ circulating column method; $\circ$ batch method; $\blacktriangle$ without preequilibration). The dashed line represents the titration curve for the polymer (right side axis in units of ml 1 N NaOH per g polymer, and these points are denoted by $\blacksquare$).

not readily reversible because acidification caused only a slow release of technetium over a period of days. The dashed curve represents a pH titration curve of the polymer and corresponds to the replacement of the chloride ion with the hydroxide ion. The approximate similarity between the two curves suggests that the pertechnetate ion can more readily replace adsorbed hydroxide ions than chloride ions. Because this polymer is highly insoluble and is resistant to

hot acids and bases and can remove large amounts of technetium from solutions, it could prove useful as a separation agent, and we are therefore investigating it further.

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8. ELECTROCHEMISTRY

8.1 Electrochemical and Corrosion Characteristics of Ion-Implanted "Near-Surface" Alloys

(E. J. Kelly, B. R. Appleton,¹ C. W. White,¹ B. D. Lichter,² N. G. Thompson²)

Ion implantation, a nonequilibrium doping technique, can be used to prepare an endless variety of "near-surface" alloys, including alloys not attainable by conventional alloying methods. A study of the electrochemical behavior of Pt-implanted titanium alloys — prepared by ion implantation (near Gaussian distribution of Pt with the peak concentration at ~30 nm from the surface), and depth-profiled (concentration of Pt vs distance from surface) by nondestructive Rutherford backscattering — has clearly demonstrated the unique advantages of ion implantation in the study of phenomena, such as corrosion and catalysis, which depend primarily upon the surface properties of a metal.³⁻⁵

The electrochemical and corrosion behavior of Pt-implanted Ti may be understood by reference to Fig. 8.1, and is described by Eq. (1), where i represents the net (i.e., observed) current per unit area of

$$i = i_d(1 - \theta) + i_{H,Ti}^+(1 - \theta) + i_{H,Pt}^+ S - i_{H,Ti}^-(1 - \theta) - i_{H,Pt}^- S \quad (1)$$

alloy surface, S is the surface area of Pt per unit area of alloy surface, θ is the fraction of the titanium surface blocked (with respect to Ti dissolution and hydrogen evolution on Ti) by the surface Pt, and i_d is the current density corresponding to the anodic dissolution of titanium. The current densities corresponding to the hydrogen oxidation and proton reduction reactions are represented by i_H^+ and i_H^- , respectively. For titanium, $i_d \gg i_{H,Ti}^+$, and for the trivial amounts of Pt involved (cf. Fig. 8.2), $(1 - \theta) \approx 1$. Consequently, Eq. (1) may be rewritten in the form,

$$i = i_{S=0} + i_{H,Pt}^+ S - i_{H,Pt}^- S, \quad (2)$$

where

$$i_{S=0} = i_d - i_{H,Ti}^- \quad (3)$$

Fig. 8.1. Effect of implanted Pt on the electrochemical and corrosion behavior of Pt-implanted Ti in H_2 -saturated 1 M H_2SO_4 (30°C).

For pure ($S = 0$) titanium under open-circuit ($i = 0$) conditions, Eqs. (2) and (3) require that $i_d = i_{H,Ti}^-$. This is shown in Fig. 8.1 by the intersection of the i_d and $i_{H,Ti}^-$ curves, and establishes the corrosion potential ($E_{corr,S=0}$) and corrosion current density ($i_{corr,S=0}$). For Pt-implanted Ti under open-circuit conditions, Eq. (2) requires that $i_{S=0} = i_{H,Pt}^+ S - i_{H,Pt}^- S$. However, as is evident from Fig. 8.1, at potentials slightly more negative than the reversible hydrogen electrode potential (E_{H_2/H^+}), $i_{H,Pt}^- \gg i_{H,Pt}^+$ and, therefore, $i_{S=0} \approx i_{H,Pt}^- S$. Consequently, as S increases (in Fig. 8.1, $S_1 < S_2 < S_3 < S_4$), the open-circuit potential given by the intersection of the $i_{S=0}$ and $i_{H,Pt}^-$ curves shifts positive relative to $E_{corr,S=0}$, and the corresponding metal dissolution rate (i_d) initially increases from $i_{corr,S=0}$ to a maximum and then decreases sharply. For a sufficiently large value of S (i.e., S_4 in Fig. 8.1), $i_{H,Pt}^+ \approx$

$i_{H,Pt}^+ S \gg i_{S=0}$ and, therefore, the potential is fixed at E_{H_2/H^+} and the corresponding corrosion rate (read from the $i_{S=0}$ curve) is very low, the goal of alloying.

In Fig. 8.2, typical open-circuit potential (E)/time (t) curves are shown for Pt-implanted electrodes upon immersion in H_2 -saturated 1 N H_2SO_4 . Following dissolution of the pre-existing air-formed oxide film, the specimens tend to activate ($E \rightarrow E_{corr,S=0}$) in the normal fashion indicated by the curve for pure titanium. As the implanted electrodes activate, preferential dissolution of Ti results in an increase in S (cutting into and moving up the Gaussian) and a corresponding increase in $i_{H,Pt}^- S$, as evidenced by the reversal in the sign of dE/dt from (-) to (+). In passing through the peak (maximum S, maximum $i_{H,Pt}^- S$) concentration of Pt given by the Gaussian profile, dE/dt again reverses sign and, eventually, $E = E_{corr,S=0}$ as the Pt is lost from the surface. Only the most heavily doped specimen remained (>30 days) at E_{H_2/H^+} .

Fig. 8.2. Open-circuit potential vs time for Pt-implanted titanium in 1 N H_2SO_4 at 30°C. Total fluence (atoms Pt cm^{-2}) and peak Pt concentration (atom % Pt): $\diamond(0,0)$; $\bullet(2 \times 10^{12}, \sim 0.001)$; $\square(1.5 \times 10^{13}, 0.006)$; $\circ(3.2 \times 10^{14}, 0.10)$; $\blacksquare(4.2 \times 10^{14}, 0.12)$; $\blacktriangle(5.3 \times 10^{14}, 0.14)$; $\triangle(1.3 \times 10^{15}, 0.31)$; $\diamond(2.8 \times 10^{16}, 9.0)$.

In Fig. 8.3, a typical potentiostatic current/time curve is shown for a rather weakly doped specimen (2.6×10^{14} atom Pt cm^{-2} total fluence) immersed in H_2 -saturated 1 N H_2SO_4 . One may assume i_d is the same as that observed on pure Ti at $E = -450$ mV vs SCE. If no accumulation of

Fig. 8.3. Potentiostatic current-time curve (solid curve) and surface concentration (atom % Pt) of platinum-time curve (dashed curve) for Pt-implanted titanium (2.6×10^{14} cm^{-2} total fluence, 0.078 atom % Pt peak concentration) in 1 N H_2SO_4 at 30°C. $E = -450$ mV vs SCE.

Pt occurs, the concentration of Pt on the surface at any instant may be calculated using $i_d(E = -450)$ and the original concentration/depth profile obtained by back scattering. This curve (dashed curve) is also shown in Fig. 8.3, with the curve shifted along the time axis to align the current and surface concentration peaks (necessary because of the initial air-formed oxide film). As the curves show, following dissolution of the oxide, the net current is initially positive, corresponding to dissolution of the metal with $S \approx 0$. As dissolution continues, the surface concentration of Pt increases (moving up the Gaussian) and i becomes negative (cathodic), i.e., $i_{H,Pt}^- S$ dominates on the right side of Eq. (2). The cathodic current peaks at the maximum in the Gaussian distribution, and then decreases (moving down the Gaussian). Ultimately, the current returns to the anodic current density observed on pure titanium at the specified potential. At the peak concentration of Pt on the surface (0.078 atom % Pt), only $i_{H,Pt}^- S$ contributes to the observed current, i.e., in Eq. (2) one has $i = -i_{H,Pt}^- S$. Consequently, if one divides the peak cathodic current by the peak concentration of Pt, one obtains the current density (A $atom^{-1}$) for the hydrogen evolution reaction on platinum. By repeating the experiment at var-

ious potentials between -300 and -450 mV vs SCE, using similarly doped specimens, and plotting $\log(\text{current density})$ vs potential, one obtains a Tafel line linear over three decades of current density (Fig. 8.4). The slope of the cathodic Tafel line is $-(2/3)(2.303RT/F)$, i.e., -40 mV/decade. This result indicates that the mechanism for hydrogen evolution on the surface

Fig. 8.4. Hydrogen evolution reaction on Pt-implanted Ti in H_2 -saturated 1 N H_2SO_4 (30°C).

alloy is fast discharge ($H^+ + e^- \rightleftharpoons H_{ad}$) on Pt, followed by H_{ad} ad-atom diffusion to Ti, followed by rate-determining electrochemical desorption ($H^+ + H_{ad} + e^- \rightarrow H_2$) from Ti. This mechanism could not have been determined without the use of ion-implanted electrodes, and demonstrates the diagnostic value of ion implantation.

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8.2 Effect of Stress on Anodic Dissolution of Titanium

(Gilbert M. Brown, E. J. Kelly)

Stress corrosion cracking (SCC) is, in part, stress-assisted electrochemistry although metallurgical and mechanical factors are also important. The corrosion of titanium has been investigated extensively by Kelly^{1,2} in acidic sulfate and chloride media, and titanium serves as a useful model for systems which have a transition from active to passive behavior. It was thought that measurement of the influence of stress on the corrosion of titanium would give some insight into the electrochemical factors which cause active-passive materials to be susceptible to SCC.

Published work³ has shown that stress has little influence on the anodic dissolution current of active metals in the elastic deformation region. However, in the inelastic or plastic deformation region, a substantial increase in current was observed for some metals, and this current approached an asymptotic limit at constant strain rate. A theoretical treatment suggested that two major factors cause the increased dissolution rate. During plastic deformation, slipping occurs and new slip planes are exposed to solution at the electrode surface to form steps. The current increase is due to the increase in the number of steps exposed to solution. In some metals, high index planes are exposed during slipping and these planes have a high activity for dissolution. Minor effects on the current are due to charging of the double layer of the new metal exposed to solution and to an increase in the surface roughness. An important conclusion from this work is that all of these influences on the observed current are proportional to the strain rate rather than the stress level.

An electrochemical cell was designed to allow previously-annealed titanium wire samples to be controlled potentiostatically in an anaerobic environment while undergoing elongation at a constant rate by use of a tensile test machine (Instron Model 1122). Despite severe experimental difficulties associated with slippage of the specimens in the grips, and with failure of various elastomeric materials used to mask the unattacked portions of the specimens, a few results of a semiquantitative nature have been obtained for electrodes in the active state. As predicted, only a minor effect was observed in the elastic region and at low strain rates ($<10^{-4} \text{ s}^{-1}$) in the inelastic region. A dramatic increase in current was observed at appreciable strain rates ($\sim 10^{-3} \text{ s}^{-1}$) in the inelastic stress region. These results differ from those observed for iron and molybdenum³ in that an asymptotic limit in current vs strain is not observed at relatively high strain rates ($\sim 10^{-2} \text{ s}^{-1}$). Instead, the current reaches a maximum and then decreases. This effect may be related to the rate of formation of monolayer, lower-valent titanium species which have been postulated to exist on the surface of actively-corroding titanium.^{1,2}

The results obtained to date are not particularly surprising in light of the theoretical work discussed above and our knowledge of the corrosion of titanium in the absence of stress. Unfortunately, the experiments have proven to be very time consuming since, initially, it takes approximately ten days to get an electrode to a steady state and only one strain rate at a fixed potential can be investigated with each sample. Since the current is a function of both strain rate and potential, a large number of samples would be required to describe such a system completely. In addition, we do not have the necessary data to ascertain the rate of conversion of bare metal to monolayer, lower-valent species in the absence of stress. In view of the time consuming nature of the experiments and the high cost of sample preparation, further work will be postponed until we have a firmer basis for interpretation of the results.

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8.3 Effect of Redox Couples on the Kinetics of Titanium Dissolution

(Gilbert M. Brown)

Earlier studies by Kelly^{1,2} have demonstrated that the reactions of Ti(III) and Ti(IV) ions in solution play a dominant role in the spontaneous cessation (auto-passivation) of localized corrosion of titanium. Localized corrosion is characterized by the simultaneous existence of active and passive surfaces in contact with the electrolyte. The product of corrosion of Ti in the active state, Ti(III), is oxidized to Ti(IV) at the passive surface. Subsequent reduction of Ti(IV) to Ti(III) at the active surface results in the passivation of the active surface; i.e., Ti(IV) functions as a cathodic depolarizer which polarizes Ti into the passive-state potential region. It is important to determine whether other redox couples, derived from dissolution of an alloying constituent, can function in the same manner. It has been shown³ that Cr(III) ions have no effect on the active-state corrosion of Ti. However, the oxidation of Cr(II) ions at the active titanium surface results in the formation of a protective Cr(III) oxide on the surface of the titanium. Thus, the action of the Cr(III)/Cr(II) couple is entirely different in nature from that of the Ti(IV)/Ti(III) couple, and consequently the search for redox couples analogous to the Ti(IV)/Ti(III) couple turned to vanadium, a common and important alloying constituent for titanium.

A literature report⁴ suggests that V(III) is the corrosion product of vanadium metal at open circuit in dilute sulfuric acid solutions; however, V(IV) appears to be the product at small anodic overpotentials.⁵ The V(III)/V(II) and V(IV)/V(III) couples have reversible potentials in the appropriate potential region to effect

the auto-passivation of titanium. The reduction of V(III) and V(IV) ions at an active titanium surface has been studied in 1 *N* H₂SO₄ at 30°C. The order of the reduction of V(IV), as determined from $(\partial \log i_c / \partial \log C_4)_E$ at steady state where i_c is the partial cathodic current at a concentration C_4 of V(IV), is reproducibly less than unity. The values are 0.83 at -530 mV vs SCE and 0.81 at -400 mV. Tafel behavior is not observed at a constant V(IV) concentration, so that $(\partial E / \partial \log i_c)_{C_4} \neq \text{constant}$. A plot of i_c^{-1} vs C_4^{-1} is linear with a positive intercept for an experiment at -400 mV, but such a plot shows downward curvature at -530 mV for small values of C_4^{-1} and a zero intercept. These results are suggestive of parallel reaction paths. One path involves rate limiting electron transfer to a solution species and the other path involves rate limiting electron transfer to an adsorbed species. The rate of the former path is more dependent on overpotential than the latter path. Further work is required to clarify the mechanism. Nonetheless, the critical concentration of V(IV) required to passivate an active titanium electrode is comparable to the concentration of li(IV) required for passivation¹ [8.4 mM Ti(IV) vs 12 mM V(IV) in 1 *N* H₂SO₄]. The reduction of V(III) at an active titanium electrode is more straightforward. A Tafel plot is linear in the potential region -500 to -620 mV vs SCE with $(\partial E / \partial \log i_c)_{C_3} = -0.12$ V, indicating the reaction mechanism is rate limiting electron transfer. Unfortunately, the concentration of V(III) required to passivate an active titanium electrode in 1 *N* H₂SO₄ is ~42 mM, a value larger than that which could reasonably be expected to be present in a crevice. If the rate of reduction of V(III) is independent of pH, this situation could improve at pH = 1 to 2.

The data in the literature for the corrosion of vanadium metal are incomplete, and further studies of the corrosion of vanadium will be required to make quantitative predictions of the corrosion behavior of Ti-V alloys. It is also of interest to determine the Ti(III), Ti(IV), V(III), and V(IV) ionic species in solution. A UV-vis-NIR spectrophotometer has been acquired,

and studies are planned to determine the species responsible for the passivation reactions.

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8.4 Corrosion of Iron in Concentrated Chloride Solutions

(A. L. Bacarella, F. A. Posey)

Studies continued on kinetic aspects of the corrosivity of pure iron in concentrated chloride solutions. In earlier studies¹ on the iron-chloride system, a numerical correlation was developed on the effects of pH (moderately acidic to neutral solutions) and temperature (up to 225°C) on the corrosion rate of a typical low carbon steel in deaerated 4 *M* NaCl. This work was directed principally towards providing a basic understanding of the corrosion behavior of ferrous metals in synthetic brines that simulated the aggressive concentrated salt solutions encountered during conversion of the heat content of geothermal brines into electrical energy. More recently, the results of these and related studies have also been used for comparison of the behavior of various metallic materials of construction in synthetic and real geothermal brines.² The current measurements are being carried out with emphasis on the influence of chloride ion concentration on the rates and mechanisms of the anodic and cathodic partial processes that determine the corrosion behavior of iron in strong chloride solutions. We expect that the results will be of general interest not only to increased understanding of the kinetics of interfacial reactions in chloride-induced localized corrosion of ferrous materials but also to specific corrosion problems such as

denting of steam generator tubes by carbon steel support plates in pressurized water reactors and anticipated corrosion behavior of iron-based materials in salt dome repositories for nuclear wastes.

During approximately the past year a large number of polarization curves have been obtained for pure iron (Johnson Matthey "Specpure") in deaerated sodium chloride solutions. Measurements were made in 0.2, 0.5, 2, 3, 4, and 5 *M* NaCl solutions at selected temperatures from 30° to 75°C; most measurements were carried out at both pH = 3 and pH = 5. Because of the need for pH control in the unbuffered chloride solutions, all measurements were made in a large (5 liter) reaction flask in which both deaeration and stirring were accomplished by a vigorous stream of purified argon or hydrogen. A considerable number of duplicate measurements have been needed under most conditions because the results have been difficult to reproduce (a not altogether uncommon occurrence in corrosion studies). In spite of the difficulties, which probably account for the relative paucity of information on this system in the literature, a number of facts seem to be established. At lower temperatures ($T < 50^{\circ}\text{C}$) the rate of the anodic, iron-dissolution reaction seems to be inverse first order in $[\text{H}^+]$ at all chloride ion concentrations; this observation agrees with those of many other investigators for systems both with and without chloride ions present. In addition, at pH = 5, the specific rate of the anodic process appears to decrease with increasing chloride ion concentration in the range from 0.5 to 5 *M*; this trend agrees qualitatively with that observed earlier with carbon steel.³ On the other hand, it is not clear that there is any significant effect of chloride ion concentration on the rate of the anodic process at pH = 3. Instead, at the lower temperatures ($T < 50^{\circ}\text{C}$) the principal influence of chloride ion concentration on the corrosion rate at pH = 3 is due to the strong effect of the increased viscosity of the solution on the limiting current for the hydrogen evolution reaction as the chloride ion concentration is

changed from 0.2 *M* to 5 *M*. The limiting current for convective diffusion of hydrogen ions to the electrode surface is affected in a complex manner by increasing chloride ion concentration because the increased (kinematic) viscosity influences both the hydrodynamic and concentration boundary layers at the electrode surface and also the stirring efficiency by gas bubbles (surface tension between gaseous and liquid phases plays an additional role).

As the temperature is increased, the situation becomes far more complex. For example, at 75°C we observe no significant effect of pH (between 3 and 5) on the rate of the anodic process. Instead, it is clear that the anodic process is under partial mass transport control, in a manner similar to that observed in studies on the mechanism of electrochemical machining.⁴ A further complication arises at the elevated temperatures, especially in relatively dilute solutions (e.g., 0.2 *M*), due to simultaneous formation of a porous magnetite layer on the electrode surface. Continued growth of the magnetite layer leads eventually to mass transport effects on both anodic and cathodic partial processes, and consequent changes in the corrosion rate with time (another source of irreproducibility).

These measurements also demonstrate the futility, in general, of attempts to estimate accurately the spontaneous corrosion rate from measurements of the polarization resistance,⁵ because under many conditions the system is under partial mass transport control and the proportionality factor between corrosion current density and polarization resistance cannot be estimated accurately from the polarization curves. A method for analysis of errors to be expected from use of curve-fitting methods for estimation of corrosion rates from polarization curves in the vicinity of the corrosion potential was presented previously.⁶ It is clear that further progress in understanding the kinetic behavior of this rather complicated corrosion system will require use of an improved electrolytic cell, one in which mass transport by forced convection is controlled in

a precise manner. Of particular interest are configurations for which the appropriate equations of convective diffusion have been solved (rotating disk electrode, various channel or annular electrodes).⁷

1. F. A. Posey and A. A. Palko, *Corrosion* (Houston) **35**, 38 (1979).
2. P. F. Ellis, II and M. F. Conover, Materials Selection Guidelines for Geothermal Energy Utilization Systems, DOE/RA/27026-1 (January 1981).
3. F. A. Posey, A. A. Palko, and A. L. Bacarella, Corrosivity of Geothermal Brines Progress Report for Period Ending December 1976, ORNL/TM-5863 (April 1977).
4. H. C. Kuo and D. Landolt, *Electrochim. Acta* **20**, 393 (1975).
5. F. Mansfeld, pp. 163-262 in Advances in Corrosion Science and Technology, vol. 6, M. G. Fontana and R. W. Staehle, eds., Plenum Press, New York, 1976.
6. Chem. Div. Annu. Prog. Rep. Feb. 29, 1980, ORNL-5685, p. 173.
7. J. Newman, p. 305 in Electrochemical Systems, Prentice-Hall, Englewood Cliffs, 1973.

8.5 Chemical/Electrochemical Treatment of Waste Photographic Liquids for Silver Recovery and Conditioning Prior to Discharge

(F. A. Posey, A. A. Palko)

Nearly 50,000 liters of silver-bearing and cyanide-bearing waste liquids are generated annually at ORNL from photographic and photo-reproduction equipment.¹ In Tennessee the acceptable discharge level of these ions is 0.05 mg/l. Since the concentrations of silver and cyanide ions in the liquids in question range from about 0.5 to 20,000 mg/l, these wastes must be treated before legal discharge to the environment or to secondary sewage treatment facilities. Currently waste liquids are stored in drums or carboys because no entirely satisfactory processes have been available which are capable of both silver removal and destruction of toxic species to the desired levels without simultaneous creation of other problems, such as sludge disposal.

Because of our experience in earlier studies on metals recovery and the design of extended-

surface-area electrolytic cells,² we were asked to assist in the solution of this problem. Initial efforts were concerned with the design and construction of cells for direct electrolytic recovery of silver from spent photographic fixer which contains approximately 5 g/l of dissolved silver along with high concentrations of thiosulfate, sulfite, halide, acetate, ammonium, aluminum, and other ions. One cell contained a multiplicity of closely spaced parallel plates operated as a cathode at controlled potential. It was expected that this cell would be used to recover most of the silver from spent fixer in the form of plated metal. A second cell, based upon use of a porous graphite cathode of high efficiency, was to be used to "polish" the effluent from the parallel-plate cell for reduction of the silver content of the solution to desired values. It is possible to design such porous-electrode cells for treatment of process streams in a rational manner.³ Our experiments on direct electrolytic silver recovery from spent fixer soon confirmed our earlier work² and the observations of Van Zee and Newman⁴ on deposition of silver onto porous carbon cathodes as well as the limitations on removal efficiency by electrolysis which were discussed by Trainham and Newman.⁵ Although many cell designs for electrolytic silver recovery units appear in the technical and trade literature every year, it is clear that no cell design will circumvent the basic limitations of the direct electrolytic method for silver removal from spent fixer to environmentally acceptable levels.

Fortunately, in the course of our studies on the electrochemical reactivity of the components of spent photographic fixer and on the conditions required for deposition of satisfactory silver plates, a process was developed which allows reduction of the silver content of spent fixer from >5 g/l to <0.5 mg/l, so that the resulting effluent may be discharged directly to the sewer system (silver concentrations below 10 mg/l are acceptable to the EPA for discharge to secondary sewage treatment facilities). No silver-containing sludges are produced by the

process, which also lowers the biological oxygen demand (BOD₅) from >20,000 mg/l to approximately 2,000 mg/l and lowers the chemical oxygen demand (COD) from >100,000 mg/l to approximately 2,000 mg/l. The process has been tested successfully on a scale which is equivalent to the rate of production of spent fixer by ORNL. Details of the process will be described in a forthcoming report.

1. R. M. Rauenzahn and Y. B. Lee, Recovery of Silver from Waste Liquids of Photoreproduction Equipment, ORNL/MIT-314 (November 1980).

2. A. A. Palko and F. A. Posey, p. 153 in Ecology and Analysis of Trace Contaminants Progress Report October 1974 - December 1975, ORNL/NSF/EATC-22 (February 1976).

3. Gilbert M. Brown and Franz A. Posey, J. Electrochem. Soc. 128, 306 (1981).

4. J. Van Zee and J. Newman, J. Electrochem. Soc. 124, 706 (1977).

5. J. A. Trainham and J. Newman, J. Appl. Electrochem. 7, 287 (1977).

9. NUCLEAR WASTE CHEMISTRY

9.1 The Effect of Water in Salt Repositories

The purpose of this program is to carry out experimental and modeling studies of the behavior of crystalline salt in the presence of saturated brine. Such studies are needed to predict those consequences of the presence of water in bedded salt that might affect the integrity of a radioactive waste repository.

During the reporting period, the study of the kinetics of salt consolidation in brine was completed, a study of the time-dependent permeability of a "grain boundary" between stressed salt crystals has been underway, and a study of the migration of brine within consolidated blocks of salt under stress was initiated.

9.1.1 The Consolidation and Permeability of Salt in Brine

(A. J. Shor, C. F. Baes, Jr., C. M. Canonico)

The following is an abstract of a recently issued topical report¹ presenting our results on the kinetics of consolidation and the loss of permeability of aggregates of salt crystals in brine:

The consolidation and loss of permeability of salt crystal aggregates, important in assessing the effects of water in salt repositories, has been studied as a function of several variables. The kinetic behavior was similar to that often observed in sintering and suggested the following expression for the time dependence of the void fraction:

$$\phi(t) = \phi(0) - (A/B) \ln[1 + Bt/\bar{z}(0)^3],$$

where A and B are rate constants and $\bar{z}(0)$ is initial average particle size. With brine present, A and $\phi(0)$ varied linearly with stress. The initial void fraction was also dependent to some extent on the particle size distribution. The rate of consolidation was most rapid in brine and least rapid in the presence of only air as the fluid. A brine containing 5 m MgCl_2 showed an intermediate rate, presumably because of the greatly reduced solubility of NaCl. A substantial wall effect was indicated by an observed

increase in the void fraction of consolidated columns with distance from the top where the stress was applied and by a dependence of consolidation rate on the column height and radius. The distance through which the stress fell by a factor of e was estimated to change inversely as the fourth power of the column diameter. With increasing temperatures (to 85°C), consolidation proceeded somewhat more rapidly and the wall effect was reduced. The permeability of the columns dropped rapidly with consolidation, decreasing with about the sixth power of the void fraction. In general, extrapolation of the results to repository conditions confirms the self-sealing properties of bedded salt as a storage medium for radioactive waste.

1. A. J. Shor, C. F. Baes, Jr., and C. M. Canonico, Consolidation and Permeability of Salt in Brine, ORNL-5774, July 1981.

9.1.2 The Permeability of a Salt Grain Boundary
(L. O. Gilpatrick, A. J. Shor, C. F. Baes, Jr.)

An apparatus was fabricated to measure the permeability to brine of a well-defined grain boundary between two NaCl crystals subjected to a (normal) uniaxial stress. The cell (Fig. 9.1), with a 1.27 cm bore, contains two cylindrical crystals in contact. The upper crystal, 1.14 cm in diameter, is stressed against a lower (anvil) crystal, 1.27 cm in diameter, by means of a piston. Rapid-setting epoxy cement was used to seal the upper crystal to the piston. Lateral creep of the crystals under prolonged stress was constrained by a slightly undersized monel sleeve. The crystal surfaces to be contacted were initially ground in a 90° jig with 400 or 600 grit carborundum paper. Saturated brine from a pressurized reservoir was fed through a 1.5 mm diameter axial hole in the upper crystal, through the annular space between the contacting crystal surfaces, and out via a collecting channel at the periphery of this "grain boundary". Axial force was applied to the piston by an air-driven ram to produce stresses from 1 to 14 MPa

Fig. 9.1. Apparatus for measuring the permeability of a salt grain boundary to brine.

(10 to 140 bars) normal to the crystal surfaces in contact.

Temperature was controlled to $\pm 0.05^\circ\text{C}$ by submerging the entire cell, its stress-bearing frame, and a salt-saturator (with filter) in an ethylene glycol bath. Saturated brine was fed to the cell at pressures always less than 10% of the axial stress and generally less than 2% in order to distort as little as possible the net normal stress across the interface. Brine flow was small and never more than a few mg per minute. Flow was continuously monitored for periods of up to a week with a recording Mettler balance. For measurements at 50 and 80°C , a reservoir was added to the brine exit line (within the thermostat) in which dodecane could be displaced by the brine. The dodecane was cooled, collected and weighed, thus avoiding the precipitation of NaCl which would have otherwise occurred on cooling the brine.

The brine flow at any given time was found to be proportional to the hydraulic pressure drop between inlet and exit lines. The relation describing laminar flow of a noncompressible fluid radially outward between two circular plates is:¹

$$dV/dt = \frac{4\pi z^3 \Delta P}{3\eta \ln(r_2/r_1)} \quad (1)$$

in which dV/dt is the volume flow rate, $2z$ is the separation distance between the plates, η is the fluid viscosity, ΔP is the hydraulic pressure drop, and r_1 and r_2 are the inner and outer radii, respectively, of the (upper) annular plate. For convenience we define a permeability P_m as follows:

$$P_m = (dG/dt)/\Delta P \quad (2)$$

in which dG/dt is the mass flow rate of the fluid. Combination of eqs. (1) and (2) — with the fluid density ρ in g/cm^3 , z in cm, viscosity η in poise, fluid flow in g/min and hydraulic pressure drop in bars — gives:

$$P_m = 6 \times 10^7 \times \frac{4\pi \rho z^3}{3\eta \ln(r_2/r_1)} (\text{g min}^{-1} \text{ bar}^{-1}) \quad (3)$$

In this equation, z may be viewed as the effective half thickness of the grain boundary; i.e., half the separation distance of the crystal surfaces if they were perfectly flat and parallel.

All results to date demonstrate that the permeability of a stressed NaCl "grain boundary" decreases with time, the rate depending on the initial condition of the mated surfaces and the magnitude of the uniaxial stress. In most runs it was found that for a constant applied stress the reciprocal permeability increased linearly with time

$$1/P_m = A + Bt \quad (4)$$

Values of A and B obtained for various conditions at 25°C are summarized in Table 9.1. In two series of measurements (Runs 20 and 70), it appeared that the parameter B had minimum values and increased as about the sixth power of the applied stress σ ,

$$B = 6 \times 10^{-13} \sigma^6 (\text{bar g}^{-1}) \quad (5)$$

giving B values in the range 10^{-4} to 10 bar/g for σ values in the range 25 to 140 bars. The remaining results at room temperature did not conform to this relationship, but showed much higher values of B for a given stress. Some characteristic of the initial crystal surfaces, some conditioning process that takes place in the presence of brine, or other factor that

Table 9.1 The permeability of salt grain boundary (20°C)^a
 $1/P_m = A + Bt$, (bar min g⁻¹)

Run	Stress ^b (bar)	Time (t)		Total brine flow (g)	A	B	Apparent thickness (2z) ^c	
		Initial (min)	Final (min)				Initial (μm)	Final (μm)
20a	23.4	0	1455	307	1.44	0.000125	8.68	8.35
20b	23.4	1559	5810	790	1.34	0.000122	8.51	7.72
20c	46.9	8312	11120	810	-53.7	0.00780	4.39	3.06
20d	34.4	11120	18300	842	13.1	0.00123	3.28	2.98
20e	25.0	18590	21190	851	4.7	0.00130	3.20	3.08
20f	46.9	21670	31700	882	11.1	0.00245	2.44	2.20
40a	31.3	8	48	2	61.4	2.32	2.28	1.76
40c	11.7	159	1384	3	139	0.116	1.82	1.47
40d	30.6	1386	4295	9	-263	0.526	1.26	0.78
40e	46.1	4320	30050	18	-4640	1.56	0.77	0.28
40f	62	30050	97310	26	43500	1.01	0.23	0.19
60a	26.6	9	69	45	23.4	1.00	3.08	2.17
60b	38	72	271	65	-135	3.05	2.23	1.11
70a	63	108	11210	71	2660	0.411	0.70	0.51
70b	92.8	11541	22780	75	1050	0.520	0.51	0.42
70c	119.4	22780	43890	77	-25240	1.80	0.39	0.26
70d	142	44045	60330	78	-292200	6.92	0.42	0.20

^aThe permeability (P_m) is the flow of brine (g/min) produced by a hydrostatic pressure drop of one bar (10⁵ Pa) across an annular grain boundary of inner radius 0.159 cm and outer radius 1.143 cm.

^bMechanical stress applied normal to the grain boundary, uncorrected for small hydraulic pressure drop.

^cHypothetical separation required if crystal surfaces are perfectly smooth (from eq. 1).

affects the value of B remains to be identified. Results presently being collected at 50 and 80°C should help with this identification.

Table 9.1 includes an effective thickness of the grain boundary (2z) which decreases with time at a given stress. This is a hypothetical separation distance of the two crystal surfaces if they were perfectly smooth and parallel. The actual surfaces, of course, contain irregularities which separate them and which define the flow channels. The points of contact between surfaces are subjected to a stress higher than the applied stress by an amount that depends on the area of contact. We shall attempt to model

the closure of such an interface using an approach analogous to that applied previously to salt consolidation,¹ but in two dimensions.

1. R. B. Bird, W. E. Stewart, and E. N. Lightfoot, *Transport Phenomena*, John Wiley Interscience, New York, 1960, pp. 106, 114.

9.1.3 Brine Migration in Polycrystalline Salt (H. R. Bronstein, A. J. Shor, C. F. Baes, Jr.)

In order to study the movement of brine under conditions simulating bedded salt in a temperature gradient, an apparatus (Fig. 9.2) was constructed in which cylinders of polycrystal-

Fig. 9.2. Apparatus for the study of brine migration in polycrystalline salt under stress.

line salt could be introduced, or prepared in place by compaction, and subjected to uniaxial stresses up to 155 bar in a temperature gradient while the contained brine is allowed to escape as a liquid, or water vapor is carried away in a gas stream.

The apparatus consists of a thick-walled (2.54 cm) monel cylinder, 10 cm in diameter and 16 cm in height, which contains the salt between two 0.63 cm thick porous nickel plates (porosity 40%). The stress on the salt is delivered by a hydraulic ram which acts on a piston bearing on the upper nickel plate. The upper and lower pistons are sealed by rubber "O" rings. Annular spaces around the porous plates collect either liquid brine or moisture removed from the surface

of the salt specimen by a flow of dry helium through the porous frits. The brine was collected and weighed directly, while the water vapor carried away by a helium sweep gas was collected and weighed by means of magnesium perchlorate traps. A temperature gradient was maintained by heaters (not shown) placed at either ends of the cylinder. The required temperatures are maintained by conventional instrumentation. Temperature was measured directly on the surfaces of the salt block with stainless steel sheathed chromel-alumel thermocouples sealed through the gas inlets.

In each of three runs (200-202, Table 9.2), a weighed quantity of sodium chloride crystals (c.p. grade, particle size 240-420 μm) was thor-

Table 9.2 Loss of brine from polycrystalline salt under stress (155 bars)

Run	Specimen Prep.	Temperature (°C)		Duration (min)	Void fraction		Water collected (g)		Volume (cm ³)	
		Top	Bottom		Initial	Final	Top	Bottom	Geometric loss	Collected as brine
200	Consol. from 240-420 μ m crystals in brine	78	100	20,700	0.042	0.032	1.0	5.1	7.46	7.16
201		75	95	2,070	0.028	0.022	0.35	13.3	4.7	15.9
202		85	65	17,000	0.034	0.0094	4.7 ^a	14.2 ^a	20.6	16.2
				20,000	0.0094	0.0091	7.4	1.8	0.20	10.8
203	Machined block brine im- pregnated	85	65	20,600	0.073	0.013	10.5	16.5 ^b	43.4	31.5
				25,000	0.013	0.011	—	6.5 ^b	1.5	7.6

^aCollected as brine.

^bUpper annulus closed. He pressure at top, 22 psig; He sweep at bottom.

oughly dispersed as a slurry in brine before loading into the apparatus. The bulk brine was removed by flow through the upper and lower outlets, the other outlets being sealed during this initial consolidation. The pressure was then released, the upper and lower piston removed, the frits washed to remove brine and dried, restored in the apparatus and pressure reapplied. In another run (203), a cylinder of salt machined from a commercial salt block¹ was dried in a vacuum oven and impregnated with a known quantity of brine determined by weighing before and after treatment. Table 9.2 summarizes the various experimental procedures employed during this investigation along with the pertinent data collected.

The kinetics of consolidation of the dispersed crystals, after allowance for a greatly reduced wall effect in the larger column, was about that predicted from the previous measurements in smaller columns (Sect. 9.1.1). As the consolidation process proceeds, the porosity of the column approaches a linear decrease with the logarithm of time, the rate of the decrease increasing with the stress and the temperature.

As Table 9.2 shows, at higher void fractions there was generally good agreement between the volume of brine lost and the volume lost by a specimen, suggesting that the principal mechanism of brine loss was by exclusion as compaction proceeds. There was clear evidence of the

effect of the temperature gradient in only one case (run 202), wherein more water vapor was lost at a warmer upper surface than at a cooler lower surface. Generally more brine was lost from the bottom of the specimen than from the top, but there was always some loss from the top. This suggests that the permeability of the specimen was not quite sufficient to accommodate the flux of excluded brine under the small hydrostatic head involved.

At some point near the end of the process of brine loss, however, migration of brine becomes more rapid than would be required for exclusion alone and it was possible to remove essentially all of the water contained in the specimen by an extended gas sweep of the top and bottom surfaces. In future measurements, greater attention will be given to this phase of the process of water loss.

1. Supplied by the Hardy Salt Company.

9.1.4 The Hydrolysis of Mg^{2+} in Concentrated Brines at 25°C

(H. R. Bronstein, C. F. Baes, Jr.)

A brief potentiometric study was made of $MgCl_2$ solutions near saturation with NaCl to investigate the hydrolysis of Mg^{2+} ion in the concentrated brines that might occur in salt

repositories. From the results, appended to a report by Jenks and Walton on the radiation chemistry of brines,¹ it appeared that the hydrolysis can be described by the same two reactions which describe behavior at lower ionic strengths:²

But somewhat modified expressions were obtained for the formation quotients of the two hydrolysis products:

$$\text{Log } Q_{11} = -11.44 - 1.022 \sqrt{I}/(1 + \sqrt{I}) + 0.045 m_{\text{Cl}}$$

$$\text{Log } Q_{44} = -41.02 + 2.044 \sqrt{I}/(1 + \sqrt{I}) - 0.154 m_{\text{Cl}}$$

(Q_{xy} is the formation quotient, I is the ionic strength, and m_{Cl} is the chloride concentration; concentrations are in molalities.) These revised expressions seem to describe the hydrolysis behavior of Mg^{2+} in MgCl_2 -NaCl solutions, 0 to 5 m in MgCl_2 and to NaCl saturation.

1. G. H. Jenks and J. R. Walton, Radiation Chemistry of Salt-Mine Brines and Hydrates, ORNL-5726 (July 1981), p. 51-55.

2. C. F. Baes, Jr. and R. E. Mesmer, p. 95 in The Hydrolysis of Cations, John Wiley Interscience, New York, 1976.

9.2 Adsorption of Ions of Interest in Nuclear Waste Isolation

(R. E. Meyer, S.-Y. Shiao, D. A. Palmer, J. S. Johnson, Jr.)

Information on the adsorption behavior on geological formations of nuclides of interest to nuclear waste isolation is necessary to estimate the rate of transport of these nuclides should they be leached by water penetrating the repository. We are systematically investigating the adsorption behavior of ions of U(VI), Tc(VII), Eu(III), Np(V), Cs(I) and Sr(II) on selected minerals over the pH range ~5-9 and over a wide range of ionic strengths. Although we have studied a large variety of minerals, we have concentrated on the clay minerals and hydrous oxides because they are likely to be

present in all types of formations. Also, because most clays and hydrous oxides have considerable sorptive capacity they are likely to dominate the sorption properties of those formations in which they are present even in relatively small amounts. Measurements over a full range of ionic strengths are necessary because the groundwaters in contact with the various types of formations proposed as hosts for repositories will cover a fairly wide range of solution species and concentrations. Thus the ionic strength of water in contact with bedded salt deposits will be much greater than that in contact with basalt. The task of defining the sorptive behavior of these nuclides for the many different conditions found in geological formations could be greatly simplified if it could be shown that fairly consistent patterns of behavior are observed. This might then allow the development of sorption models which could be used to predict behavior for those conditions not explicitly tested in the laboratory. We have previously, compared our results to that predicted by simple ion exchange equations; i.e., equations which assume no coion invasion and adsorbents which have a constant well-defined capacity, and we have shown that in some cases these equations can predict behavior with reasonable success.^{1,2,3}

Adsorption on Hydrous Oxides. For hydrous oxides, these simple ion exchange equations are not adequate to describe the results, especially at pH values from 6-9, the same range which is found in natural formations. We have therefore derived ion exchange equations for the more general case of simultaneous cation and anion adsorption for substances which have a capacity dependent upon pH and solution concentration of species. Simple cation or anion exchange equations of the type $\text{M}^+(\text{aqueous}) + \text{N}^+(\text{adsorbed}) = \text{M}^+(\text{adsorbed}) + \text{N}^+(\text{aqueous})$ are special cases of the more general equations we have developed.

These general equations predict many of the patterns observed with our measurements of uptake of ions on alumina. Fig. 9.3 shows the uptakes of Na^+ and Br^- on chromatographic alumina as a function of pH and concentration of NaBr. The

Fig. 9.3. Anion and cation uptake on alumina from NaBr solutions.

equations predict that the slopes of the logs of the uptakes with respect to pH should be $-1/2$ for anion uptake and $+1/2$ for cation uptake. Also, if the concentration is increased by a factor of 10 the uptake should be increased by the square root of 10 so that the lines should be approximately $1/2$ decade apart. The data shown in Fig. 9.3 are approximately in accord with these predictions. Similar observations were noted for adsorption of Na^+ and Br^- on ZrO_2 . These observations are described in Section 7.6.1 of this report.

Other predictions of the general equations are: (1) Near the isoelectric point there should be little or no salt dependence on sorption for amphoteric adsorbers like hydrous oxides whose capacity is dependent on pH. (2) The salt effect for adsorption of cations on hydrous oxides in basic solutions should be less than that on ideal ion exchangers by an amount which depends on the

change of uptake with concentration. (3) For adsorption of trace cations on hydrous oxides from fairly concentrated electrolytes like 0.5 M NaCl, the slope of the log of the distribution coefficient with respect to pH will be positive and should be approximately equal to $n/2$ where n is the charge of the cation. (The distribution coefficient, D , is here defined as the moles of ion adsorbed per unit weight of solid divided by the concentration in moles per liter of the ion in the solution.) Slopes of approximately $n/2$ are illustrated in Fig. 9.4 where adsorption of Cs(I), Sr(II), and Eu(III) on alumina are compared. These equations with

Fig. 9.4. Adsorption of Cs(I), Sr(II), and Eu(III) on the sodium form of gamma-alumina. Trace loading, 60-240 hr equilibration, 0.5 M NaCl.

their application to adsorption of a number of ions on alumina are described in two publications.^{4,5}

Adsorption on Mixtures of Minerals. Adsorbents in geological formations are usually complex mixtures of minerals, and the question naturally arises whether it is possible to predict sorption properties of these complex mixtures from measurements on pure minerals. We have therefore measured distribution coefficients for adsorption of Cs(I) and Sr(II) on a number of mixtures of pure adsorbents. It follows directly from the definition of the distribution coefficient that the overall distribution coefficient observed on a mixture should be equal to the sum of the distribution coefficients of each pure adsorbent multiplied by its weight fraction. For a number of systems such as adsorption of Sr(II) on mixtures of illite and montmorillonite, this relation was followed quite closely as shown by the straight line between the values of the pure components in Fig. 9.5. For other systems, straight lines were not observed. Large deviations were observed for the Al_2O_3 -illite system, and this behavior probably indicates that the solubility of alumina causes deviations because of changing solution composition. The results of these studies on mixtures have been published.⁶

1. S.-Y. Shiao, P. Rafferty, R. E. Meyer, and W. J. Rogers, "Ion Exchange Equilibria between Montmorillonite and Solutions of Moderate to High Ionic Strength," p. 297 in ACS Symposium Series 100, S. Fried, ed., Washington, D.C., 1979.

2. P. Rafferty, S.-Y. Shiao, C. M. Binz, and R. E. Meyer, J. Inorg. Nucl. Chem. **43**, 787 (1981).

3. R. E. Meyer, "Systematic Study of Metal Ion Sorption on Selected Geologic Media - Annual Report for the Period October 1978-December 1979," USDOE DOE/BETC/OR-14 (1980).

4. S.-Y. Shiao, Y. Egozy, and R. E. Meyer, "Adsorption of Cs(I), Sr(II), Eu(III), Co(II), and Cd(II) by Al_2O_3 ," J. Inorg. Nucl. Chem. (in press).

5. S.-Y. Shiao and R. E. Meyer, "Adsorption of Inorganic Ions on Alumina from Salt Solutions: Correlations of Distribution Coefficients with Uptake of Salt," J. Inorg. Nucl. Chem. (in press).

Fig. 9.5. Adsorption of Sr(II) on mixtures of montmorillonite and illite.

6. D. A. Palmer, S.-Y. Shiao, R. E. Meyer, and J. A. Wethington, "Adsorption of Nuclides on Mixtures of Minerals," J. Inorg. Nucl. Chem. (in press).

9.3 A Digital Scanner for Determination of Alpha Radioactivity Adsorbed on Surfaces

(G. D. O'Kelley, G. W. Beall¹)

A recent study² by an autoradiographic technique demonstrated that useful, although qualitative, information could be obtained concerning the relative extent of sorption of actinide elements onto specific mineral grains comprising the surface of a rock. It was considered advantageous to determine quantitatively the amounts of radioactivity sorbed at specific mineral sites on flat specimens, so that distribution coefficients could be obtained on surfaces for comparison with those obtained by bulk equilibration methods. In response to this need,

a scanning device has been assembled which serves to measure the spatial distribution of alpha radioactivity deposited on flat surfaces.

The essential detecting element of the scanning device is a position-sensitive, charged-particle detector³ (PSD) whose external circuit elements can be arranged to provide an electronic signal with amplitude proportional to the position of a detected alpha particle along the x direction. Because the PSD has no position resolution in the perpendicular, or y , direction of the sample plane, a defining slit is located over the face of the PSD which restricts the field of view in the y direction to 0.6 mm. The resolution of the PSD along the x direction is 0.5 mm over the entire aperture length of 27 mm. Interposed between the surface of the PSD and the y defining slit is a collimator array of the Soller type, widely used in x-ray spectroscopy. The purpose of this collimator is to reduce smearing of the image in the x direction due to rays emitted from the source plane at low angles. The planes of the parallel collimator elements are perpendicular to the x axis and to the detector plane and consist of 40 stainless-steel sheets, 0.13 mm thick, spaced 0.51 mm apart.

A precision stage driven by a micrometer holds the flat specimen near the collimator and serves to move the specimen in the y direction. At a given setting of the micrometer the position distribution along the x direction is recorded as an electronic pulse-height distribution on a multichannel pulse-height analyzer. In use, the specimen is advanced in increments of 0.6 mm, recording an x -position distribution at each setting.

A link has been established between the multichannel analyzer used for data acquisition and the ORNL DEC-10 computer, so that with appropriate computer software oblique projection plots can be obtained to present the data as a three-dimensional graph of the variables intensity, x , and y .

As a test of the device, a uniform source of ^{241}Am in the shape of a rectangle 1.00×1.17 mm was scanned as described above. The scanner data reproduced the shape and dimensions of the

source as expected. No corrections have been determined for variations in the detection efficiency of the PSD along the x direction. However, for the test scan the efficiency for detection of the ^{241}Am source area was about 1%, with the source near the center of the detector.

These results demonstrated that with a few minor improvements the scanner could be used as originally proposed. One additional feature which may prove useful in the future is that a pulse proportional to alpha-particle energy is available and can be recorded simultaneously with the position information. The alpha-particle energy resolution of the PSD has been measured as 50 keV, which is adequate in favorable cases for identification of nuclides adsorbed onto a surface, or for measuring simultaneously the sorption of more than one nuclide.

1. Present address: Radian Corporation, Austin, Texas 78766.

2. Chem. Div. Annu. Prog. Rep. Feb. 29, 1980, ORNL-5665 (July 1980), p. 118; G. W. Beall, G. D. O'Kelley, and B. Allard, An Autoradiographic Study of Actinide Sorption on Climax Stock Granite, ORNL-5617 (June 1980).

3. P-series, active area 8×47 mm, EG&G ORTEC, Oak Ridge, Tenn.

9.4 Recovery of Nonradioactive Palladium from High-Level Radioactive Waste

(F. J. Smith)

Nuclear waste material contains appreciable quantities of strategically important and valuable elements. We are continuing to develop methods for recovery of these materials. A fortuitous combination of nuclear and chemical properties was found that makes it possible to recover appreciable quantities of nonradioactive palladium and rhodium from fission-product residues. The method is based on an essentially complete removal of ruthenium (the precursor of nonradioactive Pd and Rh) from the radioactive palladium and rhodium. Decay of 369-d ^{106}Ru and its 30-s ^{106}Rh daughter produces nonradioactive ^{106}Pd while decay of 40-d ^{103}Ru yields nonradioactive ^{103}Rh . After an appropriate waiting period for the decay, separation of this nonradioactive palladium and rhodium from the

remaining ^{106}Ru and ^{103}Ru gives a product suitable for unrestricted commercial use.

Experimental results for the key ruthenium-palladium separation by liquid-liquid partitioning between immiscible liquid metals are shown in Table 9.3. For example, when molten magnesium containing ~0.1 at. % each of palladium and ruthenium was equilibrated with molten uranium-5 wt % chromium eutectic at 900°C, the ruthenium extracted into the uranium-chromium solution while the palladium remained in the magnesium. Separation factors of greater than 10^6 were obtained. Although providing good separations, this system has the disadvantage of requiring a high temperature, >900°C. This causes volatilization of magnesium and limits the availability of suitable container materials. Substitution of uranium-iron eutectic (89-11 wt %; mp = 725°C) for the uranium-chromium eutectic (95-5 wt %; mp = 859°C) allows for equilibration at temperatures as low as 750°C with a decrease of magnesium vapor pressure from about 100 mm to 10 mm. Ruthenium-

palladium separation factors of $>10^6$ are again obtained. Preliminary experimental measurements indicate that rhodium behaves similarly to palladium in these systems and, therefore, can also be separated from ruthenium. The distribution of palladium and ruthenium between liquid aluminum-liquid bismuth was measured at several temperatures between 700 and 900°C. It was observed (Table 9.3) that both the palladium and ruthenium essentially dissolved in the aluminum phase with little reporting to the bismuth. Thus, the aluminum-bismuth binary system does not appear promising for achieving the necessary separations for recovery of palladium and rhodium from nuclear waste.

A proposed tentative but viable separation process for recovering non-radioactive palladium and rhodium from radioactive waste would consist of the following steps

1. Noble-metal fission-product residues from the LWR head-end dissolution step (in or reduced to the elemental form) are treated with molten magnesium; molybdenum and

Table 9.3 The partitioning of palladium and ruthenium between two immiscible liquid metal systems

Temp (°C)	Equilibrium concentration (atom fraction)				Partition ratio ^a		Pd:Ru separation factor
	Ru	Pd	Ru	Pd	Ru	Pd	
<hr/>							
	<u>Mg Phase</u>		<u>U-5 wt % Cr Phase</u>				
900	$<1 \times 10^{-7}$	9.9×10^{-5}	1.1×10^{-4}	$<1 \times 10^{-7}$	$<10^{-3}$	$>10^3$	$>10^6$
900	3.0×10^{-7}	1.1×10^{-3}	1.3×10^{-4}	1.6×10^{-6}	2.3×10^{-4}	6.9×10^2	3.0×10^6
950	4.9×10^{-7}	1.2×10^{-3}	1.7×10^{-3}	2.1×10^{-6}	2.9×10^{-4}	5.7×10^2	1.9×10^6
<hr/>							
	<u>Mg Phase</u>		<u>U-11 wt % Fe Phase</u>				
750	$<1 \times 10^{-7}$	1.0×10^{-4}	3.6×10^{-4}	$<10^{-7}$	2.3×10^{-4}	$>10^3$	$>10^6$
750	9.1×10^{-7}	1.7×10^{-3}	2.4×10^{-3}	1.4×10^{-6}	3.8×10^{-4}	1.2×10^3	6.5×10^6
800	6.0×10^{-7}	1.8×10^{-3}	2.6×10^{-3}	1.5×10^{-6}	2.3×10^{-4}	1.2×10^3	5.2×10^6
850	6.7×10^{-7}	1.7×10^{-3}	2.6×10^{-3}	1.5×10^{-6}	2.6×10^{-4}	1.1×10^3	4.2×10^6
<hr/>							
	<u>Al Phase</u>		<u>Bi Phase</u>				
700	1.1×10^{-3}	1.0×10^{-3}	$<10^{-7}$	$<10^{-7}$	$>10^{10}$	$>10^{10}$	Not Measurable
700	2.0×10^{-2}	1.9×10^{-2}	$<10^{-7}$	$<10^{-7}$	$>10^{10}$	$>10^{10}$	
750	2.0×10^{-2}	2.0×10^{-2}	$<10^{-7}$	$<10^{-7}$	$>10^{10}$	$>10^{10}$	
800	1.8×10^{-2}	1.8×10^{-2}	$<10^{-7}$	$<10^{-7}$	$>10^{10}$	$>10^{10}$	
850	2.1×10^{-2}	2.0×10^{-2}	$<10^{-7}$	$<10^{-7}$	$>10^{10}$	$>10^{10}$	
900	2.0×10^{-2}	1.9×10^{-2}	$<10^{-7}$	$<10^{-7}$	$>10^{10}$	$>10^{10}$	

^aConcentration in light phase divided by concentration in heavy phase.

technetium are insoluble, but ruthenium, rhodium, palladium, silver, and cadmium are soluble. The molten magnesium solution is separated from the insoluble residue.

2. The magnesium solution is then contacted with molten uranium-chromium eutectic at 950°C, or uranium-iron eutectic at 750°C; the ruthenium is extracted from the magnesium to form a 0.10 at. % solution in the uranium alloy phase. The phases are separated.
3. The uranium eutectic phase containing the ruthenium may be contacted with a fresh supply of molten magnesium at 950°C to provide additional decontamination from the radioactive palladium and rhodium. The phases are separated.
4. The uranium eutectic ruthenium phase is allowed to freeze and is stored for a period of time to permit the $^{106}\text{Ru} \rightarrow ^{106}\text{Pd}$ and $^{103}\text{Ru} \rightarrow ^{103}\text{Rh}$ decay to occur; then it is heated, and reextracted with fresh magnesium to remove the ^{106}Pd and ^{103}Rh . This produces a solution of nonradioactive palladium and rhodium in magnesium. The separation and recovery of the palladium and rhodium can then be accomplished by conventional methods.

9.5 Actinide Chemistry Relevant to Nuclear Waste Isolation

9.5.1 Complexes of Np(V) in Aqueous Solution

(J. Halperin, J. H. Oliver)

The presence of actinide ions in solution is of concern in any scenario postulating a breach in a reactor waste repository. The investigation of the degree of aqueous complex formation of the III, IV and VI ions is of interest in this regard; in general, ions in these oxidation states tend to be accessible to the experimenter over an appreciable range of stability. However, in the case of the V oxidation state, both UO_2^+ and PuO_2^+ are relatively unstable due to disproportionation reactions and are difficult

to maintain free of species in other oxidation states. Among the actinides only NpO_2^+ lends itself readily to the study of the dioxo-actinide (V) ion in solution. The relatively large radius for coordination of the NpO_2^+ ion together with the single charge on that ion leads to a reduced tendency to form complex ions in solution. The order of decreasing tendency to form complex ions for neptunium is generally given as $\text{Np}^{+4} > \text{Np}^{+3} > \text{NpO}_2^{+2} > \text{NpO}_2^+$. The interpretation of measurements for very weak complexes needs to be made with caution to properly separate effects due to mass action equilibria and those due to changes in the ionic environment. Since we are interested in actinide ion behavior at very low concentrations, we make use of a tracer technique to evaluate these equilibria.

We have investigated the formation of the mono-sulfate complex of NpO_2^+ in aqueous solution using an organic extraction technique and tracer concentrations of ^{237}Np . Solutions of the liquid ion exchanger, sodium dinonyl naphthalene sulfonate (NaDNNS) in *n*-heptane, have been used to extract Np(V) from aqueous solution. The extraction of NpO_2^+ from 2 M NaClO_4 media is characterized by an extraction equilibrium constant of $K_x = D^\circ/(\text{NaDNNS}) = 0.36 \pm 0.02$ at 25°C and $K_x = 0.45 \pm 0.02$ at 37°C. These values are small enough to require NaDNNS concentrations of ~ 0.5 M in *n*-heptane to achieve good sensitivity. A log-log plot of D° , the distribution coefficient in the absence of ligand, versus the NaDNNS concentration yields a slope of ~ 0.9 rather than unity, suggesting that activity coefficient changes may not be negligible for these high NaDNNS concentrations.

Aqueous solutions of neptunium containing varying concentrations of sulfate ligand were equilibrated with the organic extractant. The ionic strength was maintained at $\mu = 2$ with NaClO_4 to minimize activity coefficient variations in the aqueous environment. The distribution coefficients obtained from the ^{237}Np concentrations (using liquid scintillation alpha counting) have been interpreted in terms of the stability quotient. Measurements of the equi-

librium quotients for the reaction as written in Eq. 1 for several concentrations of NaDNNS

and over a range of pH are shown in Table 9.4. Since the second acid dissociation constant of H_2SO_4 is approximately $K_2 \approx 0.1$ in this $\mu = 2$ medium, essentially all of the HSO_4^- is expected to be completely dissociated at $\text{pH} > 3$.

Similarly the acid dissociation constant of HDNNS is sufficiently large that essentially all of the DNNS is in the sodium form at $\text{pH} > 3$. The constancy of the measured equilibrium quotient over the pH range 3-7 supports the observation that Np(V) is not appreciably hydrolyzed over this range of acidity. The measured stability quotient $k_1 = 1.43 \pm 0.02$ at 25°C is approximately a factor of two lower than that reported by Rao and coworkers.¹ The relatively small value for this constant of course confirms that the sulfate complex of Np(V) in natural waters will not form to any appreciable extent. Measurements of the

equilibrium quotients over a range of NaDNNS concentrations at $T = 37^\circ\text{C}$ are summarized in Table 9.4.

The constancy of k_1 over the concentration range of NaDNNS is consistent with the extraction of a single species. Further, the temperature dependence of the equilibrium quotient supports the observation that the contribution of the entropy term to the free energy exceeds that of the enthalpy term.

Some preliminary measurements have been carried out in the Np(V)-bicarbonate system using the NaDNNS extraction technique. It was necessary to go to a higher specific activity tracer to work in the higher pH solutions characterizing HCO_3^- - CO_3^{2-} media. We have made use of the ^{239}Np tracer (2.35 day, β^- , γ emitter) at concentrations approaching 10^{-13} M , again maintaining the ionic strength at $\mu = 2.0$ with NaClO_4 . Data obtained so far allow only for reporting several qualitative observations made with Np tracer in bicarbonate media in the pH range 8-10. The pH dependence of the extraction data appear consist-

Table 9.4 Equilibrium quotients for the reaction

$$[\text{Np}] \approx 5 \times 10^{-5} \text{ M}, \mu = 2.00 \pm 0.05$$

Temp ($^\circ\text{C}$)	[NaDNNS] ^a M	pH ^a	k_1
25 $\pm$ 0.02	0.60	3.0	1.39 $\pm$ 0.05
	0.60	4.0	1.44 $\pm$ 0.03
	0.60	5.0	1.41 $\pm$ 0.03
	0.60	6.0	1.47 $\pm$ 0.07
	0.60	7.0	1.45 $\pm$ 0.03
	0.40	3.0	1.40 $\pm$ 0.04
		wt. avg.	1.43 $\pm$ 0.02
37 $\pm$ 1	0.40	5.0	1.64 $\pm$ 0.08
	0.50	5.0	1.74 $\pm$ 0.08
	0.60	5.0	1.86 $\pm$ 0.05
	0.75	5.0	1.64 $\pm$ 0.10
	0.60	3.0	1.85 $\pm$ 0.05
		wt. avg.	1.79 $\pm$ 0.09

^a[NaDNNS] accurate to $\pm 0.01 \text{ M}$, pH accurate to ± 0.1 .

ent with a bicarbonate rather than a carbonate ligand for neptunium. Up to concentrations of $\text{HCO}_3^- \approx 0.3 \text{ M}$, a single ligand complex and a comparatively small value for the equilibrium quotient appear consistent with the extraction data. There are several caveats that need to be noted regarding the interpretation of such extraction data and these are under investigation. The precise complex species formed may need to be established by independent chemical arguments; however, in favorable cases they may be deduced from the extraction dependence upon parameters such as metal ion concentration, ligand concentration and pH. The extractability of the various species by the organic extractant must be evaluated. For neptunium, some care must be taken to insure the integrity of the oxidation state, and the role of hydrolytic reactions needs to be assessed.

1. P. R. V. Rao, N. M. Gudi, S. V. Bagawdi, and S. K. Patil, J. Inorg. Nucl. Chem. **41**, 235 (1979).

9.5.2 Dioxo Uranium (VI) Carbonate Complexation in Uranium Recovery by Ion Exchange

(L. Maya)

Attempts to prepare $\beta\text{UO}_3 \cdot 2\text{H}_2\text{O}$ by an ion exchange procedure represented by

(where R-OH is a strong anion exchange resin in the hydroxide form) resulted in poor yields of the product (~50%) when the reactants were exposed to air. Evidently a competing process other than that described by Eq. (1) was taking place. After contact with the uranium solution, the resin was washed and dried. This resin released uranium when contacted with NaCl solution or acid; on contact with acid, effervescence was noted. The uranium species released was identified as $\text{UO}_2(\text{CO}_3)_3^{4-}$ by its optical and Raman spectra.

In experiments conducted to clarify the mechanism of the uranium uptake by the resin, it was determined that uranium was incorporated into the resin as a result of the following reaction:

Thus it could be inferred that reaction (2) had occurred in earlier experiments because contact with air transformed the resin from the hydroxide into the bicarbonate form. Uranium uptake is highly favored in reaction (2), leading to distribution ratios (U resin/U soln) of about 10^6 . The reaction is driven to the right because of the inherent selectivity of the resin for highly charged species and by the evolution of carbon dioxide. The process is essentially irreversible since no competing anions are present in solution that could displace the uranium.

Reaction (2) has application in the recovery of uranium from dilute solutions and for performing separations of uranium from other metal ions. Good uranium separations could be achieved by this procedure since very few elements form soluble anionic carbonate complexes.

9.5.3 Raman Spectroscopy of Dioxo Uranium (VI) Carbonato and Hydroxo Species

(L. Maya, G. M. Begun)

The Raman spectra of a number of uranium species in carbonate and alkaline solutions were obtained. The frequency of the $\text{UO}_2-\nu_1$ symmetric stretching vibration of these species was found to be sensitive to the coordination environment of the uranyl ion. This information can be used to complement that derived by other techniques for the identification of uranyl-containing species. Thus, the existence of the uranyl hemi-carbonate ion, $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$, as well as that of anionic species such as $\text{UO}_2(\text{OH})_4^{2-}$ was confirmed. The conversion of $\text{UO}_2(\text{CO}_3)_2^{2-}$ into $\text{UO}_2(\text{CO}_3)_3^{4-}$ by addition of HCO_3^- was then followed by Raman spectroscopy and ^{13}C NMR.

A correlation was observed between the ν_1 frequency of the uranyl ion and the number and nature of the ligands surrounding this ion. Using the free aquo UO_2^{2+} ion as a reference, a decrease in the ν_1 frequency was observed with increases in the number of bonds to either hydroxo or carbonato ligands. Apparently the

electron density in the UO_2^{2+} axial bonds was withdrawn by an inductive effect into the equatorial plane. An alternative explanation is that the equatorial ligands provide electron density to the uranium atom, thus partially substituting the π contribution of the axial oxygen atoms causing a weakening of the axial bonds.

9.5.4 Hydrolysis and Carbonate Complexation of Dioxo Uranium (VI) in the Neutral pH Range

(L. Maya)

This work was undertaken to clarify the nature of the uranium(VI) species formed in the neutral range at relatively low carbon dioxide partial pressures, conditions that are representative of natural waters in the environment. Evidence was found for the existence of a hydroxocarbonate species having a U/CO_3 mole ratio of two by analytical, spectroscopic and electrochemical means. This species will be referred to as hemicarbonate. A series of potentiometric titrations was conducted in order to derive the stability constants for all the species of importance under the conditions mentioned above. It was found that the hemicarbonate was indeed a dominant species in the pH range 6.0 to 8.0 at $p_{\text{CO}_2} = 10^{-3.5}$ (atm). The range of stability of the hemicarbonate decreased as the carbon dioxide partial pressure increased. Additional species of importance in the system are $(\text{UO}_2)_2(\text{OH})_2^{2+}$, $(\text{UO}_2)_3(\text{OH})_5^+$, $\text{H}(\text{UO}_2)_3\text{CO}_3$, $\text{H}(\text{UO}_2)_2(\text{CO}_3)_2^{2-}$ and $\text{UO}_2(\text{CO}_3)_3^{4-}$, all of which have been observed before. The stability constants derived for these species agreed quite well with values reported in the literature, thus adding confidence to the value derived for the hemicarbonate which had not been determined before.

9.5.5 Radioelectrochemistry of Americium Complexes

(G. D. O'Kelley)

Aqueous solutions of interest to many concepts of nuclear waste management are characterized by low concentrations, nearly neutral pH, and

the presence of a variety of ligands. Modifications of conventional coulometry and polarography permit the radioactivity of an ion in solution to be used to follow the course of the electrolysis instead of the current; in this way, measurements can often be extended to very low concentrations. Additionally, electrochemical waves can often be determined at potentials more negative than -1.5 V vs SCE without serious interference from hydrogen evolution. Waves due to different elements with similar half-wave potentials can be determined simultaneously by detecting the radiations characteristic of each radionuclide. These radiochemical variants, known as "radiocoulometry" and "radiopolarography", are limited to the determination of half-wave potentials and mechanisms of reductions to the amalgam state.

Preliminary experiments used a commercial coulometry cell¹ to aid in defining the optimum characteristics of a radiocoulometry cell with a mercury pool electrode. As an aid to studying the influence of cell parameters, a computer program was written which uses the formalism developed by Samhoun and David² to calculate the concentration of reducible ion remaining in solution as a function of time for a particular value of the difference between the applied and half-wave potentials. Experiments on the kinetics of reduction of Am^{3+} to the amalgam were in reasonable agreement with the theory.

The half-wave potential for the reduction $\text{Am}^{3+} \rightarrow \text{Am}(\text{Hg})$ is about -1.85 V vs SCE in a non-complexing medium, while in the presence of a strongly complexing ligand such as citrate, the half-wave potential can be shifted several hundred millivolts more negative. These results were confirmed using solutions containing ^{241}Am at concentrations of 10^{-7} - 10^{-8} M, and citrate as the complexing ligand. Supporting electrolytes were either LiClO_4 , $(\text{CH}_3)_4\text{NCl}$, or $(\text{CH}_3)_4\text{NClO}_4$. Although the reduction of the americium citrate complexes proved not to be reversible, the experience with radiocoulometry at very negative potentials was instructive.

The potentials of interest in most actinide studies lie beyond the onset of the hydrogen wave. If vigorous stirring is maintained,

radiocoulometry is not readily affected by hydrogen evolution; however, for studies of pH-dependent complexation, the consumption of hydrogen ions seriously alters the pH of the bulk solution in a short time and makes control of the pH difficult, even with buffering. Future experiments will emphasize the more convenient technique of radiopolarography, since at highly negative potentials the hydrogen ion concentration may be altered on a microscopic scale near the dropping mercury electrode, but the pH of the bulk solution should not change significantly.

1. EG&G Princeton Applied Research, Princeton, NJ, Model 377A.

2. K. Samiouni and F. David, J. Electroanal. Chem. 106, 161 (1980).

9.6 Lanthanide Orthophosphates as Alternate Actinide Waste Forms

9.6.1 Simultaneous Precipitation of Ter- and Tetravalent Metal Phosphates

(C. E. Bamberger, J. F. Land, J. Brynstad)

Elucidation of the behavior of tetravalent ions during the formation of tetravalent metal phosphates either by precipitation or crystallization is of interest in regard to fixation and interaction of transuranium elements in nuclear waste processing. It has been reported that during the very first separations of plutonium by "coprecipitation" with BiPO_4 from strong acid solutions, Pu(IV) was much more efficiently precipitated than Pu(III) .¹ Although it was recognized that Pu(III) and Bi(III) phosphates were isomorphous and probably different from Pu(IV) -phosphates, an unequivocal explanation was never offered because interest in the process dropped due to the advent of solvent extraction. Recently, it was reported that the plutonium in Pu -containing LaPO_4 crystals grown from a $\text{Pb}_2\text{P}_2\text{O}_7$ flux at temperatures above 1000°C was tetravalent.² In trying to understand these phenomena, several series of precipitations were made using trivalent and tetravalent cerium as a stand-in for plutonium. The precipitates were

analyzed with regard to chemical composition and x-ray powder patterns. Thermal decomposition was studied by heating the precipitates up to 1200°C under a flow of argon, and evolved oxygen was determined. The solids after ignition were also analyzed. The results obtained are summarized as follows:

- (1) Precipitates (digested at 90°C for 2-3 days) containing various amounts of Ce(IV) and Bi(III) were shown by x-ray diffraction to have two distinctive phases, hexagonal BiPO_4 and an ill-defined Ce(IV) -phosphate. The latter appears to form irrespective of the Ce(IV) -salt used (sulfate or nitrate) and of the presence of NH_4^+ . However, when NH_4^+ is present in the solution the precipitates also contain various amounts of NH_4^+ . Furthermore, the ratios $\text{NH}_4^+/\text{Ce(IV)}$ and $\text{H}_3\text{PO}_4/\text{Ce(IV)}$ affect the rate of transformation from gel to crystalline state. The x-ray diffraction pattern of the crystalline Ce(IV) -phosphate obtained invariably resembled only one of the many alleged crystalline Ce(IV) -phosphates reported in the literature,³ independent of the presence and amount of Bi(III) .
- (2) Precipitates containing various amounts of Ce(III) and Bi(III) showed, by x-ray diffraction, the presence of one phase, that of hexagonal BiPO_4 ; only when Bi(III) was absent was hexagonal CePO_4 observed.
- (3) On heating precipitates containing both Ce(IV) and Bi(III) , thermal reduction of Ce(IV) to Ce(III) occurred and the resulting solids gave the diffraction pattern of monoclinic (medium temperature) BiPO_4 . In the absence of bismuth, the ignited solids consisted of monoclinic (monazite) CePO_4 and, CeP_3O_9 . The latter was found to be present by x-ray diffraction when the ratio PO_4/Ce in the precipitates was ≥ 1.4 .
- (4) Precipitates of Ce(IV) phosphates exhibited a lower solubility than those containing Ce(III) and Bi(III) .

This work continues with emphasis on determining the stoichiometry of the Ce(IV)-phosphate in the absence and presence of NH_4^+ .

It would appear, by analogy with cerium, that the reason for Pu(IV) being more efficiently coprecipitated than Pu(III) with Bi(III)PO_4 is that the Pu(IV)-phosphate is much more insoluble than the Pu(III)-phosphate and, thus, the Bi(III)PO_4 precipitate may be acting as a nucleating agent for the Pu(IV)-phosphate precipitation. The lack of stability toward thermal reduction of Ce(IV)-phosphates [and Pu(IV)-phosphates] suggests that the reported stability of Pu(IV) in LaPO_4 formed at high temperatures is due to some stabilization effect not present in our precipitates. It may be that the reported² Pu(IV) in LaPO_4 is stabilized by an equivalent content of Pb(II);⁴ i.e., $\text{Pu(IV)}_x\text{Pb(II)}_x\text{La}_{1-2x}\text{PO}_4$. Efforts to demonstrate this have been initiated.

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3. K. H. Koenig and E. Meyn, *J. Inorg. Nucl. Chem.* **29**, 1153 (1967); G. Alberti, U. Constantino, F. DiGregorio, P. Galli, and E. Torracca, *J. Inorg. Nucl. Chem.* **30**, 295 (1968); R. G. Herman and A. Clearfield, *J. Inorg. Nucl. Chem.* **37**, 1697 (1975).

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9.6.2 Raman Spectra

(G. M. Begun, C. E. Bamberger)

The possible suitability of the rare earth monazite or zircon structured orthophosphates as long term hosts for fission products has prompted a study of the synthesis and properties of these materials. In the preceding report,¹ we reported the systematic study of the Raman spectra of high purity crystals of the rare earth orthophosphates prepared by the high temperature reaction of lanthanide oxides with molten lead pyrophosphate. The complete series of lanthanide orthophosphates (except Pm) was

studied. The results of this investigation have been published.² This data now serves as baseline data for phosphates prepared by other methods. The Raman spectra of numerous samples prepared by precipitation from aqueous solutions have been recorded.

Excellent correlation has been found between Raman spectra and other methods of analysis. In all cases the Raman spectra have proven to be more sensitive for the identification of components of mixtures and of impurities and to furnish more information than the x-ray diffraction data. A direct correlation between the heights of selected peaks assigned to orthophosphate species and those associated with metaphosphate compounds allows us to estimate the ortho/meta phosphate ratio in the products of ignition of precipitates. Thus, the ratio of intensities at 961 cm^{-1} (the strongest peak for CePO_4) and at 1194 cm^{-1} (the strongest peak for CeP_3O_9), calculated as $I_{1194}/I_{961} + I_{1194}$ shows a linear relationship with the molar ratio $[\text{CeP}_3\text{O}_9]/[\text{CeP}_3\text{O}_9] + [\text{CePO}_4]$ calculated from determinations of total phosphorous and cerium. Numerous preparations of cerium phosphate, bismuth phosphate and their mixtures have been examined and characterized.³ The comparison of spectra obtained from ignited samples of pure CePO_4 and BiPO_4 and of ignited mixtures of BiPO_4 and Ce(IV) or Ce(III) phosphates permits us to unequivocally conclude that upon ignition of the mixtures a solid solution, $\text{CePO}_4\text{-BiPO}_4$, is obtained.

Raman spectra have also been found to be very sensitive to small quantities of CeO_2 in CePO_4 . While x-ray powder diffraction methods are unable to distinguish less than 10 wt % CeO_2 in CePO_4 , Raman spectra clearly show as little as 0.2 wt % CeO_2 . Although the CeO_2 peak at 460 cm^{-1} is very intense and overlaps with a weak peak of CePO_4 , the ratio of I_{460}/I_{961} for pure CePO_4 measured for more than 10 preparations is 0.19 ± 0.03 , while for a mixture containing 1 wt % CeO_2 in CePO_4 that ratio is 1.1. The Raman spectra are proving to be very useful in identifying and characterizing the phosphates under study, and observations on actinide phosphate compounds are underway.

1. Chem. Div. Annu. Prog. Rep. Feb. 29, 1980, ORNL-5665 (July 1980), p. 123.

2. G. M. Begun, G. W. Beall, L. A. Boatner, and W. J. Gregor, J. Raman Spectroscopy **11**, 273 (1981).

3. See Section 9.6.1, this report.

9.6.3 The Application of ^{57}Fe Mössbauer Spectroscopy to the Characterization of Nuclear Waste Forms

(P. G. Huray,^{1,2} M. T. Spaar,¹ S. E. Nave,¹ J. M. Legan,¹ L. A. Boatner,³ M. M. Abraham³)

The electronic charge states and site symmetries of the radioactive ions incorporated in nuclear waste forms are of considerable importance in determining the physical and chemical properties of these materials. An in situ characterization of these ions is, unfortunately, often difficult especially when a mixture of charge states and local crystal symmetries exist. The application of Mössbauer spectroscopy represents a powerful technique for obtaining solid state chemical information.

The Mössbauer isotope ^{57}Fe has been employed in examining the fractions of these nuclei present in mixed atomic environments in a variety of waste forms. The effects of heat treatment at various temperatures, reducing atmospheres, and diverse preparation procedures, were investigated. In many cases a comparison of the resulting spectra with the spectra of well-characterized compounds permitted a quantitative stoichiometric identification to be made of a fraction of the Mössbauer nuclei. In some instances only the charge states and local crystal distortions could be determined; however, a knowledge of the experimental values of isomer shifts and electric field splittings for various compounds may allow a quantitative chemical analysis for untested waste forms containing iron.

Pure Iron Phosphate

In an effort to identify the Mössbauer spectra associated with several pure iron phosphates we have examined several products. They are:

- (a) Commercial (Alpha) $\text{FePO}_4 \cdot x \text{H}_2\text{O}$ as received,
- (b) Commercial (Alpha) $\text{FePO}_4 \cdot x \text{H}_2\text{O}$ after heating to 1200°C under flowing Ar,
- (c) Commercial (Alpha) $\text{Fe}_3(\text{PO}_4)_2 \cdot 8 \text{H}_2\text{O}$ as received,
- (d) Commercial (Alpha) $\text{Fe}_3(\text{PO}_4)_2 \cdot 8 \text{H}_2\text{O}$ after heating to 1200°C under flowing Ar,
- (e) Quartz-like FePO_4 precipitated from a molten urea solution,⁴ and heated to 800°C,
- (f) Quartz-like FePO_4 heated to 1050°C.

In Fig. 9.6 we show the Mössbauer absorption spectrum of quartz-like FePO_4 as precipitated in the molten urea process and calcined at 800°C. A single quadrupole pair of Lorentzian lines with a linewidth of ~ 0.36 mm/sec (the natural

Fig. 9.6. Mössbauer spectra of FePO_4 :
 (a) Precipitated from urea and calcined at 800°C,
 (b) Commercial with waters of hydration, and
 (c) After heating (b) to 1300°C in argon.

linewidth taking into account our equipment broadening) describes the data very well. The isomer shift (1st moment) of this pair is 0.17 mm/sec and the electric field splitting is 0.66 mm/sec. Both values are in agreement with the expected 3+ oxidation state values. Since no additional Lorentzian lines are needed for a good fit, we surmise that a single site exists for iron atoms in this compound. In Fig. 9.6(b), the Mössbauer absorption of "as received" commercial $\text{FePO}_4 \cdot x \text{H}_2\text{O}$ is displayed. Comparison of the top and middle spectra show the influence of waters of hydration. Once again a single pair of Lorentzian lines produces a good fit to the data, and the linewidth of 0.3 mm/sec suggests a single site for the iron atoms. In this case there is an isomer shift of 0.27 mm/sec and a splitting of 0.30 mm/sec which are both in the 3+ range. The reduced electric field splitting suggests that the waters of hydration provide a more symmetric site for iron atoms.

Heating the $\text{FePO}_4 \cdot x \text{H}_2\text{O}$ sample overnight under flowing Ar at slowly increasing temperatures up to 1300°C, and measuring the O_2 off-gas with a Beckman analyzer,⁵ we found that evolution started at 1050°C and was exponentially decreasing with time at the maximum temperature. Calculation revealed that ~80% of the iron should have reduced to the 2+ oxidation state based upon an expected reduction to $\text{Fe}_3(\text{PO}_4)_2$. The Mössbauer spectrum for the product is shown in Fig. 9.6(c). Here, two sets of quadrupole pairs are necessary to provide a good fit to the data. One pair with an isomer shift of 0.47 mm/sec and a splitting of 0.22 mm/sec is presumably the result of unconverted Fe^{3+} which remained in the FePO_4 state. The other pair, with an isomer shift of 1.11 mm/sec and a splitting of 2.49 mm/sec, is consistent with Fe^{2+} parameters and is presumably due to the $\text{Fe}_3(\text{PO}_4)_2$ present in the sample. The relative intensities of the two sets indicate that 87% of the iron atoms have converted to the 2+ state in partial agreement with the effluent value. Several problems exist in the analysis of this spectrum: (1) The linewidths for the two pairs are 0.72 mm/sec and

0.46 mm/sec, respectively, (this allows multiple sites in the compound); (2) The total effect is much smaller than it was prior to heating (this suggests an amorphous component with a small recoilless fraction).

This solid was later exposed to 1 atmosphere of steam at continuously increasing temperatures (up to 1000°C) and found to produce no reoxidation to the 3+ state as evidenced by the absence of H_2 evolution. The resultant Mössbauer spectrum was in agreement with this conclusion.

Iron in Rare Earth Phosphates

Employing the urea coprecipitation method and adding 6 at. % ^{57}Fe to each, powders were formed of the entire lanthanide orthophosphate series (excluding promethium). X-ray analysis confirmed that all compounds formed from the first half of the series (La, Ce, Pr, Nd, Sm, Eu, and Gd) exhibited the expected monoclinic monazite structure. Likewise all compounds formed from the second half of the series (Tb, Dy, Ho, Er, Tm, Yb, and Lu) exhibited the expected tetragonal structure typical of the mineral zircon (ZrSiO_4). X-ray form factors for iron, in comparison to the rare earths, are small and do not reveal a crystal structure for the small 6 at. % component.

All Mössbauer spectra for these compounds required two sets of Lorentzian pairs (i.e., two sites) with similar quadrupole splittings but different isomer shifts. All of the isomer shifts and splittings observed are consistent with *only* 3+ charge states for the iron ions. It is tempting to suggest that the iron atoms occupy one of two possible sites:⁶ (a) a quartz-like FePO_4 site (at least in the immediate neighborhood of an iron atom), and (b) a substitutional site for the rare earth atom in R.E. PO_4 . A discontinuity in a plot of the isomer shift vs atomic number especially lends itself to this argument when one recalls that lattice parameters in these compounds show a discontinuity at Gd.

Iron in Other Phosphates

Powders containing ~6 at. % ^{57}Fe with ScPO_4 , YPO_4 , ThP_2O_7 mixed with $\text{Th}_3(\text{PO}_4)_4$, and NpP_2O_7

were also prepared by the urea precipitation method. All spectra require two 3+ sites only, with one exception: in ScPO_4 , 25% of the iron atoms occupied a 2+ site.

Iron in Simulated Savannah River Waste Phosphates

Simulated Savannah River Waste (SRW), which has a high iron content, was coprecipitated with LaPO_4 at a 15 at. % concentration. The observed iron Mössbauer spectrum was identical to that for pure ^{57}Fe dissolved at the 6 at. % level in LaPO_4 .

Iron in Other Waste Forms

Single crystals of synthetic perovskite, CaTiO_3 , doped with 6 at. % ^{57}Fe were prepared by a flux growth technique. The Mössbauer effect spectra showed 70% Fe^{3+} and 30% Fe^{2+} with a dispersed magnetic component in evidence. The absorptions were not characterized by a sufficiently narrow width to identify single sites, and this suggests there is a highly variable local character for iron in this SYNROC phase.

Borosilicate glasses were examined: Fe_2O_3 and high-iron SRW were dissolved into a type 21 frit at 1150°C. Pure Fe^{3+} spectra were observed for both materials. By comparison, standard MCC-76-68 glass composition (which initially contains 10 wt % Fe_2O_3) exhibits the iron in a predominantly 2+ site with only a small proportion of 3+ in evidence. No magnetic component of iron was observed, indicating the absence of Fe_2O_3 in the final product.

Sol-Gel-spheres were produced from high iron content SRW. Some of the spheres were removed from the process after drying in air at 300°C. These spheres showed the pure 3+ character [see Fig. 9.7(a)]. After sintering the spheres at 1000°C in an Ar-4% H_2 reducing atmosphere, the spectra were characterized by at least three separate 2+ sites constituting 52% of the total [see Fig. 9.7(b)].

The Mössbauer isotope ^{57}Fe has been employed in a quantitative examination of in situ fractions of these nuclei present in mixed atomic

Fig. 9.7. Mössbauer spectra of Savannah River Waste in sol-gel-spheres after (a) drying in air at 300°C and (b) sintering at 1000°C in Ar-4% H_2 .

environments in a variety of waste forms. An identification of the electronic charge states and site symmetries produced from the Mössbauer isomer shifts and electric field splittings allow stoichiometry to be determined in many cases. These results will be of importance in identifying changes produced when heating procedures are employed to bring about some other desirable property such as high densities. It is clearly established that chemical changes may be brought about in such procedures.

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10. CHEMICAL PHYSICS

10.1 Structural Chemistry10.1.1 Neutron Crystallography Relating to Fast-Ion Conductors: Structure Analyses of Hydrated Lithium β -Alumina and Magnesium-Stabilized Sodium β'' -Alumina

(George M. Brown)

Hydrated Lithium β -Alumina. Water is known to be reversibly absorbed into single crystals of Na and Li β -alumina,¹⁻³ the evidence indicating that the water enters the material on the molecular scale and is located in the conduction planes. The absorbed water leads to a decrease in the ionic conductivity of single crystals of Na β -alumina.⁴ Since Na β -alumina is used as the solid electrolyte in experimental high-temperature sodium-sulfur batteries of some promise, it is important to understand on a molecular scale the hydration process and its effects on ionic conductivity. Accordingly, in the Solid State Division a study was undertaken by J. B. Bates and co-workers to develop a complete, quantitative description of the hydration process. The work on hydrated Li β -alumina described here was done in cooperation with the Solid State group, with the aim of finding out where the water molecules and the lithium ions are located in the crystal structure. Lithium β -alumina has been chosen by Bates and co-workers for convenience because it rapidly absorbs a relatively large quantity of water. At 300°C the resistivity of Li β -alumina increases by a factor of four for a sample with about 0.6 water molecule per unit cell. A brief report including the results from the diffraction work and from the hydration studies is in press.⁵

The crystal sample used was approximately a rectangular parallelepiped with dimensions $0.46 \times 2.6 \times 3.0$ mm (11.2 mg in weight). It had been hydrated at 235°C under steam pressure of ~ 80 kPa for 240 hours. It was found by x-ray precession photography to be a single crystal of good quality displaying the Laue symmetry $P6/mmm$, corresponding to the expected space group $P6_3/mmc$. The unit-cell dimensions, determined by the method of least squares from angle data of 12 carefully centered neutron reflections in the

2θ range 53-101°, are as follows: $a = b = 5.5914(6)$, $c = 22.715(2)$ Å. A total of 756 independent Bragg neutron reflections were recorded to a 2θ limit of 130° ($\lambda = 1.0153$ Å) at room temperature.

The structure analysis, by standard least-squares and difference-Fourier techniques, has led to the location of 1.55 molecules of H_2O per unit cell (0.775 molecule per conduction layer per cell), in good agreement with the composition determined from weight-loss measurements. The location of the water from the final least-squares refinement is shown in Fig. 10.1. The oxygen of the water molecule lies in the conduction plane (a mirror plane), and the molecule forms hydrogen bonds with oxygen ions directly above and below the anti-Beevers-Ross site. The water molecule and hydrogen bonds are in three-fold disorder (not shown in Fig. 10.1) about the line (z axis) through the two acceptor oxygen ions.

The location of water by neutron-diffraction analysis was of key importance in the interpretation of the hydration experiments.⁵ A peak in the infrared absorbance spectrum of hydrated Li β -alumina at 3180 cm^{-1} was assignable to the ν_1 mode of the H_2O molecule on the basis of the diffraction results. The absorbance at this wavelength was used to determine the equilibrium water concentration in the material as a function of H_2O vapor pressure and temperature and also to study the kinetics of the hydration process.

The water molecule, which in this case is not determined as precisely as is often possible, appears to have O-H bond lengths of 0.99 Å and an unusually large angle H-O-H of 114°. The proton-proton distance is 1.66 Å. It is pleasing to note that an NMR study⁶ of hydrated Li β -alumina also shows proton-proton vectors within 7° of parallelism with the z axis and a proton-proton distance of 1.65 Å.

The lithium ions in the crystal were not located by the diffraction analysis, though there were volume elements of negative density in the final difference map, some of which may correspond to the presence of lithium (a negative scatterer). The failure to locate the lithium

Fig. 10.1 Location of the H_2O molecule in the conduction plane of hydrated $\text{Li } \beta$ alumina from neutron diffraction analysis. The Li^+ ion, shown here in the Beevers-Ross site, was not located in the diffraction analysis.

probably results from a combination of factors: the small magnitude of the lithium scattering length (-0.214×10^{-12} cm); a diffuse distribution of lithium in the conduction plane; considerable "noise" in the difference map, which is a frequently occurring feature in β - and β'' -aluminas.

Magnesium-stabilized Sodium β'' -Alumina. Magnesium stabilized $\text{Na } \beta''$ -alumina (name hereafter abbreviated to $\text{Na}\beta''\text{-Mg}$) is a possible competitor of $\text{Na } \beta$ -alumina for use as solid electrolyte in sodium-sulfur batteries. The single-crystal neutron structure analysis of this material was undertaken for the same reasons that earlier determinations⁷ of β'' -aluminas were done, namely, to characterize structurally β'' -alumina crystals from the same batches that were the sources of the subject crystals for various physical studies by J. B. Bates and co-workers in the Solid State Division.⁸

It appears that the stabilizing ion Mg^{2+} (or Zn^{2+}) required to produce the $\text{Na } \beta''$ -alumina phase substitutes only for Al^{3+} ion in the $\text{Al}(2)$ sites of the crystal, not in any of the other three different Al^{3+} ion sites.^{7,10}

An important structural parameter that is available from neutron diffraction analysis of a β'' -alumina is the fraction, f , of the Al^{3+} ions in the $\text{Al}(2)$ sites that is replaced by the stabilizing ion. Since substitution of Mg^{2+} (or Zn^{2+}) for Al^{3+} requires an extra Na^+ ion in the conduction layer for charge balance, we can write a general formula such as $\text{Na}_{1+x}\text{Mg}_x\text{Al}_{11-x}$ ⁰¹⁷ to specify the contents of one primitive rhombohedral cell, where $x = 2f$ and $1 + x$ is just the number of conducting ions per conduction layer in the hexagonal cell to be expected from the fraction f of substitution of $\text{Al}(2)$. The values of $1 + x$ for $\text{Na}\beta''\text{-Mg}$ and for the three β'' -aluminas already studied ($\text{K}\beta''\text{-Mg}$, $\text{Ag}\beta''\text{-Mg}$, and $\text{Na}\beta''\text{-Zn}$) are given in the third column of Table 10.1. These values agree well with the corresponding ones from the known chemical compositions of the samples (see the last column of Table 10.1).

Table 10.1 Apparent numbers of conducting ions per layer in the hexagonal cells of four β'' -aluminas

Compound	Conducting ion per layer ($1+x$)* from neutron diffraction		
	From ion occupancies	From $\text{Al}(2)$ substitution	From chem. anal.
$\text{Ab}\beta''\text{-Mg}$	1.61	1.70	1.67
$\text{K}\beta''\text{-Mg}$	1.59	1.68	1.67
$\text{Na}\beta''\text{-Mg}$	1.80	1.71	1.67
$\text{Na}\beta''\text{-Zn}$	1.80	1.59	1.57

* See text.

The number of conducting ions per layer can also be estimated directly in neutron structure analysis by adjustment of the ion occupancy factor in least-squares refinement (see second column of Table 10.1). However, there is reason to expect a less reliable value from the conduct-

ing ion occupancy, because of the rather inadequate model that must be used in the refinement for the smeared-out density distribution of the conducting ion. The fact that for $\text{Na}\beta''\text{-Mg}$ and $\text{Na}\beta''\text{-Zn}$ the values of $1 + x$ from the conducting ion occupancies are higher than those from the fraction of $\text{Al}(2)$ substitution while the reverse is true for $\text{Ag}\beta''\text{-Mg}$ and $\text{K}\beta''\text{-Mg}$ suggests that the $\text{Na}\beta''\text{-Mg}$ and $\text{Na}\beta''\text{-Zn}$ samples may have absorbed some water into the conduction layers, where it would be expected to have the effect of increasing the apparent occupancies of Na^+ ions. It is now known that $\text{Na}\beta''\text{-Mg}$ and $\text{Na}\beta''\text{-Zn}$, especially the latter, can absorb significant amounts of water from the air.^{8b,10}

Corresponding to the apparent smaller number of Na^+ ions in $\text{Na}\beta''\text{-Zn}$ than in $\text{Na}\beta''\text{-Mg}$, as indicated from both the chemical analyses and the fraction of substitution of $\text{Al}(2)$, there should be a larger number of vacancies of Na^+ sites. The higher conductivity of $\text{Na}\beta''\text{-Zn}$ at low temperatures ($<200^\circ\text{C}$) is possibly to be attributed to these extra vacancies.^{8b}

Fig. 10.2 shows for $\text{Na}\beta''\text{-Mg}$ and $\text{Na}\beta''\text{-Zn}$ the nuclear scattering densities of the Na^+ ions in the sections at $z = 1/6$ of Fourier syntheses from

Fig. 10.2 Comparison of the Na^+ ion density distributions at $z = 1/6$ (center of conduction layer) for $\text{Na}\beta''\text{-Zn}$ and $\text{Na}\beta''\text{-Mg}$. The density contributions of other atoms have been removed. The contour interval is 0.1 (in units of $10^{-12} \text{ cm}^3/\text{\AA}$), and the lowest contour (dotted) is at the zero level.

which the contributions of all other atoms have been subtracted. These sections, which are at the centers of conduction layers, show the smeared-out density distributions characteristic of the conducting ions in β'' -aluminas. However, comparison of the two distributions in these and other sections would hardly suggest that the conductivity of the $\text{Na}\beta''\text{-Zn}$ is 10 times that of the $\text{Na}\beta''\text{-Zn}$ at 25°C , as it is.

Further discussion of our neutron diffraction studies on β'' -aluminas is in press.¹¹

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10.1.2 Crystal Structures of Three Complexes of Transition Metals with Strong π -Acceptor Ligands

(George M. Brown and J. E. Finholt¹)

Chelating strong π -acceptor ligands are of interest in connection with the stabilization of transition metals in low oxidation states that exhibit unusual chemical properties,² including the important one of activity in homogeneous catalytic reactions. We have determined by x-ray

crystal-structure analysis the structures of three complexes involving three different transition-metal elements in zero-valent states and two different π -acceptor ligands. The three compounds are named and their formulas and crystal data are given in Table 10.2. (This work

Table 10.2: The complexes studied and their crystal data

- (1) Tricarbonyl[tris[phenyl(difluorophosphino)-amino]phosphine]molybdenum,

$$\text{P}[\text{N}(\text{C}_6\text{H}_5)\text{PF}_2]_3\text{Mo}(\text{CO})_3$$
- (2) Bis- μ -[N,N-bis(dimethoxyphosphino)methylamine]bis(dicarbonylcobalt),

$$(\text{CH}_3\text{N}[\text{P}(\text{OCH}_3)_2]_2)_2\text{Co}_2(\text{CO})_4$$
- (3) μ -Carbonyl- μ -[N,N-bis(dimethoxyphosphino)methylamine]bis(tricarbonyliron),

$$\text{CH}_3\text{N}[\text{P}(\text{OCH}_3)_2]_2\text{Fe}_2(\text{CO})_7$$

	1	2	3
Space Group	$P2_1/c$	$P2_1/c$	$P2_1/m$
<i>a</i> (Å)	8.683(1)	10.809(4)	9.143(2)
<i>b</i> (Å)	28.218(7)	8.980(4)	15.977(5)
<i>c</i> (Å)	15.338(2)	27.63(1)	6.876(1)
β (°)	118.12(1)	94.10(2)	101.00(1)
<i>Z</i>	4	4	2

was done as a cooperative project with Professor R. B. King of the University of Georgia, in whose laboratory the three compounds were prepared. For each crystal, the structure solution was obtained by standard heavy-atom methods from an extensive data set, and refinement was done by the method of least squares.

Compound 1. This compound, $\text{P}[\text{N}(\text{C}_6\text{H}_5)\text{PF}_2]_3\text{Mo}(\text{CO})_3$, whose cage-like structure³ is shown in Fig. 10.3, is the first example of a tridentate chelating ligand containing three PF_2 groups, which are very strong π -acceptors. The compound was identified by our structure analysis after it was produced as an unexpected product in the reaction of N,N-bis(difluorophosphino)aniline, $\text{C}_6\text{H}_5\text{N}(\text{PF}_2)_2$, with $\text{fac}-(\text{CH}_3\text{CN})_3\text{Mo}(\text{CO})_3$. The structure of 1 makes it clear that in the reaction there was an unprecedented elimination of PF_3 from $\text{C}_6\text{H}_5\text{N}(\text{PF}_2)_2$:

Fig. 10.3 The structure of $\text{P}[\text{N}(\text{C}_6\text{H}_5)\text{PF}_2]_3\text{Mo}(\text{CO})_3$ (1), showing the bond lengths (Å) of principal interest (with their estimated deviations in parentheses). The atoms are represented by their thermal ellipsoids of 10% probability (hydrogen atoms not shown).

This is probably a template reaction involving as intermediate the molecule $\text{fac}-(\text{C}_6\text{H}_5\text{N}(\text{PF}_2)_2)_3\text{Mo}(\text{CO})_3$, in which $\text{C}_6\text{H}_5\text{N}(\text{PF}_2)_2$ acts as a monodentate ligand and in which the proximity of the three uncomplexed PF_2 groups facilitates elimination of PF_3 to form the tridentate ligand $\text{P}[\text{N}(\text{C}_6\text{H}_5)\text{PF}_2]_3$ in place on the molybdenum atom.

The Mo-P bond lengths, averaging 2.343 Å, and the Mo-C bond lengths, averaging 2.050 Å, provide striking evidence of the strong π -acceptor character of the PF_2 groups. The Mo-P bonds are among the shortest ever observed for trivalent phosphorus ligands bound to molybdenum, and the Mo-C bonds are among the longest ever observed for carbonyl groups similarly bound. These bond lengths are essentially identical within experimental error with the corresponding lengths 2.369(1) Å and 2.063 Å in $\text{Mo}(\text{CO})_5\text{PF}_3$ ⁴ and 2.063(3) Å in $\text{Mo}(\text{CO})_6$,⁵ from gas-phase electron-

diffraction analysis in each case. Some other relevant bond-length comparisons are available.⁶ Since the Mo-C bond order in Mo(CO)_6 may be assigned^{7,8} a value of 1.5, it follows then from the bond-length data that the Mo-C and Mo-P bond orders in $\text{Mo(CO)}_5\text{PF}_3$ and in **1** must all be about 1.5. We conclude, then, that each ligating group of the tridentate ligand in **1** is about as strong a π -acceptor as the CO molecule or the PF_3 molecule.

Compound 2. Recently, Professor King and co-workers have been studying the coordination chemistry of the bidentate ligand $\text{CH}_3[\text{P}(\text{OCH}_3)_2]_2$ in order to ascertain the effects of substituting methoxy groups for the fluorine atoms in $\text{CH}_3\text{N}(\text{PF}_2)_2$, whose coordination chemistry has already been extensively studied.² Some differences in coordination behavior are to be expected because the methoxy group is less electronegative and bulkier than the fluorine atom. Compound **2**, $\{\text{CH}_3[\text{P}(\text{OCH}_3)_2]_2\}_2\text{Co}_2(\text{CO})_4$, is the first complex of the ligand $\text{CH}_3[\text{P}(\text{OCH}_3)_2]_2$ to have its structure determined.⁹

Fig. 10.4 is a stereoscopic drawing of the molecule of compound **2**. It includes as labels

the bond lengths of principal interest. The Co(1)-Co(2) distance of 2.698(1) Å in the binuclear molecule corresponds to a metal-metal bond and is quite close to the Co-Co distances found in complexes containing the $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{-Co}_2$ unit.¹⁰

The most interesting feature of the structure of **2** in the crystal is the difference between the coordination polyhedra of the two Co atoms. Each cobalt atom is five-coordinate, since each is linked to the other cobalt atom, to two phosphorus atoms, and to two carbonyl groups. However, in the crystal the two cobalt atoms are not related by symmetry, and the two coordination polyhedra are distinctly different. The situation is a most unusual one: in the same molecule two identical metal atoms with identical sets of ligands display approximations to the two different coordination polyhedra characteristic of coordination number five, namely, the square pyramid and the trigonal bipyramid. The polyhedra can be seen from Fig. 10.4 to be as described. The Co(1) polyhedron approximates a tetragonal pyramid, and the Co(2) polyhedron approximates a trigonal bipyramid. Since stereo-

Fig. 10.4. Stereoscopic drawing of the molecule of $\{\text{CH}_3[\text{P}(\text{OCH}_3)_2]_2\}_2\text{Co}_2(\text{CO})_4$ (**2**) with bond lengths (Å) of principal interest. Atoms are represented by their thermal ellipsoids of 20% probability (hydrogen atoms not shown).

chemical nonrigidity is a common feature of five-coordinate complexes,¹¹ the difference between the two polyhedra probably arises from the packing in the crystal of a flexible molecule that is symmetrical in solution.

Compound 3. The binuclear structure of 3, $\text{CH}_3\text{N}[\text{P}(\text{OCH}_3)_2]_2\text{Fe}_2(\text{CO})_7$, is shown in Fig. 10.5. This structure was established unequivocally by the x-ray analysis in contradiction to the conclusion from the original chemical work that the compound was the mononuclear chelate $\text{CH}_3\text{N}[\text{P}(\text{OCH}_3)_2]_2\text{Fe}(\text{CO})_3$. The conclusion from repetition of the chemical work is in agreement with the x-ray result, though the reason for the original disagreement remains obscure.

Fig. 10.5 Drawing of the molecule of $\text{CH}_3\text{N}[\text{P}(\text{OCH}_3)_2]_2\text{Fe}_2(\text{CO})_7$ (3) with bond lengths (Å). Hydrogen atoms are not shown. The molecule has exact mirror symmetry in the crystal.

The complex 3 is closely related structurally to the complex $\text{CH}_2[\text{P}(\text{C}_6\text{H}_5)_2]_2\text{Fe}_2(\text{CO})_7$ (4), whose structure has been determined by x-ray analysis,¹² and to the complex $\text{CH}_3\text{N}(\text{PF}_2)_2\text{Fe}_2(\text{CO})_7$ (5), whose structure has been inferred from analytical and infrared data.¹³ The bond length Fe-Fe in 3 is 0.05 Å shorter than in 4. The Fe-P bond length of 2.192(1) Å in 3 is about 0.06 Å shorter than the corresponding average bond length in 4, con-

sistent with the expected superior π -acceptor property of the phosphorus atoms in 3. Except for the Fe-P and Fe-Fe bonds the corresponding bonds in the two compounds -- that is, those that occupy corresponding positions and involve the same kinds of atoms -- are essentially identical in their lengths, within the errors of the determinations. In particular, the slight lengthening in 3 of bond Fe-C(2) expected to accompany the shortening of the Fe-P bond in the trans position is not observed. Corresponding valence angles in the two molecules are also remarkably close to each other. A crystal-structure analysis of 5 would allow comparison of the structures of 3 and 5, which should be informative concerning the relative strengths of the PF_2 and $\text{P}(\text{OCH}_3)_2$ groups as π -acceptors.

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10.1.3 Intramolecular Potential Functions From Observed Crystal Structures

(W. R. Busing)

The crystal structures of 1,8-diphenylnaphthalene (DPNAP)¹ and 1,4,5,8-tetraphenylnaphthalene (TPNAP)² show a remarkable difference in the out-of-plane strains of the naphthalene nucleus. These strains can be measured by the in-ring torsion angles χ shown in Fig. 10.6, 1.6° and 10.8° for DPNAP and TPNAP, respectively.

Fig. 10.6 Molecules of 1,8-diphenylnaphthalene (DPNAP) and 1,4,5,8-tetraphenylnaphthalene (TPNAP) showing the average conformation angles observed in the crystal structures.

The average magnitudes of the ring-ring torsion angles ϕ are also somewhat different in the two compounds, namely 66.4° and 53.4° respectively.

Computational models of these crystals have been constructed in which the molecules of DPNAP or TPNAP have been divided into 11 and 15 rigid segments, respectively, defined so as to permit flexibility of the naphthalene moiety while all bond distances are held constant.

The energy of each model is computed using a potential function which includes the exp-6-11 nonbonded interaction of Williams and Starr,³ a torsion potential of the form $V_\phi = E_\phi (1 - \cos^2 \phi)/4$ to represent the conjugation energy of the ring-ring links, and a similar expression in χ which tends to keep the naphthalene nucleus planar. Quadratic potentials are also included for the in-plane and out-of-plane ring-link bends.

Four parameters of this intramolecular potential function were adjusted to give the best fit to the experimental crystal structure when the energy of a model is minimized with respect to the lattice parameters, the rotation and translation of the molecule as a whole, and the molecular geometry. The numbers of structural variables were 26 and 20 for DPNAP and TPNAP, respectively. Table 10.3 shows that there is good agreement between the observed and calculated crystal structures.

Also listed in Table 10.3 are the torsion angles of the isolated molecules calculated from the model. Examination of these results for the

Table 10.3 Observed and calculated structural parameters for 1,8-diphenylnaphthalene (DPNAP) and 1,4,5,8-tetraphenylnaphthalene (TPNAP).

	Crystal				Isolated Molecule
	Obs	Calc	Calc-Obs	%	Calc
DPNAP					
a(Å)	8.58	8.40	-0.18	-2.1	
b	20.03	19.84	-0.19	-0.9	
c	9.72	9.67	-0.05	-0.5	
$\beta(^{\circ})$	116.7	115.6	-1.1		
ϕ	-66.4	-66.9	-0.5		-55.4
χ	1.6	2.0	0.4		6.8
TPNAP					
a(Å)	6.46	6.46	0.00	0.0	
b	24.33	24.21	-0.12	-0.5	
c	8.02	7.91	-0.11	-1.4	
$\beta(^{\circ})$	114.3	114.3	0.0		
ϕ	-53.4	-52.6	0.8		-61.9
χ	10.8	11.3	0.5		7.7

crystals and isolated molecules shows clearly that, because the crystals have different structural arrangements, the crystal packing forces have different effects on the ring-ring torsion angle ϕ , increasing its magnitude from 55.4° to 66.4° in DPNAP and reducing it from 61.9° to 53.4° in TPNAP. At the same time the naphthalene distortion angle χ is reduced in DPNAP and increased in TPNAP in going from molecule to crystal. Further calculations for isolated molecules of both substances show that forcing the phenyl rings to be more nearly coplanar with the naphthalene moiety has a prying effect which increases the out-of-plane strain in this moiety.

Clough, Kung, Marsh, and Roberts⁴ propose another explanation for the difference between the out-of-plane strains for these molecules. They suggest that the stress on the 1,8 side of the naphthalene nucleus can be relieved by in-plane changes of distances and angles on the 4,5 side in DPNAP. In TPNAP, on the other hand, both sides are stressed similarly, and out-of-plane distortions provide the only relief. Calculations on a hypothetical molecule of DPNAP using the naphthalene bond distances and angles from TPNAP show that such in-plane differences could explain some, but not all, of the observed out-of-plane strains.

The present work shows that crystal packing forces are the major cause of this difference. By twisting the phenyl rings away from and toward the naphthalene plane in DPNAP and TPNAP, respectively, these forces reduce and increase the out-of-plane distortions from the values that are calculated for the isolated molecules.

10.1.4 X-Ray Diffraction Studies and Models of Some Simple Molecular Liquids

(A. H. Narten, E. Johnson, A. Habenschuss¹)

Simple molecular fluids consist of molecules which interact with weak attractive forces. Most homonuclear diatomics fall into this category and have therefore been extensively studied by computer simulation and other statistical mechanical methods. These model calculations predict that the structure of these liquids should change in a systematic way with the elongation of their constituent molecules, defined as $L^* = L/\sigma$ (bond length/atomic diameter).

To test these predictions, we have measured the x-ray diffraction patterns of four diatomic liquids and derived the intermolecular atom pair distribution functions, $g(r)$, from the data. Of the liquids studied, only nitrogen and bromine are homonuclear diatomics. The other two, ethylene and ethane, are "pseudodiatomics" in that the hydrogen atoms in these molecules are mere bulges in the electron density distribution which, viewed from the carbon nucleus, have a sizeable angular spread. The scattering of x-rays from these molecules can hence be described by a single form factor for methylene and methyl groups. The carbon-carbon atom pair distribution functions thus derived from the data are compared with the corresponding functions for liquid nitrogen and bromine in Fig. 10.7.

The main first peak in each of the curves is followed by a shoulder which develops into a second peak with increasing elongation of the molecule. This structure is explained as follows: When two molecules touch, there is at least one highly probable intermolecular distance at $r = \sigma$, and two others between σ and $L + \sigma$. Beyond $L + \sigma$ there is therefore a sudden drop in probability, producing a shoulder or peak at that distance. Another interesting feature is that the structure beyond $L + \sigma$ is gradually washed out as the elongation increases. All these features are in good qualitative agreement with results from computer simulations.² The simula-

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Fig. 10.7 Intermolecular atom pair distribution functions derived from x-ray diffraction.

tions show, in addition, that the transformation of the shoulder at $L+\sigma$ into a peak is due to an increase of T-shaped configurations, since in this orientation there are two atom pair distances approximately equal to $L+\sigma$.

We have calculated atom pair distribution functions for 2-site models of these liquids using the reference interaction site model (RISM).³ The sites, located at the atomic positions, were assumed to interact with exp-6 potentials. Such a 2-site model predicts the structure of liquid nitrogen in good agreement with experiment.⁴ The distribution function calculated for such a model of liquid ethylene is in poor agreement with the curve derived from experiment,⁵ and the model fails completely to predict the structures of liquid ethane⁶ and bromine.⁷ In particular, the 2-site model does not predict the secondary peak at $L+\sigma$. The computer simula-

tions² indicate that this peak, caused by T-shaped configurations, arises from quadrupole-quadrupole interactions between molecules. Such electrostatic potentials which arise from a localized distribution of charge can be modelled by point charges assumed to lie on the molecular axis, with magnitudes and separation chosen to give the desired quadrupole moment. RISM calculations for such 3-site models of liquid ethane and bromine are under way.

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10.1.5 Atom Pair Distribution Functions of Liquid Water at 25°C From Neutron Diffraction

(W. E. Thiessen, L. Blum,¹ A. H. Narten)

Enormous effort has been invested in experimental determinations of the properties of water, in attempts to interpret these properties in terms of molecular interactions, and in the development of models with which known properties can be correlated and unknown properties predicted. Despite the effort, our factual knowledge is meager and our understanding rudimentary. An example is the structure of liquid water, described by the three atom pair distribution functions $g_{OO}(r)$, $g_{OH}(r)$, and $g_{HH}(r)$. Only the function $g_{OO}(r)$ is known² with sufficient accuracy to test proposed models of liquid water.

Neutron diffraction is a unique tool for probing the structure of water, because the hydrogen atoms cannot be "seen" with adequate precision by other techniques (x-ray, electron diffraction). This was recognized in the pioneering work of Wollan and Schull³ who, in 1946, measured the first neutron diffraction patterns of liquid water at the X-Pile in Oak Ridge. The existence

of two stable hydrogen isotopes with different coherent scattering lengths suggests that one could perform the standard isotopic substitution experiments⁴ on water, and obtain the three partial structure functions. In practice, however, the very large incoherent cross-section of light hydrogen obscures the structural information contained within the coherent scattering. This means that in order to obtain sufficiently good statistics for the coherent scattering cross-sections very large numbers of neutrons have to be counted. We have used a dedicated diffractometer at the High Flux Isotope Reactor to obtain neutron data of very high statistical accuracy for four mixtures of light and heavy water containing 0.1%, 35.79%, 67.89%, and 99.75% deuterium.⁵ Another problem is the complex nature of the interaction of thermal neutrons with light nuclei such as hydrogen. Inelastic and recoil effects make the extraction of the static coherent scattering function from the measured effective cross-sections difficult. We have solved this problem by constructing the dynamic scattering function for sufficiently realistic models of water and integrating over the energy transfer.⁶ The static coherent scattering functions for the four mixtures were then analyzed to yield the three partial structure functions from which the three atom pair distribution functions were obtained by Fourier inversion. The results are shown in Fig. 10.8.

The oxygen atom pair distribution function, $g_{OO}(r)$, derived from the neutron data is not significantly different from that obtained previously from x-ray diffraction.² This curve contains information about the positional correlation between centers of molecules in liquid water. Principal features are an asymmetric distribution of nearest neighbors centered at 2.85 Å, which overlaps with the distribution of tetrahedrally coordinated second neighbors near 4.5 Å. This overlap of first and second neighbor distance distributions has been interpreted⁷ in terms of a complex near neighbor

Fig. 10.8 Intermolecular atom pair distribution functions for liquid water at 25°C.

coordination sphere which cannot be explained by tetrahedral coordination alone.

The function $g_{HH}(r)$ describes the distance distribution between hydrogen atom pairs in different water molecules and, hence, contains information about orientational correlations in the liquid. Principal features are a near neighbor distribution centered at 2.29 Å which overlaps with the distribution of second neighbors near 3.9 Å. The function $g_{OH}(r)$ shows a narrow distribution of first neighbors at 1.86 Å which does not overlap with the distribution of second neighbors near 3.2 Å. A nearest neighbor O...H distance of 1.86 Å, a corresponding O...O distance of 2.86 Å, and an intramolecular O-H distance of 0.96 Å⁵ suggests that most water molecules are connected to their nearest neighbors through straight hydrogen bonds.

The oxygen atom pair distribution function $g_{OO}(r)$ derived from x-ray diffraction has already provided a crucial test of water models in computer experiments.⁸ The function $g_{OH}(r)$ and $g_{HH}(r)$ derived in this study will provide an even more sensitive test of proposed models for

liquid water. This should lead, eventually, to a realistic statistical mechanical theory of liquid water.

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10.1.6 Small Angle X-Ray and Neutron Scattering from Polydisperse Ludox Samples

(R. Triolo and H. R. Child¹)

An important step in the process of analyzing small angle diffraction curves of polydisperse systems is the inversion of experimental data to obtain size distribution functions. Several methods are currently available, each presenting some positive aspects as well as some negative ones. The ideal situation would be the one in which synthetic size distributions obtained by mixing components of different sizes can be analyzed by the different methods, giving the same answer.

Unfortunately in nature no system is strictly monodisperse and very often polymodal and polydisperse distributions are encountered. Systems of this type are common in the Enhanced Oil Recovery (EOR) technology as well as in the coal extract technology.

Here we present some preliminary data on polydisperse colloidal silica suspensions (Ludox) as well as bimodal polydisperse suspensions obtained by mixing different samples of Ludox.

Experimental. Six grades of Ludox colloidal silica are commercially available: AM, AS, HS, SM, LS, and TM. The stabilization of the suspension is due to a slight negative charge on the surface of the particle. One of the grades (AS) uses ammonium ions as counterions, the other five grades use sodium ions as counterions. The type AM, in addition to this, has also some Al atoms replacing Si atoms on the surface.

We decided to study three types which have the same chemical composition, but differ in the size of the particles as determined with TEM. Typical properties (before dilution) are presented in Table 10.4. We have studied all the three types

Table 10.4 Typical Properties of Ludox Colloidal Silica

Type	SM	HS	TM
Conc. (v/v)	30.00	40.00	30.00
Conc. SiO ₂ (wt %)	~30.00	~40.00	50.00
Diameter (Å)	75.00	135.00	235.00
Viscosity at 25 C (cP)	6.50	26.00	40.00
Density at 25 C (g/ml)	1.22	1.31	1.39

and some of their mixtures with both small angle x-ray and neutron scattering. The machines used were the 10 M SAXS instrument at ORNL and the 30 M SANS instrument at HFIR. All the dilutions of the samples have been done volumetrically with D₂O, in order to achieve maximum contrast for the SANS experiments. The same solutions were also used for the SAXS study. Experimental results have been obtained in the concentration range 40% to 0.05% (v/v) when x-rays were used and in the concentration range 40% to 0.5% (v/v) when neutrons were used. In addition to this we also studied some mixtures SM-TM and HS-TM at the highest concentration.

Discussion. For a polydisperse system of interacting spherical particles the scattering intensity at a given value of k will be given by²

$$I(k) = \alpha \sum_i \phi_i(k) S_i(k) \quad (1)$$

where α is a proportionality constant which depends on the nature and the concentration of the scattering centers and on the instrument used, $\phi_i(k) = (\sin(kr_i) - kr_i \cos(kr_i))^2 / (kr_i)^6$ is the scattering due to the isolated particle, and $S_i(k)$ is the interparticle structure function. In the simple case of a monodisperse system, the summation in (1) will contain only one term. At small k 's $I(k)$ will then appear as an interaction peak due to the combination of the decreasing function $\phi_i(k)$ and the increasing function $S_i(k)$.³ Model calculations⁴ show that usually $S_i(k)$ is essentially constant for values of k greater than the value of k_p of the maximum in the interaction peak. This in turn means that the slope of $I(k)$ vs. k is essentially due to $\phi_i(k)$ for $k > k_p$. For dilute non-interacting particles, the term $S(k)$ is essentially constant and equal to 1 except for very small values of k , so that $I(k)$ becomes proportional to $\phi_i(k)$. In this case one can easily relate the scattering curve to the Guinier radius R_G through the equation

$$I(k) = I(0) \exp(-k^2 R_G^2 / 3). \quad (2)$$

If the system is not dilute enough, it is still meaningful to calculate R_G using the data obtained for $k > k_p$, where $S(k)$ is constant.

In Table 10.5 we present the results obtained for three pure samples of Ludox at several different concentrations. It can be noted that

Table 10.5 Values of the Guinier radius, R_G (in Å), for three samples of Ludox at various concentrations (SAXS data)

Type	SM	HS	TM
Dilution			
1:10	58.9	83.0	133.0
1:20	58.9	83.0	133.0
1:25	58.5	82.4	136.0
1:50	58.5	81.5	135.0
1:100	56.5	81.5	133.0
1:200	54.1	80.5	131.0

the values of R_G obtained are essentially concentration independent, even at high concentrations.

These values are consistent with the values of R_G calculated from the scattering curves of mixtures of Ludox SM and TM (Fig. 10.9) and HS and TM (not shown here). In the case of mixtures we

Fig. 10.9 SANS curves for mixtures of undiluted Ludox SM and TM samples: (●) 95% SM and 5% TM; (Δ) 90% SM and 10% TM; (○) 80% SM and 20% TM; (□) 70% SM and 30% TM.

found a double interference peak; the first peak is due essentially to interaction between TM particles; the second peak is due to interaction between the smaller particles (SM or HS). The intermediate region is affected by the "mixed" interaction SM-TM (or HS-TM). This has a small effect on the values of R_G obtained on the right side of the first and of the second peak, respectively. As a consequence of the presence of two components, the value of R_G for the TM particles is about 15% smaller than in pure TM and the value of R_G for the SM (or HS) is about 15% higher than in pure SM (or HS).

Inversion of scattering data. We are presently analyzing the above mentioned data with all the methods currently available: these include

Schmidt's method,⁵ Glatter's method,⁶ and Vonk's method.⁷ As an example, in Fig. 10.10 we show a typical experimental curve (●) and a calculated one (○) using the size distribution function (shown in Fig. 10.11), obtained with a modified version of Vonk's program. The data refer to a sample of Ludox HS diluted 1:50 with D₂O. The experimental curve is actually a combination of three different curves obtained with the detector set at different distances. The distribution function shown in Fig. 10.11 agrees well with TEM determinations.

Fig. 10.10 Experimental (●) and calculated (○) scattered intensity for a solution of 0.6% (v/v) Ludox HS in D₂O.

Fig. 10.11 Size distribution function obtained by inversion of the experimental data of Fig. 10.10.

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10.1.7 Structural Studies of Nucleosomes

(G. Bunick, E. Uberbacher)

Nucleosome x-ray diffraction studies. A new crystal form of chicken erythrocyte nucleosomes has been discovered. The crystals are flat tri-

angular plates up to 0.5 mm in length and relatively thin. X-ray diffraction experiments suggest an orthorhombic lattice with $a=220 \text{ \AA}$, $b=170 \text{ \AA}$, and $c=60 \text{ \AA}$. The space group is most likely $P2_12_12$, and the unit cell volume is consistent with one nucleosome per asymmetric unit. The resolution limit of diffraction (approx. $13 \text{ \AA}$) is most likely the result of having thin crystals; thus it is expected that the resolution will improve as thicker crystals are grown.

Analysis of nucleosome-HMG complexes by small-angle neutron scattering. A preliminary analysis of scattering curves for nucleosomes and nucleosome-HMG 14 in 0%, 25%, 50%, 75%, and 100% D_2O suggests an increase by approximately $3 \text{ \AA}$ in the radius of gyration of the DNA when HMG 14 is complexed in a 2:1 ratio with nucleosomes. The increase in radius of gyration of the DNA after HMG 14 addition is interpreted as a relaxing or loosening of the CNA-histone interactions. The observed change is consistent with the hypothesis that *in vivo* HMG proteins induce structural changes which are necessary for the recognition of potentially transcribable regions within the chromatin. The measured radius of gyration for protein increases by about $1 \text{ \AA}$ when HMG 14 is complexed with nucleosomes. This change is most likely due to the added HMG protein itself, and it is not thought to be an indication of any conformational change within the histone core of the nucleosome.

10.2 Atomic and Molecular Collisions

10.2.1 Carbon Reactions in Molecular Beams

(H. F. Krause)

Gas-phase carbon reactions involving carbon atoms and polymers (C , C_2 , C_3 , ..., C_n) are of chemical interest and they occur in a wide variety of man-made and natural environments. Basic understanding in this area may be particularly applicable in the fields of combustion, high-temperature chemistry and astrophysics. The feasibility of studying carbon reactions by the use of molecular beam methods has been demonstrated recently.^{1,2}

The carbon beam (principally C , C_2 , C_3) is produced by a graphite evaporation source operating up to 3600°K . The thermally excited $C(^1D)$ population is less than 1%. After the carbon beam is narrowly collimated, pulsed by a rotating slotted disk, and completely cleansed of any charged particle beam fractions, it travels a fixed flight length before colliding with reagent gas in a cell (single collision conditions, 0.5 mTorr). Since each carbon constituent, C_n , arrives at the reaction zone in different time-dispersed packets, it is possible to identify the reactant by measuring the time-of-arrival of reaction product signals. Molecules formed in reaction are detected and internal state analyzed by detecting their laser-induced fluorescence (LIF) or chemiluminescence.

I. Velocity-Selected Study of Rotational Excitation in the Reaction:

Recent improvements in the experimental technique used to study vibrational excitation in reaction (1),³ have permitted the improved state-selected experiment reported here. In this study the $CN(X^2\Sigma^+)$ molecules, detected by the LIF technique, are measured in coincidence with carbon traveling at $4 \times 10^5 \text{ cm/sec}$, where the beam is about 95% pure C atoms. The reagent NO has a Boltzmann rotational distribution at 300°K .

Rotational populations formed in collision, shown in Fig. 10.12, are derived from rotationally resolved LIF spectra obtained on the

Fig. 10.12 $CN(X^2\Sigma^+, v=0)$ rotational population produced by reaction of velocity-selected C atoms ($v = 4 \times 10^5 \text{ cm/s}$) with NO .

CN(X + B) system. Although the product rotational distribution is non-thermal, populations in the highest levels ($K > 14$) can be fit approximately to a Boltzmann rotational distribution using a temperature of about 800°K. But, product populations in the lowest states ($k < 7$) are larger than those given by the Boltzmann fit and are not proportional to the rotational degeneracy. On the average, product excitation exceeds the NO reactant excitation by about 10 rotational quanta. The suggested structure at low K may be indicative of a bimodal distribution. Different distributions could arise if more than one potential energy surface were involved. It is worth noting that three doublet and three quartet surfaces adiabatically correlate reactants and products.

In Fig. 10.12, experimental populations are compared with a rotational distribution calculated by assuming that the product flux distribution in phase space is uniform, subject only to the conservation of total energy. The average product rotational energy predicted by this distribution is about five times higher than

that observed. Conservation of both energy and angular momentum in the collision can support much more rotational excitation than is observed.

Gross disagreement with experiment suggests that the reaction proceeds via a "direct" mode rather than through "complex" formation. The redistribution of total available energy (2.00 eV) observed (translational 80%, vibrational 15%, rotational 5%), may be indicative of CN-O breakup from a weakly bent conformation. Higher rotational and lower vibrational excitation would be anticipated if the breakup conformation were severely bent.

II. Identification of the Chemiluminescent Reaction:

The most interesting portion of a typical wavelength scan (200-450 nm) of the chemiluminescence is shown in Fig. 10.13. The peaks in the emission spectrum can be explained completely in terms of the $\text{SO}(\text{A } ^3\pi, v \rightarrow \text{X } ^3\Sigma^-, v')$ band system where $v = 0, 1, 2, 3, 4$, and perhaps $v = 5, 6$.

Fig. 10.13. $\text{SO}(\text{A } ^3\pi; v \rightarrow \text{X } ^3\Sigma^-; v')$ emission spectrum produced by collisions of C with SO_2 (0.42 nm FWHM). Band origins ($J = J' = 0$) corresponding to bands having the largest Franck-Condon factors are indicated for each multiplet component of A.

Vibrational populations in $\text{SO}(\text{A } ^3\pi)$ decrease monotonically with increasing v . The $\text{SO}(\text{B } ^3\Sigma) + \text{CO}$ product chemiluminescent channel (exoergic by 0.353 eV) must be of minor importance because no band emission from very intense $\text{SO}(\text{B} \rightarrow \text{X})$ transitions is discerned in the vicinity of 266.6, 274.6, and 283.0 nm ($v=1$ to $v=4,5,6$ respectively). In addition, no signals are observed in the regions around 339.3, 351.4, and 364.2 nm where the $\text{SO}(\text{B} \rightarrow \text{X})$ transitions for the $v=0$ to $v=11,12,13$ bands would appear.

Photon arrival distributions for the $\text{SO}(\text{A} \rightarrow \text{X})$ emission uniquely identify the reactant carbon species as C. A typical experimental distribution for dispersed photons (260 nm region of Fig. 10.13) is shown in Fig. 10.14. The data are compared with calculated reaction flux distributions (C and C_2 with SO_2) assuming that a) the energy dependence of the total reaction cross section varies as $E^{-1/3}$ over the entire experimental energy range ($E < 1.10$ eV) and

b) the velocity distributions of the reactants are Boltzmann. The energy dependence of the cross section noted above is expected for an exoergic process where long range forces predominate (attractive r^{-6} potential with a repulsive centrifugal barrier). Referring to Fig. 10.14, the calculated distribution for the atomic carbon reactant fits experimental data very well. A calculated distribution assuming an energy independent reaction cross section is noticeably inferior to that shown in Fig. 10.14.

The fact that chemiluminescence from the $\text{SO}(\text{A} \rightarrow \text{X})$ band system predominates and no emission from the $\text{SO}(\text{B} \rightarrow \text{X})$ system is identified can be explained by the use of adiabatic correlation arguments, which are illustrated in Fig. 10.15. It can be seen that reactants in the ground state correlate to the observed $\text{SO}(\text{A } ^3\pi) + \text{CO}(\text{X } ^1\Sigma)$ product channel on two triplet surfaces. There are no other triplet surfaces available for the ground state reactants

Fig. 10.14. TOA distribution for the $\text{SO}(\text{A} \rightarrow \text{X})$ emission in a narrow region around 260 nm. Data are compared to calculated reaction flux distributions for the C and C_2 carbon beam components with SO_2 ($T=3370^\circ\text{K}$).

to correlate to the $\text{SO}(\text{B } ^3\pi) + \text{CO}(\text{X } ^1\Sigma)$ product channel because the third triplet surface originating with ground state reactants correlates to ground state products. The correlations for the lowest product channels are the same as those shown in Fig. 10.15 when the planar geometry is relaxed to the C_1 point group (no symmetry, $\text{A}' = \text{A}'' = \text{A}$ in Fig. 10.15). A lower limit on the rate coefficient for reaction (1) is estimated to be $k = \langle v\sigma \rangle = 1.5 \times 10^{-11} \text{ cm}^2/\text{s}$ (for $\langle v \rangle = 2.5 \times 10^5 \text{ cm/s}$).

Fig. 10.15 Adiabatic correlation of reactants and products (C_∞ symmetry). The observed specificity of $\text{SO}(\text{A } ^3\pi)$ production over the $\text{SO}(\text{B } ^3\Sigma)$ product is explained. Efficient production of SO in lower lying levels is predicted.

Since reaction (2) is the only known carbon atom chemiluminescent reaction which yields emission in the UV spectral region (where detection efficiencies are high), it could form the basis for a convenient and very sensitive detector of carbon atoms in environments where ambient light backgrounds in the IR and visible spectral regions are high.

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10.2.2 Collisional Electron Detachment of Cl^- with Diatomic Targets

(B. K. Annis and S. Datz)

Energy loss and angular intensity distributions for the neutral chlorine product formed in detachment collisions have been obtained for NO, O_2 , and CO targets in the energy range 150–300 eV ($E_{\text{rel}} = 60 - 140 \text{ eV}$). In the case of CO the energy loss spectrum exhibited two peaks corresponding to detachment channels in which approximately 6 and 12 eV were absorbed. The energy loss data are plotted in Fig. 10.16 as a function of a reduced parameter, τ , which is defined as the product of the collision energy and scattering angle. The lower energy loss is

Fig. 10.16. Most probable values of kinetic energy absorbed in collisions of Cl^- with CO versus $\tau (\equiv E\theta)$.

commensurate with the charge transfer to the 2π resonant state of CO^- and the high-loss channel is appropriate to the excitation of the $\text{A } ^1\pi$ state of CO. The possibility that the $1p^0$ auto-detaching channel of Cl^- was involved is precluded on the grounds that there was no evidence for the formation of the analogous autodetaching state of F^- in separate experiments with F^- and CO. As in the case of our earlier results with

an N_2 target,¹ the low angle scattering was dominated by the 12 eV channel. Within the general context of atomic and molecular collisions, low-angle, high-energy-loss scattering is atypical. We will return to a possible explanation for this observation after a brief summary of our results on related systems.

Examples of energy loss data for NO and O_2 targets are shown in Fig. 10.17. High-energy-loss, low-angle scattering was not observed.

Fig. 10.17 Energy loss spectra for NO and O_2 targets.

The dominant low-angle energy loss for NO is centered at about $5\frac{1}{2}$ eV, while that for O_2 is noticeably lower at 4 eV. At larger angles there is an indication that another channel is opening in the $Cl^- + NO$ scattering. In contrast with this a second peak centered at about 6 eV is readily apparent in the data for O_2 . This channel subsequently dominates the detachment scattering at higher angles. Resonant states of NO^- are known to exist in the range 0.7-2.5 eV and the observed energy losses are in accord with charge transfer to these states. The 4 eV peak in O_2 is also appropriate to the formation of O_2^- in an autodetaching state; however, since the energy loss is also commensurate with direct ejection of the electron into the continuum, the exact nature of the detachment process remains equivocal.

The angular differential cross sections for N_2 , CO, NO, and O_2 have been measured and have been found to differ substantially from one another. The data that we have accumulated demonstrate that collisional detachment by the simple atmospheric diatomic molecules proceeds in a complicated and highly specific manner. From a practical point of view, this work suggests that the use of collisional detachment in the production of fast neutral beams can result in unexpected energy spreads and angular divergencies.

A detailed understanding of collisional detachment will require the use of several potential surfaces for the triatomic collision complex. Typically these surfaces are formulated with substantial difficulty and use fragmentary information obtained by infrared and optical spectroscopy, photo dissociation, and electron scattering. In view of the specific behavior of the detachment collisions that we have observed, we feel that scattering experiments of this type will provide useful tests of such surfaces.

As an example of this possibility, we consider the angular differential cross sections for detachment by NO and Ar targets² as shown in Fig. 10.18; and note that the scattering is shifted to lower angles for NO. There is some

Fig. 10.18 Angular differential cross sections for NO, O_2 , and Ar. Vertical lines on NO and Ar data show location of calculated threshold scattering angles.

potential information relevant to these targets which suggest that this angular shift is explicable. The essence of the argument is that the potentials for $\text{Cl}^- + \text{Ar}$ and $\text{Cl} + \text{Ar}$ are repulsive and cross at a positive value of the potential energy. On the other hand, a stable NOCl molecule is known to exist; and comparison with potentials for $\text{K}^+ + \text{NO}$ and $\text{Ar} + \text{NO}$ which are isoelectronic with $\text{Cl}^- + \text{NO}$ establishes that the curves cross near the bottom of the attractive well for NOCl . A simple classical calculation of the minimum scattering angle which occurs when the colliding particles just reach the crossing points shows that the attractive well substantially reduces the scattering angle for $\text{Cl}^- + \text{NO}$ below that of the repulsive $\text{Cl}^- + \text{Ar}$ system.

The results suggest that a bound excited state such as shown in Fig. 10.19 for $\text{N}_2\text{CO} + \text{Cl}$ can explain the unusual high-energy-loss, low-angle scattering that was observed in these

Fig. 10.19 Schematic potential energy functions.

systems. Since O^- is isoelectronic in the outer shell with Cl , we have included a simplified version of the potentials for N_2O^- as suggested by calculations of Krauss et al.³ which supports the hypothesis of a bound excited state.

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10.2.3 Radiation from Channeled Electrons

(S. Datz, M. J. Alguard,¹ R. L. Swent,¹ R. H. Pantell,¹ B. L. Berman,² S. D. Bloom,² J. U. Andersen,³ E. Laegsgaard³)

The potential function for an electron penetrating a crystal with sufficiently small transverse energy with respect to crystal planes or axes produces a series of bound eigenstates in which the particle can be trapped. Such a particle is said to be planar or axially channeled. We have reported radiative spontaneous transitions between the eigenstates which result in electromagnetic radiation with a photon energy spectrum that has peaks corresponding to the Doppler-shifted transition energies for 28- to 54-MeV electrons planar channeled in Si. This year we report on quantitative fits of the spectral lines with theory, the occupation lengths of bound states in electron planar channeling, the temperature dependence of the spectral lines and the existence of bound two-center ("molecular") states in electron axial channeling in diamond. The high energy (54 MeV) electron planar channeling data was obtained with the electron linear accelerator at Lawrence Livermore Laboratory and the low energy (4 MeV) axial channeling data was obtained using a Van de Graaff accelerator at Aarhus University in Denmark.

Figure 10.20 shows data obtained with 54 MeV electrons in Si (17.4 μm thick). The dashed curve shows the spectrum obtained in a random orientation (normal bremsstrahlung) for the same electron fluence. The remainder consists of a broad continuum arising from free-to-bound state transitions and a set of peaks resulting from bound-to-bound state transitions. Peaks labelled (1) through (5) result from $\Delta n = 1$ transitions between adjacent eigenstates. The peak marked (1) is from the first excited state

Fig. 10.20 Photon spectrum from 54-MeV electrons in 17.4 μm thick Si. Points are for {110} channeling orientation and dashed line is for a "random" direction. Spectra are not corrected for detector response.

($n = 1$) to the ground state ($n = 0$). Peak (2) is from $n = 2$ to $n = 1$, and so on. The small peaks at higher energies come from $\Delta n = 3$ transitions.

The photon energies and FWHM linewidths listed in Table 10.6 for $\Delta n = 1$ transitions are obtained from a least-squares curve fitting to the data in Fig. 10.20. The calculated photon energies were obtained by the Aarhus group using many-beam, dynamical theory and a Doyle-Turner approximation to the silicon atomic Hartree-Fock potential averaged in the plane and accounting for thermal vibrations at a temperature of 300°K. The agreement is remarkably good; the largest disagreement with experiment is only $\sim 2.5\%$ at the $n = 1$ to $n = 2$ transition where perturba-

tions of the planar potential due to thermal vibration of the atoms is a maximum.

Using a Lorentzian line shape, the linewidths were determined and are listed in the fourth column of Table 10.6. The coherence length ℓ_n for a state is the mean distance for which an electron remains in that state. An effective coherence length for a transition is defined as

$$\ell_{nn'}^{-1} = \ell_n^{-1} + \ell_{n'}^{-1}.$$

Incoherent scattering interrupts the oscillation and causes a linewidth contribution

$$\Delta E_{nn'} = 2\gamma^2 \beta c \hbar \ell_{nn'}^{-1},$$

where $\beta = 1$ is the ratio of the particle velocity to the velocity of light. The resulting $\ell_{nn'}$ are listed in Table 10.6. The coherence lengths decrease with decreasing quantum number because the lower-lying states are more localized near the atomic planes, and the electrons are therefore scattered more frequently by thermal vibrations and atomic electrons. If these scattering events caused irreversible transitions to non-bound states, the population of a state would decay on the scale of a coherence length; and the population of the lower states would decay more rapidly. Moreover, since the coherence lengths are all $< 1 \mu\text{m}$, it would be expected that crystals of $\sim 20 \mu\text{m}$ would show little radiation above the bremsstrahlung level. To determine the occupation lengths, i.e., the length over which the initial occupation of a given level drops to $1/e$ of its initial value,

Table 10.6 Characteristics for line radiation for 54 MeV ($\gamma = 107$) electrons in bound states of {110} of silicon

Transition $n \rightarrow n'$	Photon Energy (keV)		Linewidth (keV)	Coherence Length (μm)	Occupation Length for State n (μm)
	Calc.	Exp.			
1 $\rightarrow$ 0	125.3	122.5	19.5	.231	165
2 $\rightarrow$ 1	89.0	88.8	14.4	.312	45
3 $\rightarrow$ 2	64.5	64.3	10.5	.429	17
4 $\rightarrow$ 3	49.0	49.1	7.8	.577	13
5 $\rightarrow$ 4	38.4	38.3	7.0	.642	10

of a given n level the line intensities were measured as a function of crystal thickness. The results are shown in the last column and can be seen to be two orders of magnitude greater than the coherence lengths.

The data can be explained if it is assumed that the scattering events which terminate coherence are more likely to produce transitions to other bound states rather than to cause dechanneling. In this case, electrons could oscillate between bound states on a length scale of less than one micron, and yet move from the bound to unbound states on a length scale of tens of microns. Furthermore, if transitions to neighboring states are most likely, then only the uppermost state has appreciable coupling to the unbound states; and this would explain why the lowest states have the longest occupation lengths. Occupation probabilities would be determined by a Markov process with a perfectly reflecting boundary at $n = 0$ and a highly absorbing boundary at $n > 5$. That this upper boundary is not perfectly absorbing can be adduced from the presence of continuum to bound state radiation which underlies the peak structure in Fig. 10.20.

These considerations indicate that the calculation of the radiation intensity for a transition requires a specification of the transfer rates between states. The resulting coupled rate equations must then be solved to obtain the occupation probabilities as a function of penetration distance. The experiments also demonstrate that the intensity obtainable from channeling radiation is not limited by the coherence lengths but by the occupation lengths which can be two orders of magnitude greater.

As mentioned above, the potential into which the electrons are trapped is a properly averaged sum of atomic potentials in the plane in which the thermal vibrations must be taken into account. Larger vibrational amplitudes raise the bottom of the well without much affecting the upper portion of the well. This is demonstrated in Fig. 10.21 which shows channeling radiation spectra for (110) planar channeling in Si as a function of crystal temperature. The

Fig. 10.21 Photon spectra from 54-MeV electrons planar channelled in (110) Si as a function of crystal temperature.

$n = 1$ to $n = 0$ transition is most strongly affected giving shifts of almost 20 keV with a temperature rise of only $\sim 150^\circ$. The upper states are progressively less affected by the changes at the bottom of the well. A complete theoretical treatment of these effects is in progress.

Electrons entering a crystal close to low index crystal axes are bound in the two dimensional potential made up by the atoms in a row ("string potential"). The eigenstates here require two quantum numbers n and ℓ . Radiation from transitions between these states of this type in Si have been reported by the Aarhus group. In a collaborative effort axial channeling radiation in diamond was studied (the diamond was loaned to us by Prof. F. Selschop of the University of Witwatersrand in South Africa). Radiation from a $2p-1s$ transition in $\langle 111 \rangle$ diamond axial channeling is shown in the upper portion of Fig. 10.22. (In this case $\sim$ half the measured linewidth is due to detector resolution.) In the lower portion of Fig. 10.22 we show the spectrum obtained with channeling in a $\langle 110 \rangle$ direction. Four lines of width equivalent to the $\langle 111 \rangle$ line can be deconvoluted from this spectrum. The transition in the $\langle 110 \rangle$ case is also a $2p \rightarrow 1s$ transition but with one important difference; i.e., the states

Fig. 10.22 Photon spectra from 4 MeV electrons axially channeled in the $\langle 111 \rangle$ and the $\langle 110 \rangle$ directions in diamond.

in question are "molecular" (two "string" atoms) and not atomic (one "string" atom). This comes about because in a $\langle 110 \rangle$ direction two strings lie in close proximity to each other. Hence an approximately exponential potential from one string overlaps the potential of the adjacent pair string, giving a local maximum midway between the strings. The $1s$ level lies well below the local maximum but the $2p$ level lies above it. Hence a proper description involves binding to both strings and the "atomic" $2p$ state must be treated as a set of molecular states: $2p\pi_u$, $2p\pi_g$, $2p\sigma_u$, and $2p\sigma_g$. The maximum effect is in the $2p\sigma_g$ which appears at the lowest energy. Quantitative interpretation of these state splittings depends on the detailed electron density distributions in the diamond lattice and is presently under development.

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10.2.4 Photoelectron Spectrometry of Free Atoms and Metal Vapors with the Use of Synchrotron Radiation

(M. O. Krause, T. A. Carlson)

The design features of a new gas phase electron spectrometry system for the study of free atoms and molecules, with the aid of synchrotron radiation, have been described in the last annual report.¹ In the intervening period, this system has been built and successfully field tested at a synchrotron radiation source. Although the computer controlled data acquisition system is not yet implemented, the use of temporarily available semi-automatic equipment for data handling has allowed us to carry out several studies during the two beam time periods (including the testing period) we have had at the Synchrotron Radiation Center in Wisconsin. These studies include measurements of the photoelectron angular distribution for a number of free molecules, described in the companion report, and several atomic species, described below.

The experimental setup^{2,3} follows the original concept¹ in all essential features: two spherical sector plate electrostatic energy analyzers can be rotated in tandem about the axis of a polarized photon beam and accept photoelectrons within a small cone from an enclosed source cell which can be biased; permanent gases or atomic vapors can be used; and the system is windowless, yet preserves the vacuum integrity of the photon source by means of high gas flow impedances between the main chamber and two successive pumping stages. The sole use of turbomolecular pumps was found to be satisfactory to achieve a base pressure of 4×10^{-8} Pa (3×10^{10} torr) in the last pumping stage adjacent to the monochromator, or about 6×10^{-8} Pa at an operating pressure of typically 2×10^{-2} Pa in the source cell. Under these conditions, our windowless gas phase

system can be used safely and efficiently at any photon source to measure photoionization cross sections, branching ratios, and photoelectron angular distributions in atoms and molecules over a wide range of photon energies, from a few eV to some photon source dependent cutoff in the 100 eV or 1000 eV range. In our initial experiments, a toroidal grating monochromator supplied a narrow photon beam with a resolution between 1 Å and 5 Å in the energy range from 15 eV to 110 eV.

The Xe 5p spin-orbit components. The photoeffect in the outer regions of xenon affords a sensitive probe of both the many-body and relativistic aspects of atomic structure and dynamics. This holds true especially if, in the measurement of partial cross sections and the angular distributions, the spin-orbit components are separated and the energy range covered spans several electronic subshells that are capable of interacting with one another. We measured³ the angular distributions of photoelectrons ejected from the Xe 5p_{3/2} and Xe 5p_{1/2} levels and derived the corresponding asymmetry parameters $\beta_{3/2}$ and $\beta_{1/2}$, and the cross section or branching ratio $\sigma_{3/2}:\sigma_{1/2}$. Both properties, β and σ , are closely related to the wave functions of the bound and continuum electrons and, hence, reflect the many-electron interactions and relativistic effects that are contained in the wave functions. The values of $\beta_{3/2}$ and $\beta_{1/2}$ obtained between $h\nu = 19$ eV and $h\nu = 105$ eV are plotted in Fig. 10.23 and compared with various theoretical predictions. We find that the single-particle, relativistic Dirac Fock (DF) calculation agrees poorly with the experimental data, and the many-electron theories, both the non-relativistic and the relativistic random phase approximations (RPA and RRPA), agree well with the experiment. Evidently, the many-electron interactions, which involve the 5p, 5s, and 4d subshells, are much more important in determining the behavior of β than the relativistic effects. However, if we form the difference $\Delta\beta = \beta_{3/2} - \beta_{1/2}$, the comparison with theory made in Fig. 10.24 indicates, not surprisingly,

Fig. 10.23 The asymmetry parameter β for the Xe 5p doublet. Our data ($\circ$, $\bullet$) are compared with the predictions of the Dirac Fock (DF) model, the random phase approximation (RPA) and the relativistic random phase approximation (RRPA). A detailed discussion is given in Ref. 3.

Fig. 10.24 The difference $\Delta\beta$ of the asymmetry parameter of the Xe 5p spin-orbit components. Our data ($\circ$) are compared with the DF and RRPA theoretical results.

that the relativistic effect is dominant in this quantity which specifically distinguishes the spin-orbit components. The single particle DF calculation predicts the general behavior, while the many-body effects, included in the RRPA calculation, add mainly some fine structure in $\Delta\beta$. The measured branching ratio $\sigma_{3/2}:\sigma_{1/2}$ is in agreement only with the theoretical predictions that include both the many-body and relativistic effects. This is to be expected since σ like β would be strongly

influenced by many-electron interactions, while the splitting of σ into its components $\sigma_{3/2}$ and $\sigma_{1/2}$ is, by its nature, a relativistic effect.

These results on Xe give the first experimental assessment of the roles that the many-body and relativistic effects play in the medium Z range of the periodic table. The results show that the RRPA theory is capable of accurately predicting the electronic properties in a rare gas atom as Xe. The results, we feel confident, may also be transferred to other elements of medium Z whether they are isolated or incorporated in molecular and condensed structures. This possibility of extrapolation is important because theoretical models that are as sophisticated as the RRPA model have not been developed to date for more complex systems.

The 4d multiplet of atomic silver. The high temperature oven included in our new photoelectron spectrometry system offers the opportunity of studying metal vapors and, by that, many open-shell atoms. Open-shell atoms, which account for about 70% of the elements, have rarely been studied due to the difficulties of theoretically treating atoms that lack spherical symmetry and the experimental problems of producing and controlling atomic vapors of suitable density. However, to better understand and predict the electronic properties of aggregate systems made up of this large class of atoms, it is important to know the purely atomic properties which can be seen in the isolated atom.

In the first study of a high temperature metal vapor with the aid of synchrotron radiation, we measured the angular distribution of the 4d photoelectrons of atomic silver between 20 eV and 45 eV.⁴ We obtained the asymmetry parameter β for the 4d subshell and for the individual term components (1D_2 , $^3D_{1,2,3}$) that result from the coupling of a hole in the 4d level with the outermost 5s electron. Thus we were able to delineate any effects that may be associated with the term structure. The photoelectron spectrum of the Ag 4d ($^1,^3D$) quartet recorded at $\phi = 0^\circ$ and $\phi = 90^\circ$ relative to the polarization direction of the photon beam is shown in Fig. 10.25. The nearly equal intensity of the

Fig. 10.25 Photoelectron spectra of the 4d level of atomic silver measured in the perpendicular to the polarization direction of the photon beam provided by a synchrotron radiation source. Spectra were recorded in 13 min at each angle.

Ag 4d quartet observed at the two angles indicates a nearly isotropic distribution of the photoelectrons. By contrast, the Kr $4p_{3/2}$ line, which served as a calibration standard, is much more intense in the $\phi = 0$ direction.

The measured β values for the 4d subshell are compared in Fig. 10.26 with the only available theoretical calculation, which is based on the single Hartree-Slater model. Both theory and experiment display the same energy dependence, but theory underestimates the absolute values by 0.4 to 0.6 units in β . Our analysis of the term structure shows a very small dependence of β on the term structure. This implies that the anisotropic or exchange interactions of the outgoing photoelectron with the ionic core states (1D , 3D) are quite similar. In the future, we will extend the energy range of our measurements and intend to include copper and other metal vapors in our work on open shell atoms. This, we hope, will be a first step in the direction of establishing systematics of the electronic properties of open shell atoms, and of laying an experimental base for the development of a

Fig. 10.26 The asymmetry parameter β of the Ag 4d ($1,3D$) quartet compared with the Hartree-Slater (HS) predictions. A detailed discussion is presented in Ref. 4.

more realistic theory for open shell systems than is presently available.

This work, in which the new ORNL gas phase electron spectrometry system was used for the first time, profited greatly from the support given by E. M. Rowe and his staff of the Synchrotron Radiation Center, University of Wisconsin, in Stoughton, Wisconsin. The collaboration with P. R. Woodruff who participated in the studies of xenon and silver is especially acknowledged.

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10.2.5 Angle-Resolved Photoelectron Spectroscopy of Free Molecules with the Use of Synchrotron Radiation

(T. A. Carlson, M. O. Krause, F. A. Grimm,¹ J. W. Taylor,² D. Mehaffy,² P. R. Keller²)

In the 1960's the field of molecular photoelectron spectroscopy was established.³ In this

area of research a mono-energetic line source (HeI radiation) was used to determine the ionization potential associated for each of the valence shell molecular orbitals. Determination of the ionization potentials by photoelectron spectroscopy has become one of the most important of the experimental bases for understanding the electronic structure of molecules. Photoelectron spectroscopy also contains data regarding photoelectronic cross sections for the different orbitals, information fully as important as the ionization potentials. Full exploitation of the cross section data from photoelectron spectroscopy has not been possible, however, until there became available an intense, continuous source of photons, which could be monochromatized, and whose energies would span from the ionization threshold to considerably above the ionization threshold for the various different orbitals. Such a source is a dedicated facility producing synchrotron radiation.

We have undertaken a comprehensive program for using synchrotron radiation for angle-resolved photoelectron spectroscopy of atoms and molecules. From these data we extract both partial and differential photoelectric cross sections for the individual orbitals as a function of photon energy. Partial cross sections are relative cross sections for the different electron orbitals in a given atom or molecule. The differential cross section is the cross section of a given orbital at a given angle and is measured as a function of angle. For a randomly orientated molecule the differential cross section within the dipole approximation is given in terms of the angular asymmetry parameter, β , as

$$\frac{d\sigma}{d\Omega} = \frac{\sigma_{\text{total}}}{4\pi} [1 + \beta P_2(\cos \theta)]$$

where θ is the angle between the polarization vector and the direction of the ejected photoelectron and P_2 is the second order Legendre polynomial.

In Table 10.7 are listed the studies thus far carried out in our research program. The list is quite extensive, particularly with regard to the study of the angular asymmetry parameter, β , for polyatomic molecules. The success of the program has been helped by the invaluable collaboration of J. W. Taylor and his students at the

Table 10.7 Summary of studies on angle resolved photoelectron spectroscopy of molecules using synchrotron radiation^a

Molecule	ORNL Spectrometer	β Value	Partial σ	Special Features	MSM Calculations	Photon Energies (eV)
N ₂		X		vibrational states	X	18-31
N ₂	X	X	X	satellite structure	X	44-60
CO ₂		X		shape resonance, vibrational states	X	15-70
CS ₂	X	X	X	shape resonances, Cooper minimum	X	13-70
COS	X	X	X	shape resonances	X	13-40
CH ₃ Cl		X				13-31
CH ₂ Cl ₂		X				13-29
CHCl ₃		X				13-29
CCl ₄	X	X	X	Cooper minimum	X	13-80
C ₂ H ₂		X		vibrational states	X	12-27
C ₂ H ₄		X			X	12-27
n butene		X				13-29
cis butene		X				13-29
trans butene		X				13-29
HBr	X	X	X	core shell behavior	X	80-110
Br ₂	X	X	X	core shell behavior	X	80-120
CH ₃ Br	X	X	X	Cooper minimum		20-50
CH ₃ Br	X	X	X	core shell behavior		80-110
furan		X				13-28
benzene		X			X	12-27
perfluorbenzene		X				12-27
SiF ₄		X		core shell behavior		115-150
Si(CH ₃) ₄		X		core shell behavior		110-150
NH ₃		X		vibrational states		15-25

^aResearch carried out by ORNL members and their collaborators at the Synchrotron Radiation Center (Tantalus I), Stoughton, Wisconsin.

University of Wisconsin and by F. A. Grimm at the University of Tennessee. Initial experiments were carried out on a spectrometer built at the University of Wisconsin. More recent experiments were carried out on a new electron spectrometer, designed and built at Oak Ridge, which is briefly described in the companion report on atoms. In these experiments measurements were made of the partial cross sections as well as the angular asymmetry parameter. Plans are underway for future collaboration on a beam line, particularly designed for gas phase studies over a wide range

of energies, to be installed at the new Synchrotron Radiation Storage Ring (Aladdin) at Stoughton, Wisconsin.

The topics of research presently being pursued concern themselves with (1) the survey of partial cross sections and β values for the various molecular orbitals and the evaluation of theoretical methods for predicting these cross sections, in particular the multiple scattering method; (2) the study of shape resonances and their effect on β and vibrational structure; (3) the behavior of the Cooper minimum in molecular

orbitals; (4) systematic behavior of organic compounds, particularly with respect to π orbitals for unsaturated molecules; (5) the nature of many-body excitations including electron shakeup and configuration interaction; (6) effects on the partial cross sections and β values just above the threshold of core shell ionization.

This report will limit itself to that work which has been principally carried out by Oak Ridge staff members, i.e., the studies on nitrogen, the triatomic molecules, the study of the Cooper minimum in CCl_4 and the investigation of core shell effects on Br compounds. Most of this work was carried out on the ORNL electron spectrometer which has recently become operational.

Evaluation of the MSM for Calculating Molecular Photoelectron Cross Sections. One of the overall aims of our research program is to test theory with regard to its efficacy for predicting photoelectric cross sections. This in turn tests the concepts of molecular orbital theory and the basic nature of the dynamics of photoionization in a molecule. The present interest has been concentrated on the multiple scattering method (MSM) with its use of a muffin tin potential. Although highly approximate this method can be used in a wide variety of molecules, both simple and complex, and can be used to calculate the angular asymmetry parameter, β , as well as partial cross sections.

Since earlier work in the literature has concentrated on diatomic molecules, we have taken the next step to triatomic molecules. Experimental studies using synchrotron radiation have been carried out on CO_2 ,^{4,5} CS_2 ,⁶ and COS ,⁶ and comparisons are made with earlier calculations.⁷ Still more recent unpublished results have illustrated the importance of carrying out such studies to higher photon energies (to at least 50 eV above threshold and in some instances higher). In summary, comparisons between experiment and theory show that the MSM does well for CO_2 and for the least tightly bound orbitals of CS_2 and COS . Difficulties are observed, however, for the deeper orbitals of CS_2 and COS . Part of the explanation may lie in theoretical difficul-

ties in handling the relaxation of deeper orbitals and in coping with a permanent dipole such as COS possesses.

Turning to more complex organic molecules, good agreement was obtained between the experimentally determined β 's and those calculated by the MSM for the valence orbitals of both ethylene⁸ and acetylene and to a more limited extent also those of benzene.

The multiple scattering method has now proven itself in a number of cases, and it will be one of our tasks to ascertain what regions of study will require further improvement.

In Fig. 10.27 we present a typical investigation of one of the orbitals of CS_2 . The calculations give a reasonable overall agreement with experiment. The positions of the maximum and minimum are sensitive functions of the molecular potentials as well as the details of the nature of the calculations. The effects of shape resonance and the Cooper minimum, which will be subsequently discussed, are also indicated.

Fig. 10.27 Angular asymmetry parameter, β , as a function of photon energy for the first band in the photoelectron spectrum of CS_2 corresponding to the $X^2\Pi_g$ state of the ion following photoejection of an electron from the $2\pi_g$ orbital. Solid circles ● taken with TGM monochromator, open circles ○ taken with 1 meter Seya monochromator. Solid line is from theoretical calculations using MSM (ref. 5). Presence of effect of shape resonance and Cooper minimum found in calculations indicated by arrows.

Shape Resonances. Shape resonances are important in the photoelectron spectroscopy of molecules. They manifest themselves experimentally as broad maxima in the partial cross section curves of individual molecular orbitals. They arise as the result of absorption into states that couple directly with the continuum. In addition to the partial cross sections, shape resonances strongly influence the behavior of the angular asymmetry parameter, β , which in some instances may be more pronounced than the effect on the partial cross sections.

One of the best experimental documentation of a shape resonance was seen in the fourth band of CO_2 .^{2,3} The observed dip in β as a function of photon energy was clearly evident and afforded theory not only a qualitative but quantitative evaluation. Calculations using the multiple scattering method⁷ did predict a minimum in the region found by experiment, but it was too sharp. Swanson et al.,⁹ by including changes in β due to changes in the internuclear distances, demonstrated in their calculations a broadening of the shape of the minimum, in better agreement with experiment.

Strong variations in the β values of the different vibrational bands for the $X\Sigma_g^+$ states in N_2 were investigated as a function of photon energies.¹⁰ The results were shown to be in agreement with calculations¹¹ which affirmed the dependence was due to a shape resonance. Somewhat remarkable is that this effect is felt at a considerable distance in energy from the actual value where the resonance itself takes place.

Cooper Minimum. The Cooper minimum has been well studied in atomic physics.¹² A minimum in the photoelectron cross section occurs as the result of a change in sign in the matrix element describing a transition to one of the permissible continuum channels. Though of a more complex nature, similar phenomena may also be expected to occur in molecules, particularly for lone pair orbitals of elements heavier than the second row in the periodic table.

We have examined the angle-resolved photoelectron spectra of the valence orbitals of CCl_4 and CS_2 from ionization threshold to photon energies

of 80 eV. We find strong evidence for a Cooper minimum in the first band of CS_2 and for the first three bands of CCl_4 . To our knowledge, these are the first studies of such an effect in molecules. Even more striking experimental evidence of the Cooper minimum than the partial cross section is the rapid drop in the angular asymmetry parameter, β , as a function of photon energy. (The positions of the minimum for the cross section and β value are not identical but are usually close.) Comparison between lone pair molecular orbitals of sulfur and chlorine with atomic argon show strong qualitative similarities (cf. Figs. 10.27, 10.28). Examination in greater detail of the data on the Cooper minima for β derived from the three lone pair orbitals of CCl_4 (t_1 , t_2 , and e) show, however, distinctive differences (Fig. 10.28). The minima occur at slightly different photoelectron energies (from 31 to 36 eV) and the shape of the β curves vary. Most interesting is the fact that the fourth band in the photoelectron spectrum of CCl_4 , which has been previously determined to be primarily due to the carbon-chlorine bond, also exhibits a slight but broad depression in the β value near the Cooper minimum.

Fig. 10.28 Angular asymmetry parameter, β , as a function of photoelectron energy for the first four bands in the photoelectron spectrum of CCl_4 . Designation is given to the orbital corresponding to the observed band. For comparison, data on Ar 3p are also plotted [R. G. Houlgate et al., *J. Electron Spectrosc.* 9, 205 (1976)].

These and other features are being examined theoretically by use of the multiple scattering method. It is anticipated that the Cooper minimum will provide an especially sensitive and selective tool for the experimental investigation of molecular orbitals.

Threshold Effects for Core Shells. Calculations have demonstrated that both photoelectric cross sections and angular distributions are strongly affected by the molecular potential when photoionization occurs just above the threshold for K shell ionization. In particular Grimm¹³ has shown using multiple scattering theory that, up to 2 Rydbergs above the Cls and Ols binding energies, the β value for several small molecules was substantially different. It is anticipated when the Aladdin Storage Ring is put into operation that studies will be carried out on the K shells for a variety of gaseous molecules containing boron, carbon, nitrogen, and oxygen.

It seemed reasonable to assume that threshold effects would also occur with other core shells and we chose for study the 3d shell of bromine and the 2p shell of silicon. In Fig. 10.29 are plotted the angular asymmetry parameters, β , for

Fig. 10.29 Angular asymmetry parameter, β , as a function of photoelectron energy as the result of photoionization in the 3d shell of bromine. Dependence of β on chemical environment is demonstrated by comparing results on three different molecules: HBr, Br₂, and CH₃Br. For comparison, data on Kr are also shown. Theoretical results are from D. J. Kennedy and S. T. Manson, Phys. Rev. A 5, 227 (1972).

photoionization in the 3d orbital of HBr, Br₂, and CH₃Br, and for comparison the 3d subshell of Kr. The results of the three molecules plotted against photoelectron energy coalesce at higher energies, but between 5 and 15 eV above threshold there is a distinct difference in β between the three species. (A similar result was also reached for different silicon compounds.) Atomic krypton gives results that are qualitatively similar to those of the bromine compounds, and not surprisingly resembles most closely the data of HBr, which is isoelectronic with Kr. Results were also taken on the cross sections as a function of photoelectron energy but the shapes of all these bromine compounds and Kr were the same within experimental error. In this case β values seemed to be more sensitive to the nature of the molecule.

The molecular threshold effects seen for the 3d orbital are not as dramatic as predicted for 1s orbitals, but they are measurable. It may not always be practical to examine the K shell of a given element. Multiple scattering calculations are underway to evaluate the chemical effects in the 3d shell of bromine, and it is felt that valuable chemical information can be gained from the study of cross sections and β values just above the core shells of most elements.

Electron Shakeup and Configuration Interaction.

As the result of photoionization, a final state arises that generally has the same configuration of the initial state except that a single orbital electron has been removed. It may also occur that a number of other final electronic states arise, some of which are ascribed to electron shakeup or in the more general case to configuration interaction. These states are seen in the photoelectron spectrum as additional bands shifted from the main peak by the energy of excitation. This process is particularly prevalent for the deeper valence shells. Krummacher et al.¹⁴ have recently studied the cross sectional behavior of structure in N₂ in the ionization potential region from 25 to 40 eV. We have extended their study by examining the β values for the principal peaks in this region as a

function of photon energy from 45 to 60 eV. An attempt is being made to calculate the angular distribution for an excited state which is believed to correspond to the major satellite peak that occurs in the photoelectron spectrum at 29 eV.

Another interesting case of excitation occurs in the spectrum of CS_2 . The fifth band has been traditionally ascribed to photoionization of the $4\sigma_u$ orbital. Recent calculations, however, have suggested that it is in fact a strong satellite peak¹⁵ arising from photoionization in the $2\pi_u$ orbital. In Fig. 10.30 we have plotted the experimental partial cross section for the fifth

Fig. 10.30 Partial cross section of the fifth band in the photoelectron spectrum of CS_2 as a function of photon energy. Dashed line is from theoretical calculations on photoionization of the $4\sigma_u$ orbital (ref. 5). The solid line is derived by multiplying the experimental cross sections for the second band $(\pi_u)^{-1}$ by a partition ratio of 0.23 obtained from configuration interaction calculations (ref. 15).

band in the photoelectron spectrum of CS_2 as a function of photon energy. The calculated cross sections for the $4\sigma_u$ orbital are in poor agreement with experiment. If we, however, assume that excitation accompanies photoionization of the $2\pi_u$ orbital ($2\pi_g \rightarrow 3\pi_u$), and further assume that the partitioning of the cross sections between the ground and excited states is constant with photon energy, then a good fit can be made to the experimental data.

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10.3 Reactive Intermediates by Electron Spin Resonance

10.3.1 Equilibrium Dissociation of Bibenzyl

(H. Zeldes, R. Livingston)

Electron spin resonance (ESR) is being used to study free radicals present during the pyrolysis of fluids which are of interest in coal and combustion chemistry. An ESR spectrometer developed^{1,2} for this purpose includes a heated silica capillary in which pyrolysis takes place on a flowing fluid. The heated capillary traverses the microwave cavity of the spectrometer and may be used at temperatures up to 700°C and pressures to 21 MPa (200 atm).

In earlier work^{3,4} we reported the presence of 1,2-diphenylethyl in concentrated solutions

of bibenzyl in benzene and the presence of benzyl in dilute solutions of bibenzyl in toluene. This was a consequence of the equilibrium

for which K_C was found¹ to be 10 ± 3 at 560°C . More recently we determined that the fractional amount of irreversible decomposition of bibenzyl is greatly inhibited by toluene and that it becomes exceedingly small in very dilute solutions of bibenzyl in toluene. This encouraged us to measure the equilibrium constant for the dissociation of bibenzyl in toluene solution,

using ESR to assay the concentration of benzyl.

The ESR assay involved a comparison of A_∞ for benzyl with A_∞ for a stable reference radical of known concentration where A_∞ is the second integral of the signal from the radical after subtracting baseline (first derivative of the absorption) for essentially infinite field limits. We had much difficulty in determining A_∞ by integration. The signal was weak, and there were lines close to the lines most suitable for assay measurements. For this reason we deduced A_∞ from parameters of a matching simulation of a small relatively strong part of the spectrum. The program to simulate includes correction for the distortion of lineshape caused by high modulation of the spectrometer with a uniform modulation amplitude over the entire sample. In fact the modulation is not uniform, and we needed to determine the maximum ratio of modulation amplitude to linewidth we could safely use and to determine, for use in simulations, the modulation amplitude most representative of the sample as a whole. These determinations were made from studies of the reference stable free radical 4-hydroxy-2,2,6,6-tetramethylpiperperidine-1-oxyl (Tempol) whose ESR couplings are known and which is available in pure crystalline form. A_∞ for Tempol was evaluated for a range of modulations and microwave powers and for air-saturated and He-scrubbed solutions (with linewidths of 2.15 and

0.31 G respectively) using both the integration and the simulation method, and consistent results were obtained.

Measurements on bibenzyl solutions were made at 590°C and 620°C at 20.7 MPa (3000 psi) and 13.8 MPa (2000 psi). Lower temperatures were excluded, as the radical concentrations became too low for reliable assay. With higher temperatures the rate of irreversible decomposition of bibenzyl became too high for the highest concentrations of bibenzyl. The concentration of bibenzyl was varied by a factor of four with mole fractions ranging from 0.0029 to 0.0116. Values of $[\text{benzyl}]^2/[\text{bibenzyl}]$ deduced from the measurements were constant, within expected experimental error. Lower concentrations of bibenzyl were not used partly because the signals became weaker and partly because there was also a benzyl radical signal when only the toluene solvent was pyrolyzed. The latter was shown not to be excessive at the concentrations used. The contact time was varied by varying the flow rate to gain evidence that the contact times (in the order of 1 second) were not excessive. Decomposition products accumulate during the contact time, and these may react irreversibly with the benzyl radical.

The experimental accuracy was not sufficient to justify reporting the equilibrium constant K_C (on a molar basis) for reaction (2) at the two rather closely spaced temperatures which were used. For this reason the constants at the two temperatures were separately corrected to the intermediate temperature of 605°C and then averaged to give the final value. In making this correction the Arrhenius activation energy for reaction (2) in the reverse direction was taken to be zero, and that in the forward direction was taken to be 62.4 kcal/mole which is an average of selected literature values. These values of K_C at the two pressures are shown in Table 10.8. The closeness of the two values is partly fortuitous as each value of K_C is estimated to be correct only to within a factor of 1.7. The values of the equilibrium constant K_p in pressure units (Table 10.8) were computed from $K_p = K_C ZRT$ where Z is the compressibility factor of toluene, R is the gas con-

Table 10.8. K_c and K_p and estimated values^a of γ_1 , γ_2 , and K for the equilibrium dissociation of bibenzyl in toluene at 605°C

P (MPa)	$10^{10} \times K_c$ (mol/liter)	$10^{10} \times K_p$ (atm)	γ_1	γ_2	$10^{10} \times K$ (atm)
20.7	0.75	45	0.73	0.33	73
13.8	0.75	42	0.78	0.35	73

^a γ_1 and γ_2 are activity coefficients of toluene (in place of $C_6H_5\dot{C}H_2$) and of bibenzyl respectively. K is the thermodynamic equilibrium constant = $(\gamma_1^2/\gamma_2)K_p$.

stant, and T is the absolute temperature. To calculate the thermodynamic equilibrium constant $K = f_1^2/f_2$ where f_1 and f_2 are fugacities of benzyl and bibenzyl, use was made of the "partial fugacity rule" which states that the fugacity of a gas in a mixture is equal to its mole fraction x_i times the fugacity f_i^0 of the pure gas at the temperature and pressure of the mixture.⁵ Accordingly $f_i = x_i f_i^0 = (x_i P)(f_i^0/P) = P_i \gamma_i$ where γ_i is the activity coefficient and P_i is the partial pressure of component i , and $K = (\gamma_1^2/\gamma_2)K_p$. The activity coefficients may be estimated from the critical temperature and pressure and from the law of corresponding states.⁵ Since the critical constants for the benzyl radical are not known we assumed that they would be close to those of toluene. Table 10.8 shows the estimated values of γ_i and the calculated values for K at the two pressures. These two values of K should be exactly the same. Their very close agreement is largely coincidental in view of the large error.

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10.3.2 Hydrogenolysis of Bibenzyl in Toluene and Benzene Solutions

(R. Livingston, H. Zeldes, and L. W. Vernon¹)

In the last annual report² mention was made of the pyrolysis of bibenzyl in solution at a high pressure where ESR spectra were obtained from the steady-state concentration of free radicals present during pyrolysis. The primary initiating reactions are generally regarded^{3,4} to be:

In earlier work² it was shown that pyrolysis in toluene solution gives an ESR spectrum with benzyl radical predominating whereas in benzene solution the 1,2-diphenylethyl radical predominates. The equilibrium constant for (2) was measured and found to be 10 ± 3 at 560°C and 10.3 MPa (1500 psi)

Vernon⁵ has studied the hydrogenolysis of bibenzyl. Upon hydrogen uptake the yields of benzene and ethylbenzene are greatly enhanced, and a free radical mechanism was proposed in which molecular hydrogen is consumed by its reaction with benzyl radical. This suggested the present ESR experiments in which the steady-state concentration of radicals, especially benzyl radical, is monitored with and without the addition of molecular hydrogen to the system and the results correlated with the yields of final chemical products. This would give greater insight into the validity of the proposed mechanism. Our ESR equipment has been modified to permit a continuous and accurately metered flow of hydrogen to be injected into the flowing liquid sample just prior to heating to pyrolytic temperatures. Various concentrations of bibenzyl in toluene and in benzene have been pyrolyzed with and without added hydrogen, the steady-state ESR spectra have been observed, and GC analyses have been made of the final chemical products.

An important aspect of the work has been to show a direct *experimental* link between the radicals observed by ESR and the final chemical products. In a typical experiment, 2% solutions of bibenzyl in toluene and in benzene were pyrolyzed at 553°C without added hydrogen. A spectrum of benzyl radical was observed in toluene solution. The calculated ratio of radicals from equilibrium (2) and this concentration of bibenzyl in toluene shows that 90% are present as benzyl radical consistent with the experimental observation. With the observed spectral intensity the 10% content of 1,2-diphenylethyl radical was not quite large enough to be observable. In benzene solution the reverse reaction in (2) is suppressed since essentially no toluene is present, and the distribution of radicals is rate controlled. Experimentally, 1,2-diphenylethyl radical predominates, and although the spectra are weak a fair approximation is one-third benzyl radical and two-thirds 1,2-diphenylethyl radical. Currently accepted views^{3,4} on the pyrolysis of bibenzyl show that all chemical products require 1,2-diphenylethyl radical as an intermediate, and many of the products also require benzyl radical. 1,1-Diphenylethane and 1,2,3,4-tetraphenylbutane are formed from the 1,2-diphenylethyl radical. GC analyses in the above experiments show both of these products to be present in benzene solution where a substantial amount of 1,2-diphenylethyl radical was observed. Neither product was found in toluene solution where the amount of this radical was found to be greatly suppressed. 1,2,3-Triphenylpropane is a coupling product of 1,2-diphenylethyl and benzyl radicals. This product was found in both solutions, but the amount in toluene solution was only one-third that in benzene solution consistent with the relatively small amount of 1,2-diphenylethyl radical present in toluene solution. Similarly, all of the other products normally found in the pyrolysis of bibenzyl were observed, and in every case the amount present in toluene solution was greatly suppressed. This is one of the very few examples of directly observing labile radical intermediates and experimentally demon-

strating their relation to final chemical products in a pyrolytic process.

Upon injecting molecular hydrogen prior to pyrolysis the yields of benzene and ethylbenzene are greatly enhanced as reported by Vernon.⁵ The yields of other products are not significantly changed. Results for benzene yields in toluene solution are shown in Fig. 10.31. The mole percent bibenzyl is indicated in the figure, and the lowest curve is for pure toluene. The steady-state concentrations of benzyl radical observed by ESR are also listed on a relative scale of zero to ten. A listing of zero for pure toluene does not mean that benzyl radical is absent; it means that the steady-state concentration is below the detectability limit of the equipment. We have seen benzyl radical during the pyrolysis of pure toluene at a higher temperature. The hydrogenolysis of toluene is consistent with Benson and

Fig. 10.31 Effect of hydrogen on the benzene yield from bibenzyl in toluene solution, 9.0 MPa (1300 psi).

Shaw's⁶ theory. Adding bibenzyl to toluene (Fig. 10.31) gives a greatly enhanced rate of hydrogenolysis to form benzene and is consistent with Vernon's⁵ theory. Both theories depend on the reaction of molecular hydrogen with benzyl radical. The enhanced effect with bibenzyl is attributed to the greater degree of dissociation of bibenzyl to form benzyl radical as compared to toluene. The relative concentrations of benzyl radical as determined by ESR (Fig. 10.31) are consistent with this view. The yields of ethylbenzene upon hydrogenolysis in toluene and in benzene solution have also been determined, and the results lend support to the free radical

mechanisms of Benson and Shaw⁶ and of Vernon.⁵ Further details have been prepared for publication elsewhere.

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11. THEORETICAL CHEMISTRY

11.1 Atomic and Molecular Interactions with Solids11.1.1 Enhanced Raman Scattering from Adsorbed Molecules

(O. H. Crawford)

Anomalously intense Raman scattering was observed by Fleischmann and co-workers a few years ago in the course of their efforts to measure the Raman spectrum of pyridine adsorbed on a silver electrode in an electrochemical cell. Since then it has been discovered that numerous species have their Raman scattering cross sections enhanced by factors of up to a million when adsorbed on rough silver, copper, or gold. This new phenomenon, surface-enhanced Raman scattering (SERS), has attracted great interest because of the novelty of the effect and its implications for interfacial science and technology. These range from new information on molecule-surface interactions to the prospects of a method for the *in situ* detection of species adsorbed on catalysts at process temperatures and pressures. Numerous theories have been proposed for SERS, but the origin of the effect is still controversial.

We have developed a theory for enhanced Raman scattering from adsorbates on metal particles, with application to sols and supported metal catalysts. The Raman intensity is derived from quantum mechanical perturbation theory, using a model that takes account of the plasma resonances in the metal particle. The influence of metal species, the particle size, the dielectric properties of the medium, and the nature of the adsorbate are addressed. The theory cannot yet be properly tested, for lack of appropriate experimental data; but, in its simplest form, it is consistent with measured SERS from roughened metal surfaces. If verified, this theory will allow predictions to be made concerning the possibility of obtaining SERS from substrates other than silver, copper, and gold. It will also help determine whether and how *in situ* spectroscopy of adsorbates on supported metal catalysts might be accomplished.

11.1.2 Energy Loss of Fast Ions in Crystalline Solids

(O. H. Crawford)

The rate of energy loss of fast ions (i.e., the stopping power) is an important factor in radiation damage. Knowledge of its values is necessary for modern solid-state technologies such as ion-beam modification of materials, also. Moreover, it is interesting in the context of basic physics. Most applications of stopping power involve crystalline materials. These are not properly handled by existing theory, which, for the most part, was derived for structureless media.

This year, we have developed theories for the two aspects of crystalline stopping power, i.e., (1) for ions in channels between crystal planes or axes, and (2) for ions not in channels. These cases will be discussed separately, in turn.

A simple scheme was invented for predicting channel stopping power, starting from experimental values of the optical constants and computed electron densities, data that are available for most systems of interest. Calculated and measured¹ values are compared in Fig. 11.1, as a function of distance from channel midplane, of stopping power in the {001} channel of gold. Agreement is good (just outside experimental error). Because of certain high-velocity approximations that enter, this theory is expected to be best when the ion's velocity is large compared to that of the electrons near its path. Therefore, the theory should do best near the channel center, and this is what is found. The theory of Esbensen and Golovchenko² (EG) is seen in Fig. 11.1 to be much less accurate. Further support for the theory comes from Fig. 11.2, which shows stopping power^{1,3} along the channel midplane, as a function of velocity.

The Bethe-Bloch formula for the stopping power is generally considered to be (asymptotically) exact for stopping powers of real materials toward fast ions, even though its derivation restricts it to structureless media, e.g., electron gases. We derived the exact asymptotic

Fig. 11.1 Stopping power for channeled ions, divided by the square of the ion charge, as a function of the distance from the channel midplane.

Fig. 11.2 Stopping power in a channel midplane, divided by the square of the ion charge, as a function of the energy per unit mass of the ions.

high-velocity stopping power formula for crystals this year, and found notable structure effects, which are missing in the Bethe-Bloch formula. In particular, the stopping power

(for nonchanneled ions) is predicted to vary with direction of motion, in optically anisotropic media, such as, for example, graphite.

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11.2 Statistical Mechanics

(Elijah Johnson)

One of the main goals of statistical mechanics is the development of methods for obtaining accurate thermodynamic and structural information from a knowledge of the forces between particles of the system of interest. In last year's Annual Progress Report a recent theoretical method for determining structural and thermodynamic information was discussed.¹ The equations on which this method is based are apparently exact. This distinguishes it from all other practical theoretical methods previously proposed. It means that if appropriate numerical methods for solving the equations involved are developed, then results of arbitrary accuracy will be obtainable, and thus that even systems with strong attractive forces such as ionic systems would be treatable theoretically.

Three sets of results obtained by using this method are discussed below. These results may be used to partially assess the method. More results must be obtained before it can be fully assessed. The results of such an assessment will probably be either that the mathematical methods, graph theory and topological reduction, used to obtain the basic equation used here has rather interesting shortcomings when applied to statistical mechanics or that the basic equation is indeed exact.

All of the systems discussed here obey classical mechanics and they have a pairwise additive potential energy function. The basic quantities

of interest are the two and three particle distribution functions. The quantity $\rho^2 g^{(2)}(r_1, r_2)$ is the probability density for finding one particle at position r_1 and a second particle at position r_2 . Here ρ is the particle number density and $g^{(2)}(r_1, r_2)$ is the pair distribution function. The particle number density is the average number of particles in the system divided by the volume. Likewise $\rho^3 g^{(3)}(r_1, r_2, r_3)$ is the probability density for finding three different particles at the positions r_1 , r_2 , and r_3 . Here $g^{(3)}$ is the three-particle distribution function.

It has been known since 1963 that $g^{(3)}(r_1, r_2, r_3)$ is equal to $g^{(2)}(r_1, r_2)g^{(2)}(r_1, r_3)g^{(2)}(r_2, r_3) \times [1 + E(r_1, r_2, r_3)]$ where E is a known functional² of $g^{(2)}$. This means that for classical, pairwise additive potential energy function systems that the three-particle distribution function is completely determined by the pair distribution function. In 1980 a variational procedure for finding E was presented.¹ Before this variational method was proposed, no accurate method for finding E was available.

To find the two unknowns $g^{(2)}$ and $g^{(3)}$ from the forces between particles a second equation must be used in conjunction with the equation provided by the variational principle. There are a number of equations available which relate $g^{(2)}$ to $g^{(3)}$. The equation most suited for use with lattice gases is an equation derived by Raveché and Mountain.³ The BG or BGY equation⁴ is well suited to be used with the variational equation when atomic fluids are treated. Once $g^{(2)}$ is known, thermodynamic properties may be obtained rather easily.

Lattice Gases. Lattice gases differ from regular fluids in that particles of lattice gases are confined to sites on a lattice. One, two, and three dimensional lattice gases are of interest. Lattice gases are useful for treating critical phenomena,⁵ and they are being used in particle⁶ and surface physics.⁷ They have a number of other uses as well. Some results for one- and two-dimensional lattice gases will be presented here. The distances between all neighboring sites of the one-dimensional lattice gas

treated are equal, and the two-dimensional lattice discussed here is a square lattice.

One-dimensional lattice gases. Since the thermodynamic and structural properties of one-dimensional lattice gases with finite range interactions may be obtained analytically using the transfer matrix method,⁷ the accuracy of results obtained by using the variational equation in conjunction with the equation of Raveché and Mountain may be assessed by comparison with the results of the transfer matrix method.

The thermodynamic variables of interest here are ρ and the absolute temperature T . The nearest-neighbor interaction lattice gas is specified once the nearest-neighbor interaction u is known. The exact pair distribution function⁸ $g^{(2)}(0, r)$ and the variational pair distribution function $g_v^{(2)}(0, r)$ expressed as $(r; g^{(2)}, g_v^{(2)})$ for $\rho = 0.5$ and $\beta u = -1$ follows: (0;0,0), (1;1.245,1.257), (2;1.060,1.072), (3;1.015,1.022). Here $\rho = 0.5$ means that half of the lattice sites are occupied and $\beta = 1/k_B T$ where k_B is the Boltzmann constant. The results of the variational method are within about one percent of the exact results. It has been shown that the variational method yields exact results for $E(r_1, r_2, r_3)$ at least for one-dimensional lattice gases,⁹ so the one percent differences between the exact and variational $g^{(2)}$ are due to the numerical method involved. To obtain $g_v^{(2)}$ it was necessary to perform a trapezoidal rule integration over the density in order to solve the equation presented by Raveché and Mountain³ and it was also necessary to assume that $g_v^{(2)}(r) = 1$ for $r > r'$ where r' is a suitable value of r . For the results presented above, the trapezoidal rule integration grid size is $\Delta\rho = 0.025$ and r' is equal to 4. The difference between $g_v^{(2)}$ and $g^{(2)}$ may be made smaller by making $\Delta\rho$ smaller and r' larger.

Two-dimensional lattice gases. Unlike the one-dimensional lattice gases, no exact results are available for the general two-dimensional lattice gas. L. Onsager solved the two-dimensional nearest-neighbor interaction lattice gas problem¹⁰ when $\rho = 0.5$. Exact thermodynamic results are available for this special two-

dimensional lattice gas at those thermodynamic states for which $\rho = 0.5$. Exact structural properties for this special case have not yet been presented. The transfer matrix method which yields exact results for finite range interaction, one-dimensional lattice gases cannot be used to solve two-dimensional lattice gas problems. Part of the power of the variational method coupled with an integral equation such as the equation provided by Raveché and Mountain is that it is no more difficult to apply it to two- or three-dimensional lattice gases than it is to apply to one-dimensional lattice gases.

The variational pair distribution function $g_v^{(2)}(0,0,x,y)$ for the two-dimensional nearest-neighbor interaction lattice gas expressed as $(x,y;g_v^{(2)})$ for $\rho = 0.5$ and $\beta u = -\frac{1}{2}$ follows: $(0,0;0)$, $(1,0;1.12)$, $(1,1;1.03)$, $(2,0;1.02)$, $(2,1;1.01)$, $(2,2;1.00)$. No results are currently available to compare with this $g_v^{(2)}$ to assess its accuracy, but it is very likely that it is as accurate as $g_v^{(2)}$ is for one-dimensional lattice gases.

Atomic Fluids. Lattice gas systems are being studied because they are scientifically important, because they are particularly well suited to treatment by the variational method being discussed here, and because they are useful to the assessment of this method. But the ultimate goal of the development of the variational method is the treatment of atomic and molecular systems of practical importance. One step in the direction of this goal is the treatment of the hard sphere fluid which is discussed next.

In the variational equation an integration over the positions of five particles must be performed. The integrand of the integrals involved are products of $g^{(2)}$. These integrals may be obtained accurately by expanding $g^{(2)}$ in a linear combination of Gaussian functions:

$$g^{(2)}(r) = 1 - \left(1 + \sum_{i=2}^n a_i\right) \exp(-\alpha_1 r^2) + \sum_{i=2}^n a_i \exp(-\alpha_i r^2).$$

The Gaussian parameters α_i and the expansion coefficients a_i may be obtained by least squares

fits. The Monte Carlo¹¹ $g^{(2)}$, the variational $g^{(2)}$ for a least squares fit with $n = 1$, and the superposition approximation $g^{(2)}$ at $\rho d^3 = 0.298\sqrt{2}$ are presented in Table 11.1.

Table 11.1 The Monte Carlo, BGY, and BGY with the superposition approximation hard sphere pair distribution functions $g^{(2)}(r)$ for $\rho d^3 = 0.298\sqrt{2}$

r/d	Monte Carlo	BGY, $E \neq 0$	BGY, $E = 0$
1.0	1.906	1.794	1.755
1.2	1.390	1.392	1.371
1.4	1.107	1.141	1.132
1.6	0.967	0.991	0.990
1.8	0.920	0.937	0.938
2.0	0.978	0.965	0.966

Here d is the hard sphere diameter. The superposition approximation $g^{(2)}$ is the pair distribution function obtained by assuming that $E(\kappa_1, \kappa_2, \kappa_3) = 0$ and solving the BGY equation. The variational $g^{(2)}$ is obtained by using the variational equation to find $E(\kappa_1, \kappa_2, \kappa_3)$ and using this E in the BGY equation. The Monte Carlo $g^{(2)}$ is very close to the exact $g^{(2)}$.

As can be seen from the table, the variational $g^{(2)}$ obtained by using the Gaussian function fit to $g^{(2)}$ in the variational equation step is more accurate than the superposition approximation $g^{(2)}$, but in order to obtain a variational $g^{(2)}$ as accurate as the Monte Carlo $g^{(2)}$ it will be necessary to use more than one Gaussian function to fit $g^{(2)}$ in the variational step of the calculation.

The calculations described here were performed in order to assess an apparently exact variational method for obtaining thermodynamic and structural information on classical systems. More calculations must be performed in order to fully assess the method, but the present results support the view that the method can be used to obtain results which are more accurate than that obtainable from other integral equation methods.

The difficulty that stands in the way of the immediate widespread application of the variational method is the long computational time

involved in using it. For example, the results presented for the two-dimensional lattice gas required about 20 minutes on the IBM 3033 computer. One way to partially overcome this computation time problem is to develop more efficient computer programs. This is being pursued.

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11.3 Theoretical Chemical Kinetics of Bimolecular and Unimolecular Processes

11.3.1 Theoretical Investigation of Vibrational Energy Transfer in Polyatomic Molecules

(D. W. Noid, M. L. Koszykowski,¹ M. S. Child²)

Nonlinear dynamics has been the subject of intense study in recent years.³ In this article, we present a summary of our recent work in this field, in which nonlinear dynamics is applied as related to two aspects of this problem. The two are (1) correlation functions in the quasiperiodic and stochastic regime, and (2) a detailed examination of local and normal modes in H₂O.

The mode energy correlation function (i.e., $\langle E_n E_n(t) \rangle$ where E_n is the energy in the n th normal mode) is important not to molecular spectra, but to reaction rate theory. Some chemically interesting experiments involve the excitation of a given bond or mode, for example in infrared multiphoton absorption, with subsequent decay of the excitation energy into other modes.

We have numerically evaluated several different correlation functions using microcanonical averages.⁴ As expected, the correlation function in the quasi-periodic regime is oscillatory and is shown in Fig. 11.3.

Fig. 11.3 Correlation function for quasiperiodic motion.

In the chaotic regime, it has been previously postulated that the correlation function will behave exponentially. The correlation function in the chaotic regime has, in addition to the usual property present in all regimes given by

$$c(0) = \langle a \cdot a(0) \rangle = \langle a^2 \rangle,$$

also the property that

$$c(\infty) = \langle a \cdot a \rangle = \langle a \rangle \langle a(\infty) \rangle = \langle a \rangle^2.$$

In general, $\langle a^2 \rangle \pm \langle a \rangle^2$ and $c(t)$ will decay to some value. From the present system, we expect $\frac{c(\infty)}{c(0)} \sim 3/4$ in the chaotic regime, which is consistent with the results shown in Fig. 11.4. We

Fig. 11.4 Correlation function for chaotic motion.

have modeled the memory functions of Figs. 11.3 and 11.4, with the result in the chaotic regime being

$$c(t) = a + (b \cos \omega_1 t + c) e^{-dt} + f \cos \omega_2 t,$$

and in the quasiperiodic regime

$$c(t) = a' + b' \cos \omega_1 t + f' \cos \omega_2 t,$$

with a corresponding result in the memory function. The correlation functions of molecular systems are currently under investigation.

Local and Normal Modes in H_2O . Recently there has been much experimental interest in the higher overtone spectra of X-H stretching vibrations. Also, for the spectrum of water, it has been observed that the approximation of using a separable potential is adequate for most purposes. A recent paper by Lawton and Child⁵ examined the classical mechanics for a nonbending model of water using the Sorbie-Morrell potential⁶ and found that there existed two

qualitatively different types of trajectories. The quasiperiodic trajectories were labeled as either being normal mode or the local mode trajectories. Using the Poincare surface of section, they were able to quantize various states and later to determine the relative amount of phase space for each type of state.

However, this method is difficult to extend to more degrees of freedom.

The water molecule was chosen for this study so that a comparison can be made with the work of Lawton and Child. The potential of Sorbie and Morrell⁶ has trajectories of the type shown in Figs. 11.5 and 11.6. In Fig. 11.5, a typical normal mode trajectory is shown and the two types of local mode trajectories are shown in Figs. 11.6a and 11.6b. For each of these trajectories, we can examine the behavior of the dynamical quantity $A(t)$ defined as

$$A(t) \equiv Q_1(t) A_2(t)$$

Fig. 11.5 A normal mode trajectory which is approximately the (0,0) eigentrajectory.

Fig. 11.6 (a) A local mode trajectory which is a (2,0) eigentrajectory.
 (b) Symmetry local mode trajectory as in Fig. 4a.

and $\langle A(0) A(t) \rangle$ average over one trajectory as a function of time. The normal mode behavior of these two functions is shown in Fig. 11.7, while the local mode behavior is shown in Fig. 11.8. As can be determined from the two figures, the normal mode $A(t)$ oscillates around zero, while the local mode $A(t)$ oscillates either + or - and its average value is clearly non-zero.

Fig. 11.7 Plot of $A(t)$ and $\langle A(0) A(t) \rangle$ for the trajectory in Fig. 11.5.

Because of the large differences between $\langle A \rangle$ for local and normal mode trajectories, it is possible to use this to numerically distinguish them. A Monte Carlo sample of trajectories finds three sets of $\langle A \rangle$. A group is centered around 0 and the other two sets at + and - some non-zero value. We are currently extending this work to larger molecules.

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Fig. 11.8 Plot of $A(t)$ and $\langle A(0) A(t) \rangle$ as in Fig. 11.7 for trajectories in Figs. 11.6a and 11.6b.

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11.3.2 Semiclassical Study of Infrared Multi-Photon Dissociation

(D. W. Noid, J. R. Stine¹)

Theoretical calculations have shown, in agreement with experiments, that the infrared double laser dissociation process of polyatomic molecules is more efficient than the single laser dissociation process.^{2,3} In a recent calculation,⁴ the two-laser excitation of hydrogen fluoride with linearly polarized lasers was considered and it was found that the fraction of molecules that absorb energy varies considerably with the angle between the electric field vectors of the two lasers. The fact that enhancement of excited molecules in the parallel linearly polarized configuration as compared with the perpendicular linearly polarized configuration increases with lower laser powers was demonstrated in Ref. 5.

The classical equations of motion describing the energy absorption of hydrogen fluoride in the presence of two infrared lasers have been described in Ref. 3. Briefly, the time dependent Hamiltonian, H , is considered as a sum of the unperturbed Hamiltonian for the oscillator, H_0 , and the laser interaction Hamiltonian, $H_1 \cdot H_1$ is given by

$$H_1 = r^{-1} \mu(r) [\underline{x} C_x + \underline{y} C_y],$$

where r is the internuclear distance of the oscillator with components $\underline{x}$, $\underline{y}$, and $\underline{z}$. The function $\mu(r)$ is the r dependent electric dipole moment of hydrogen fluoride. Also,

$$C_x = \epsilon_1 \cos(\omega_1 t + \psi) + (\epsilon_2 \cos \phi) \cos \omega_2 t,$$

$$C_y = (\epsilon_2 \sin \phi) \cos \omega_2 t,$$

where ϵ_1 and ϵ_2 are the electric field strengths of the two lasers ω_1 and ω_2 are their respective frequencies. The quantity ϕ represents the angle between the electric field vectors and ψ , the phase difference between the two lasers, is a random number in the interval (0,2). Here the angle between the electric field vectors of the two lasers is fixed at either zero degrees (parallel linearly polarized) or ninety degrees (perpendicular linearly polarized) and the rela-

tive phase difference between the two lasers is randomly distributed.

The energy absorbed by each molecule in an ensemble of 500 randomly oriented hydrogen fluoride molecules is monitored as a function of time. The maximum energy (and hence the maximum rotational-vibrational state) attained for each trajectory during an interaction time of 1.2 ps is then binned. Typically the ensemble consists of two sets of molecules; those that remain near their ground state and those that are in an excited rotational-vibrational state.

Energy absorption of ensembles of randomly oriented hydrogen fluoride molecules are examined in the presence of two lasers. For each calculation, the lasers are assumed to have the same frequencies ($\nu_1 = \nu_2 = 3843.2 \text{ cm}^{-1}$) and the same powers ($\epsilon_1 = \epsilon_2$). Four laser powers are considered here and are 1.63, 2.60, 3.25, and 4.55 terawatt/cm². At each laser power, a histogram of the classical analog of the vibrational quantum was made for the cases where the electric field vectors are parallel and when they are perpendicular. Figure 11.9 shows these distributions for a laser power of 3.25 terawatt/cm². Approximately 19 percent of the ensemble is pumped into an excited vibrational state for the perpendicular case whereas this fraction is about 33 percent for the parallel case.

The results for some of the laser powers considered are given in Table 11.2. It is

Table 11.2 Fraction of molecules excited for different laser powers

Laser Power (Terawatt/cm ²)	Parallel	Perpendicular	Ratio
4.55	0.507	0.492	1.03
3.25	0.303	0.188	1.61
2.60	0.146	0.032	4.56
1.63	0.002	0.000	--

seen that the ratio of the fractions for the parallel to the perpendicular cases is larger for low laser powers and approaches unity for high powers. We expect that lower laser powers

can be used to obtain similar effects if the ensemble is in the presence of the lasers for longer times.

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11.3.3 Semiclassical Calculation of Bound States

(D. W. Noid, R. A. Marcus,¹ M. L. Koszykowski²)

Semiclassical methods recently developed for N-dimensional nonseparable systems have been successfully applied to both resonant and non-resonant systems.³ An extension to the previous work has focused on a model potential of H_5O_2^+ which has a multidimensional barrier.

Hydrogen bonding, which has drawn much attention in the literature, plays an important role in biochemical and chemical reactions. A hydrogen bond is formed when a covalently bound hydrogen atom forms another bond to a second atom.

It has previously been found that the one-dimensional treatment of hydrogen bonded systems is inadequate and requires a multidimensional study. Although hydrogen bonded systems have been extensively studied experimentally, theoretical calculations in two dimensions have just recently been initiated, and it is hoped that the methods developed here will be useful to future studies of these systems and to their generalization to higher dimensions.

The potential calculated by Janoschek, et al.,⁴ uses a linear model of H_5O_2^+ . Equilibrium distance for O-O was taken as 2.7 Å, and it is in good agreement with the observed van der Waals contact distance of $2.72 \pm .04$ Å. The coordinate designated x is the displacement of the proton from the center of the bond, and the

y coordinate is the displacement of the O-O from an equilibrium distance of 2.7 Å. The Schrödinger equation computed for this model was

$$\left[-\frac{1}{2m_H} \frac{\partial^2}{\partial x^2} - \frac{1}{m_O} \frac{\partial^2}{\partial y^2} + a_{00} + a_{20}x^2 + a_{40}x^4 + a_{01}y^4 + a_{21}x^2y + a_{02}y^2 \right] \psi(x,y) = E\psi(x,y). \quad (1)$$

Since the center of the O-O bond coincides with the center of mass, x and y are Jacobian coordinates to which Janoschek, et al., found the reciprocal reduced masses to be $1/m_x = 1/m_H + 1/m_O$ and $1/m_y = 2/m_O$. Because $m_O > m_H$, one can use $1/m_y = 1/m_H$ to permit comparison with Janoschek, et al., who used this approximation. m_O and m_H refer to the mass of the oxygen and hydrogen atom in atomic units.

With the aid of a SCF-MO-LC (LCGO) calculation,⁴ the coefficients $a_{k\ell}$ and $b_{k\ell}$ were determined and are given in Table 11.3, in atomic units, together with the definition of atomic units.

Table 11.3 Parameters Used in Eq. (1) for O-O distance of 2.7 Å

$a_{10} = 0.01338$	$a_{01} = -0.01941$
$a_{20} = -0.07206$	$a_{21} = 0.05226$
$a_{40} = 0.09701$	$a_{02} = 0.03983$
Energy: 1 a.u. = 27.21 eV	
Time: 1 a.u. = 2.42×10^{-17} sec.	
Distance: 1 a.u. = 0.529 Å	

Primitive semiclassical calculation of the eigentrajectory involves evaluating the value of $\oint p_x dx$ and also $\oint p_y dy$. Since the potential energy term is symmetric in x and the trajectories are also symmetric, the value of the phase integral $\oint p_x dx$ for both box trajectories will be equal. Then the quantization condition becomes (in units of $\hbar = 1$)

$$(n_1 + \frac{1}{2})2 = \oint_{\text{Right}} p_x dx + \oint_{\text{Left}} p_x dx,$$

and by symmetry

$$p_x dx = (n_1 + \frac{1}{2})$$

Because this method at this level neglects the tunnelling, the splittings of the even and odd levels are not found. The agreement between our calculation and a quantum calculation is very good, as shown in Table 11.4.

Table 11.4

State	Quantum ⁴ Eigenvalue	Semiclassical Eigenvalue
(0,0 ⁻)	.00666	.00696
(0,0 ⁺)	.00699	.00696
(0,1 ⁻)	.00855	.00897
(0,1 ⁺)	.00896	.00897
(0,2 ⁻)	.0105	.0110
(0,2 ⁺)	.0109	.0110

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11.3.4 Theoretical Investigation of Scattering Theory in the Quasiperiodic and Stochastic Regime in a Laser Field

(D. W. Noid, W.-K. Liu¹)

The classical dynamics of nonseparable anharmonic systems has been intensely investigated recently. At low energies, the trajectories follow a rather regular or quasiperiodic motion, and are confined to N-dimensional invariant tori in the phase space (the Kolmogorov, Arnold-Moser Theorem).² At higher energies, the motion is no longer confined to an invariant tori and tends to fill all of the allowed phase space, and is termed by various authors as stochastic or chaotic.² In this case, canonical invariants, called the action variables J_i , can be found on the tori:

$$J_i = \oint_{C_i} p \cdot dq \quad (1)$$

where q and p denote collectively the canonically conjugate coordinates and momenta, respectively, and C_i is a topologically independent path in phase space. The energy eigenvalues of the system can then be obtained semiclassically by quantizing J_i :³

$$J_i = (n_i + \delta_i)h \quad (2)$$

where n_i is an integer and δ_i is a known constant, usually 0 or 1/2.

Although much of the work in this field has been done on the study of stationary states of nonlinear systems, the interactions of such systems with external influence such as an applied laser field or a colliding partner also have received attention. The energy transfer process during a collinear collision between a particle and an anharmonic oscillator system has been investigated classically.⁴ In many experimental situations, absorption of radiation by a molecule takes place in the presence of colliding partners.

A model system for the collinear collision between a triatomic molecule and an oscillating target was considered. The target Hamiltonian is given by⁴

$$H_{\text{vib}} = \frac{1}{m} p_x^2 + p_y^2 + y^2 + D(\exp[-2\gamma(x-y)] - 2 \exp[-\gamma(x-y)]) \quad (3)$$

representing a harmonic oscillator coupled to a Morse oscillator. The interaction between the projectile and the target is assumed to be a Lennard-Jones potential of the form

$$V(x,z) = 4\epsilon \left\{ \left(\frac{\sigma}{z-x} \right)^{12} - \left(\frac{\sigma}{z-x} \right)^6 \right\} \quad (4)$$

The parameters in eqs. (3) and (4) are chosen to be $m = 1$, $D = 10.0$, $\gamma = 0.25$, $\epsilon = 4.0$, and $\sigma = 1.0$. The presence of a laser field provides a driving force for the system, and our model interaction is represented by

$$H_L = \epsilon_L x \cos(\omega_L t) \quad (5)$$

The total Hamiltonian for the system with a projectile of momentum p_z is thus given by

$$H = p_z^2 + H_{\text{vib}} + V(x, z) + H_L. \quad (6)$$

Before simulating the collision process, the eigentrajectory for the target Hamiltonian (3) corresponding to several vibrational energies, E_{vib} , and a given x -mode vibrational quantum number n_x was located by the method of surface of section³ when the motion was quasiperiodic. One thousand phase space points (x, y, p_x, p_y) were chosen along this eigentrajectory as initial values for starting the trajectories for the collision process. The Hamiltonian (3) was found in Ref. 4 to exhibit stochastic motion when $E_{\text{vib}} \geq 2.0$. For this case, $E_{\text{vib}} = -1.5$, a Monte Carlo sample of phase space was used for the target Hamiltonian. With p_z chosen to be a given negative value and z chosen to be large enough such that $V(x, z)$ is very small, the system of Hamilton's equations

$$\dot{q} = \frac{\partial H}{\partial p}, \quad \dot{p} = -\frac{\partial H}{\partial q}, \quad (q = x, y, z, \quad p = p_x, p_y, p_z) \quad (7)$$

with H given by eq. (6) were integrated numerically for each of the 1000 initial vibrational phases. The trajectory was stopped when p_z became positive and z was large enough such that $V(x, z)$ practically vanished where the collision process was considered to be completed. The energy transfer was calculated from

$$\Delta E = (p_z^f)^2 - (p_z^i)^2 \quad (8)$$

where p_z^f, p_z^i are the values of p_z in the beginning and the end of the trajectory, respectively. Finally, ΔE was averaged over the 1000 trajectories to yield a value for the averaged collisional energy transfer $\langle \Delta E \rangle$.

In a recent study,⁵ the behavior of the average collisional energy transfer $\langle \Delta E \rangle$ as a function of the laser frequency ϵ_L , field strength ω_L , and the initial translational momentum p_z^i and E_{vib} was investigated. The frequencies of the laser are chosen to be off-resonant from those of the target so that no appreciable absorption occurs during the course of a collision event, and the energy impact to the projectile derives solely from the vibrational energy of the target. The initial vibrational

energy of the target, E_{vib} , is chosen to lie below the dissociation energy of the target, and in the quasiperiodic regime with $E_{\text{vib}} = -4.5$ and $n_x = 1$, as discussed in Ref. 4.

Fig. 11.9 illustrates the dependence of $\langle \Delta E \rangle$ on ω_L for $E_{\text{vib}} = -4.5$ and $\epsilon_L = 0.025$ and for three different values of p_z^i . In all cases, it is observed that by tuning the laser at different frequencies, the energy transfer can either be enhanced or diminished. It should be noted that the plots have only a few data points because of the expense in running the calculation and that these points are connected with straight lines.

Fig. 11.9 Plot of $\langle \Delta E \rangle$ versus ω_L for three values of p_z ($p_z = 1.15$, o; $p_z = 1.05$, Δ; $p_z = 0.95$, □) with $\epsilon_L = 0.025$.

It is interesting to examine the effect of adding energy to the target Hamiltonian to the laser field-collision process. For two examples of ω_L (1.625 and 1.725) and one value of p_z^i (0.95), the values of $\langle \Delta E \rangle_{\text{laser}} - \langle \Delta E \rangle_{\text{no laser}}$ are plotted in Fig. 11.10 as a function of E_{vib} for which $n_x = 1$ when the motion is quasiperiodic and a Monte Carlo sample at $E_{\text{vib}} = -1.5$. Figure 11.10 demonstrated that the decrease in $\langle \Delta E \rangle$ becomes larger when the target motion has more energy in n_y with $n_x = 1$. As also found in Ref. 4, the energy transfer in the collisional process changes abruptly when the target motion becomes stochastic. It appears from these calculations that the laser has a smaller effect for stochastic motion. One explanation may be that the laser field can create resonant or

Fig. 11.10 Plot of $\langle \Delta E \rangle_{\text{LASER}} - \langle \Delta E \rangle_{\text{NO LASER}}$ versus E_{vib} for $p_z = 0.95$, $\epsilon_L = 0.025$; and two values of ω_L ($\omega_L = 1.625$, $\square$; $\omega_L = 1.725$, $\circ$).

near resonant transfer process when the motion is quasiperiodic, but is unable to change the dynamics for stochastic motion.

We found that it appears the collisional energy transfer shows many interesting features in the presence of a laser, and its effect could be monitored by varying the strength and frequency of the laser field, as well as the relative linear momentum of the colliding system.

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12. INORGANIC CHEMISTRY OF HYDROGEN CYCLES

C. E. Bamberger, M. R. Bennett, K. D. Brookhart,¹ P. R. Robinson²

In seeking alternatives for recently developed cycles involving Ce(IV)/Ce(III) and phosphates³ and titanates,⁴ reactions of CeO₂ with NaBO₂, Na₂B₄O₇ and H₃BO₃ were studied at continuously increasing temperatures up to 1200°C, while monitoring O₂ evolution. No reaction occurred with NaBO₂, but 20% of the expected O₂ was obtained with Na₂B₄O₇. The reactions of CeO₂ with H₃BO₃ (or B₂O₃·xH₂O) all evolved nearly 100% of the expected O₂, with the maximum P_{O₂} at about 1180°C. Analysis of the resulting solids by X-ray diffraction indicated that they were mixtures of CeBO₃ and Ce(BO₂)₃; however, the 100% line of the latter did not agree with literature (ASTM card file) values. While these results are completely consistent with those of Weidelt⁵ published in 1970, they are, however, in contradiction with those of a recent Russian publication⁶ in which it is claimed that for CeO₂ to react with H₃BO₃ it is necessary that at least 1 wt % of another rare earth has to be present.

Reaction of Ce(III)-borate mixtures with steam at continuously increasing temperatures up to 1000°C evolved only traces of H₂; thus, reoxidation of Ce(III) to Ce(IV) will have to be accomplished with more basic reagents, such as Na₂CO₃. This was not tested because the difficulty of hydrolyzing the resulting alkali metal borates would not be conducive to an attractive cycle. Exploratory tests in which the hydrolysis of Ce(III) borates with aqueous HCl solution was attempted indicated that such borates were quite stable; this property may be of value for some other applications (e.g., nuclear waste).

In attempts to develop a thermochemical cycle for the decomposition of HBr which could be coupled to other reactions to form a water-splitting thermochemical cycle it was found that V₂O₃ does not react with HBr(g) despite the negative free energy change calculated for the reaction. But V₂O₃ reacts with HBr(aq) yielding [VBr₂(H₂O)₄]Br·2H₂O, *I*. Thus, a study of the thermal behavior of compound *I* was considered of interest. From experiments using macro and

micro amounts of *I*, respectively, in an inert gas flow furnace and TGA apparatus, and from analysis of the solid and gaseous products by chemical methods, x-ray diffraction and thermal conductivity the following sequence for the decomposition of *I* was deduced:

The product of reaction 3 could also be formulated as "V₂O₃·H₂O". (H₂ found: 1.4 wt %; expected 1.2 wt %).

The main overall decomposition reaction for *I* can be represented by the sum of Eqs. (1) to (4):

Measurements of evolved H₂ indicated that parallel to the above scheme, 2-4% of the V(III) present (Eq. 3) is involved in other reactions, possibly one of which is a disproportionation reaction. The overall parallel reaction can be represented by

These results are in contradiction with those of Amirova et al.⁷ who have assumed that all of *I* undergoes disproportionation. Results of exposing *I* and also V₂O₃ to flowing steam (~10⁵ Pa) at continuously increasing temperatures up to 1100°C indicated that the large amounts of H₂ evolved are due to the following reaction:

Based on our experience we are led to believe that the inconsistencies reported in the literature (too numerous to review here) regarding the thermal behavior of various vanadium oxybromides may be due to differences in composition (variable amounts of protonated species such as OH^- and H_2O in the sphere of coordination of vanadium).

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13. MOLTEN SALT SYSTEMS

13.1 Composition Profiles of Molten Salt Mixtures Electrolyzed in Porous Media

(C. E. Vallet, D. E. Heatherly, J. Braunstein)

We previously have reported: (1) predictions of current-induced composition gradients resulting from Faradaic, migrational and diffusional processes in molten salt mixtures, with the possibility of solid phase formation at the electrodes of batteries and fuel cells employing molten salt electrolytes;¹ (2) potentiometric measurements of composition gradients near the electrodes in electrolyzed $(K, Ag)NO_3$ ² and $(Na, Ag)NO_3$;³ (3) atomic absorption (AA) analysis of sections of quenched electrolyzed melt; (4) preliminary measurements by scanning electron microscopy with energy dispersive x-ray fluorescence (SEM/EDX). More complex calculations⁴ for molten LiCl-KCl predict similar concentration gradients. Qualitative evidence has been reported recently for such gradients in LiCl-KCl electrolyzed between LiAl electrodes,⁵ and for solid phase precipitation in LiAl/LiCl-KCl/FeS cells.^{6,7}

Here we present the results of new experiments with $AgNO_3$ - $NaNO_3$ contained in yttria felts, electrolyzed between silver electrodes, and quenched. The aim was a quantitative determination of the entire composition profile by SEM/EDX.⁸ The tortuosity coefficient of the matrix also was determined from measurement of the electrical conductance and porosity of electrolyte-filled Y_2O_3 matrices. These measurements are compared with the predicted composition profiles in the model system, $NaNO_3$ - $AgNO_3$, with known diffusion coefficient, transference number and activity coefficients. The experimental procedures developed are applicable to molten salt battery electrolytes.

Porosities of Y_2O_3 felts placed in an electrolysis cell were determined from the weight of salt extracted from quenched felts. The porosity (volume fraction of voids), ϵ , measured on the cells used for conductance measurements is 0.90 ± 0.02 . Electrical conductance of the salt-filled felts was obtained from measurements of the IR drop across the Ag electrodes. The

conductance results obtained at 300°C are summarized in Fig. 13.1. The conductivities of 0.2 $AgNO_3$ -0.8 $NaNO_3$ contained in yttria felts of differing thickness, κ_f , are shown in the inset. The mean conductance, $0.629 \pm 0.039 \Omega^{-1} cm^{-1}$, is the solid horizontal line.

Fig. 13.1. Current-voltage curves and conductivity (inset) at 300°C of 0.8 $NaNO_3$ -0.2 $AgNO_3$ - Y_2O_3 felts for differing electrode separations. Separation/cm: 1, 0.157; 2, 0.159; 3, 0.316; 4, 0.322; 5, 0.328; 6, 0.449; 7, 0.610.

The conductivity of the free electrolyte, κ_0 , measured at the same temperature by Wetmore, is $0.9623 \Omega^{-1} cm^{-1}$. The tortuosity coefficient, calculated as $\sqrt{\epsilon \frac{\kappa_0}{\kappa_f}}$, is applied to the diffusion coefficient measured¹⁰ in the free electrolyte.

SEM/EDX analysis of the composition profile has the advantage of excellent distance resolution ($\sim 50 \mu m$) for profiles typically extending over 0.3 cm. However, quantitative measurements require careful calibration with standards, whose compositions bracket those in the electrolyzed samples, prepared by identical procedures. Seven standards were prepared, with composition ranging from 0.05 to 0.30 $AgNO_3$ mole fraction. The calibration curve is calculated, with corrections for the variation in depth of penetration of the electron beam into the

sample (Z), x-ray absorption by the sample (A), and secondary fluorescence enhancement of lighter elements by heavier ones, (F), computed from the atomic properties using the FRAME program.¹¹ The normalization factor 3.17 gives the smallest standard deviation from the experimental data but is slightly larger than the value $I_{Ag}^0/I_{Na}^0 = 2.55 \pm 0.3$ that we measured with pure silver sheet and NaCl optical grade monocrystal. A difference of this magnitude may be attributed¹² to uncertainties in the penetration of the electron beam assumed in the FRAME program.

Figures 13.2 and 13.3 summarize the SEM/EDX analysis of composition profiles in two electrolyzed Y_2O_3 felts. AA analysis of sections of quenched electrolyte, reported earlier,³ and SEM/EDX measurements are mutually consistent and have comparable uncertainty (5-6%), but SEM/EDX gave far better distance resolution of the profile (50 μ m). The points are the data, with no smoothing, and the dashed curve is the predicted profile, calculated with no adjustable parameters. The same data are shown as a solid line representing a seven point moving average to smooth out some of the fluctuations arising from irregularities of the surface and possibly from

Fig. 13.2. SEM/EDX: • Data, — 7 point moving average ---- Predicted profile.

Fig. 13.3. SEM/EDX: • Data, — 7 point moving average ---- Predicted profile.

nonuniform distribution of salt in the Y_2O_3 matrix. The average distance resolution is better than 50 μ m, even with this smoothing. Figure 13.2 shows the profile measured after a shorter electrolysis time (2 minutes) at 0.08 A cm^{-2} . The EDX determinations in the region within 0.09 cm from the anode show the near independence of the diffusion layers at the two electrodes, as predicted. Figure 13.3 gives the profile measured after electrolysis at an identical current density and a longer time (5 minutes). The deviations of the calculated compositions from the SEM/EDX data are smaller than the dispersion observed for the calibration standards. The standard deviation between measured and predicted compositions is 0.02 mole fraction $AgNO_3$. The smoothed experimental profile confirms the merging of the two diffusion layers predicted for the longer electrolysis time.

The above quantitative measurements of current induced composition gradients in molten nitrate mixtures, and their comparison with the predictions, demonstrate: the validity of the model; the applicability of the measurements and calculations to the analysis of composition gradients in LiCl-KCl and other molten salt battery elec-

trolites; usefulness of SEM/EDX for measurement of localized composition gradients in porous media.

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13.2 Current Induced Composition Gradients in Molten LiCl-KCl Battery Electrolytes

(C. E. Vallet, D. E. Heatherly, S. Cantor, J. Braunstein)

Basic studies have demonstrated the establishment of current-induced composition gradients in mixed molten salt electrolytes. Such gradients have been measured in $\text{AgNO}_3\text{-NaNO}_3$ melts electrolyzed between silver electrodes, and predicted in mixed molten salt battery electrolytes.¹ Composition shifts, if large enough, can produce significant deleterious effects, such as solid phase precipitation in or near the electrodes of molten salt batteries, including the $\text{LiAl/LiCl-KCl/FeS}_x$ battery. Quantitative measurements are needed to determine the extent of the gradients and to find means to reduce them.

Previous AA analysis and SEM/EDX data demonstrated qualitatively the current-induced composition changes in LiCl-KCl eutectic electrolyzed between LiAl electrodes.² During the past year we have obtained the first quantitative measurements of the shape of the composition profile.

A new electrolysis cell, shown in Fig. 13.4, was designed and constructed to prepare samples for measurement of current-induced composition gradients. The new cell facilitates assembly of electrodes and porous matrix to be filled with electrolyte, provides for improved electrode-electrolyte contact, can accommodate a powdered alloy electrode and simplifies quenching of the salt before sectioning and analysis. Measurements of porosity of the matrix by extraction of the quenched salt gave a porosity of 86%; the measured porosity when the yttria felts are filled with nitrate mixtures is 90%.¹

Fig. 13.4 Electrolysis cell

A SEM/EDX calibration was carried out for quantitative evaluation of electrolyte compositions from measurements of the K/Cl count (peak area) ratio. Seven standards were prepared from melts of weighed-in composition ranging from 0.25 to 0.6 mole fraction KCl; the mixtures were introduced into the porous Y_2O_3 matrix in a cell, quenched and cut in a procedure identical, except for electrolysis, with that used for electrolyzed samples. Quenched electrolyzed samples of LiCl-KCl eutectic were prepared using either two solid two-phase LiAl ($\alpha + \beta$) electrodes or a solid cathode and powdered LiAl anode.

Profiles measured in two cells electrolyzed under similar conditions are shown in Fig. 13.5. The SEM/EDX results (horizontal bars) were smoothed by averaging the measurements with a "moving window" of width $\pm 0.05 \times$ the reduced distance. This smoothing reduced the fluctuations with much smaller loss of distance resolution than that occurring with sectioning, is

Fig. 13.5. Cell #1: Electrolysis 152 s; 0.20 A cm^{-2} ; Electrode separation 0.401 cm. Cell #2: Electrolysis 242 s; 0.25 A cm^{-2} ; Electrode separation 0.416 cm. $\square$ Atomic absorption and width of the analyzed section, — SEM/EDX and width of the moving window, ---- Predicted profile, — Least-squares quadratic fit to AA and SEM/EDX data.

model-independent, and demonstrates the current-induced composition gradients. (The bars thus represent overlapping groups of points spanning less than 0.15 mm.) The AA results are obtained by analysis of lithium and of potassium in the salt extracted from sections cut parallel to the electrodes. The sections, of thickness about 0.4 mm, are not contiguous. The dashed line is the predicted profile calculated numerically. The solid line curves are least-squares quadratic fits to the data with a simple empirical function of the reduced distance, ξ .

$$x_{\text{KCl}} - 0.415 = A(\xi - 0.5)^2 \text{ for } \xi > 0.5;$$

$$x_{\text{KCl}} - 0.415 = -B(\xi - 0.5)^2 \text{ for } \xi < 0.5.$$

The standard deviations of these fits are slightly less than 0.04 mole fraction KCl. This relation had been found to represent reasonably well the predicted compositions for the experimental conditions reported. The fitted compositions are within about 6 mole percent of those predicted. Examination of deviation plots of the data (from a least-squares line) suggest the possibility that part of the observed fluctuation may represent real composition differences, perhaps produced by nonuniform electrolysis and by inhomogeneity during quenching.

SEM/EDX analysis was initiated of quenched electrolyzed LiCl-KCl eutectic in a powdered LiAl anode and in the adjacent Y_2O_3 separator. In Fig. 13.6 elemental mappings of chlorine, potassium, and yttrium in a quenched electrolysis cell with a porous upper electrode demonstrate the filling of the electrode pores by the melt.³ Preliminary SEM/EDX measurements, from a cell electrolyzed 240 s at 0.25 A cm^{-2} and quenched, show a composition gradient across the geometric interface between the porous electrode and the LiCl-KCl- Y_2O_3 electrolyte. Scans within large areas ($\sim 10^{-4} \text{ cm}^2$) gave large counts of chlorine but almost no counts of potassium, suggesting that LiCl precipitation had occurred within the porous anode as the composition crossed the liquidus line during electrolysis.

Fig. 13.6. Electron micrograph and EDX chemical mapping of cell with powdered LiAl electrode.

The experimental procedures developed in nitrate mixtures thus provide quantitative measurements of current induced composition changes in the LiCl-KCl eutectic battery electrolyte, and means to study the distribution of reactants and products in the electrodes and electrolyte.

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13.3 Composition Gradients in Electrolyzed Molten Chloroaluminates

(C. E. Vallet, J. Braunstein)

Molten alkali chloroaluminates have been proposed as battery electrolytes in order to

exploit low equivalent weight negative electrode materials such as Na, Al or Li, high electrolyte conductance, and relatively low melting points ($<200^{\circ}\text{C}$). Systems include an aluminum-chlorine cell with NaCl-KCl- AlCl_3 electrolyte,¹ and a cell with negative electrodes of LiAl or NaAl in LiAlCl_4 or NaAlCl_4 , respectively.² More recently, Mamantov has reported³ a cell with an $\text{Na}/\text{Na}\beta\text{Al}_2\text{O}_3$ negative electrode and SCl_4 /tungsten positive electrode, where the SCl_4 is stabilized in an acidic (AlCl_3 rich) melt of NaCl and AlCl_3 (NaAlCl_4 - NaAl_2Cl_7) as $\text{SCl}_3\text{AlCl}_4$. As part of an attempt to characterize sources of polarization, we have adapted our computations of current-induced composition profiles, and the resultant mass-transport polarization, to chloroaluminate systems. Initial calculations are for composition profiles in melts electrolyzed between $\text{Na}/\text{Na}\beta\text{Al}_2\text{O}_3$ and Al electrodes. Simulation of the processes at the Al electrode is simpler than at the SCl_4/W electrode, and provides a

starting point for the more complex calculations. Results of the calculations are compared to measurements of Katagiri and Mamantov.⁴

The ion flows considered in the calculation are the result of faradaic processes at the Al and Na electrodes, electromigration and diffusion. The reactions at anode and at cathode may be written

resulting in an increase in the average NaCl concentration and in the basicity of the melt, represented by the equilibrium $2\text{AlCl}_4^- \rightleftharpoons \text{Al}_2\text{Cl}_7^- + \text{Cl}^-$.⁵ The diffusion-migration equation is written in terms of flows of the ion constituents Na and Al in the reference frame of the chloride ion constituent. In this frame, the Na^+ ions are the principal current carrying constituent (i.e., $t_{\text{Na}}^{\text{Cl}} = 1$; $t_{\text{Al}}^{\text{Cl}} = 0$),^{5,6} which is equivalent to the transference numbers of the species AlCl_4^- and Al_2Cl_7^- , relative to sodium, being equal to their respective mole fractions. In the numerical solution, the volume change is taken into account by modifying the distance mesh in each time step to provide volume elements containing equal quantities of chloride ion constituent. The calculated stoichiometric mole fraction of AlCl_3 is related to the species concentrations (in ion mole fractions) of AlCl_4^- , Al_2Cl_7^- and Cl^- via the above equilibrium.^{5,7}

After one minute of electrolysis of 0.55 AlCl_3 -0.45 NaCl at a current density of 57 mA cm^{-2} and an electrode separation of 0.2 cm, with a diffusion coefficient of the order of $10^{-5} \text{ cm}^2 \text{ s}^{-1}$, the calculation would predict (if there were no convection mixing) a composition change at the Al cathode, x_{AlCl_3} , from 0.55 to 0.49; i.e., from acidic to basic. The corresponding change in chloride ion (species) concentration is from 3×10^{-7} to 8×10^{-3} . The diffusion layer thickness is about 0.04 cm, and there is no composition change at the sodium electrode from the species considered in this

calculation. With complete mixing, the average melt composition would have changed only to $x_{\text{AlCl}_3} = 0.54$.

Katagiri⁴ has made preliminary emf measurements of melt composition changes at the cathode in melts of the above composition at four current densities between 15 and 115 mA cm^{-2} . Plots of composition versus square root of time are linear for electrolysis times up to about thirty seconds, and the reciprocals of the slopes are proportional to the reciprocals of the current densities, suggesting a diffusion process. The apparent value of D , $4-8 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, calculated from the initial slopes of these plots,⁷ is reasonable compared with the value of 2×10^{-6} reported^{6,7} for the composition 63 mole percent AlCl_3 in view of the difference of composition and uncertainties in geometry and convection. For the short electrolysis times, our numerical predictions also are in reasonable agreement with the measured compositions. At longer electrolysis times the slopes of the composition-square root of time plots level off, probably because of convection. The measurements nevertheless confirm the qualitative predictions that significant acidity changes can occur at the Al cathode even with convection.

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13.4 Lithiation Equilibrium of Nickel Oxide

(J. Braunstein, H. R. Bronstein, S. Cantor, D. H. Smith)

The ternary system Ni-O-Li provides oxide phases whose chemistry is important for the understanding of high temperature corrosion of nickel alloys, electrocatalysis and controlled valence in solids. Of particular interest in this system is the triangle bounded by the compositions NiO, Li₂O, and Ni₂O₃, and especially the region near the line joining the compositions NiO and LiNiO₂. This region would include solid solutions of Li₂O or of Ni₂O₃ in the (cubic) NiO lattice, requiring defects such as interstitial Li⁺ ions for the former, and vacant cation sites for the latter, in order to maintain electroneutrality. However, the energetics of defect formation appear to favor equal numbers of Li⁺ and Ni³⁺ ions replacing pairs of Ni²⁺ ions.¹ Thus, the reaction of NiO or Ni with oxygen and with oxides of lithium can be described in terms of the formation of a solid solution of LiNiO₂ (with possible dissociation) in NiO with mole fraction y of LiNiO₂ and (1-y) of NiO

The solid phase is often designated by the cation fraction, x, of Li⁺; i.e., Li_xNi_{1-x}³⁺Ni_{1-2x}O, or Ni_{1-x}Li_xO, where x = y/(1+y). Although many of the electronic, optical and magnetic properties of this system have been measured, there is little information on the key chemical properties that determine the Li⁺ content, represented by the equilibrium (1), and the rate of approach to equilibrium;¹ these are the free energy of formation and excess chemical potentials of the solutes, and the chemical diffusion coefficient. The experiments reported here were the start of a study of the chemistry of the lithiation reaction.

Reaction vessels were gold boats containing solid samples, initially Ni, NiO, or Ni_{1-x}Li_xO, immersed in molten Li₂CO₃-K₂CO₃; the melt serves as a flux in which Li₂O activity is controlled by fixing temperature, Li/K ratio, and CO₂

pressure. The vessels were enclosed in silica tubes under a flowing gas mixture, O₂/CO₂ (at pressure slightly above atmospheric) which fixes the oxidizing potential. Other results were derived from analysis of lithium in oxidized nickel electrodes removed from electrochemical cells with Li₂CO₃-K₂CO₃ electrolytes. The lithiated nickel oxide samples were leached with acetic acid to remove adhering electrolyte. Lithium content in the nickel oxide (i.e., the value of x or of y) is obtained from x-ray diffraction measurements of the unit-cell parameter. The calibration curve of unit cell volume versus lithium content was derived from published x-ray data on samples analyzed for Li⁺ and (in some cases) Ni³⁺.² The x-ray method was checked on some of our samples by lithium analysis via atomic absorption spectroscopy.

Table 13.1 shows cation fractions, x, for samples of differing initial form exposed to different temperatures, oxygen potentials, and lithium oxide activities (ratios of Li₂CO₃ activity to partial pressure of CO₂) for differing lengths of time. The last column, K', is the empirical concentration equilibrium constant for the reaction

$$K' = (p_{\text{CO}_2}/a_{\text{Li}_2\text{CO}_3})^{1/2} p_{\text{O}_2}^{-1/4} [y/(1-y)] \quad (2)$$

The thermodynamic equilibrium constant may be written $K = K' \gamma_{\text{LiNiO}_2} / \gamma_{\text{NiO}}$ and rearranged to

$$\ln K' = \ln K - \ln(\gamma_{\text{LiNiO}_2} / \gamma_{\text{NiO}}) \quad (3)$$

The last term vanishes at vanishing concentration of LiNiO₂, and the two activity coefficients are related through the Gibbs-Duhem equation. With sufficient data, a plot of ln K' vs a function of y would extrapolate to the thermodynamic equilibrium constant at vanishing y, and the limiting slope would give the deviations from Henry's Law in the solid solution. The preliminary data here show little dependence of K' on

Table 13.1 Lithiation of NiO

T (°K)	Sample ^a form	x _{Li₂CO₃}	O ₂ /CO ₂	p _{O₂} (atm ^{1/2})	$\left(\frac{a_{\text{Li}_2\text{CO}_3}}{p_{\text{CO}_2}}\right)^{1/2}$	Time (hr)	x	K ^b
923	p	0.62	0.5	0.76	0.67	435	0.035	0.12 ₂
	p					1167	0.052	
	Ni					1167	0.059	
	Ni					1167	0.058	
823-973	el					1080	0.045	0.094
	el					1080	0.046	
	el					13000	0.042	
1093	p	1.0	9.0	0.97	3.16	212	0.207	0.11 ₈
	p					405	0.218	
	Ni					91	0.203	
	Ni					405	0.028	
	Ni					740	0.203	
	Ni	0.62	4.0	0.95	1.22	700	0.107	0.11 ₈
	Ni					1320	0.107	
	s.c.					1320	0.021	
	s.c.					1900	0.022	
	s.c.					2530	0.021	

^aInitial form of sample:

p polycrystalline NiO

Ni sintered Ni metal or Ni powder

el sintered Ni electrode removed from electrolysis cell with Li₂CO₃-K₂CO₃-LiAlO₂ electrolyte tile analogous to molten carbonate fuel cell cathode.³²

s.c. Single crystal NiO (0.1 mm thickness)

^bReference state for solid is infinite dilution of LiNiO₂ in NiO

composition, or of temperature, with a mean value value of 0.11 ± 0.02 over a threefold variation of oxygen pressure and an order of magnitude variation of Li₂O activity.

Equations (1) and (1') correspond to addition of Li⁺O²⁻ to the NiO lattice, coupled with oxidation of a Ni²⁺ ion to Ni³⁺ ion for each Li⁺. Since the lattice remains virtually unchanged, and mobilities are higher for the electrons or holes than for the ions, the bulk equilibration rate is probably determined by the Li⁺ diffusion coefficient. The time required

to reach a stationary value of x appeared to be several hundred hours, except for the single crystals, which were hundreds of times thicker than the particle size of the polycrystalline material; diffusion times would be of the order of 10⁴ times longer, probably accounting for the low values of x. In order to ascertain that equilibrium was approached, samples with x = 0.2, prepared previously under high O₂ and Li₂O activities, were subsequently exposed to conditions under which Ni or NiO powders had reached values of only 0.06. The value of x dropped

from 0.2 to 0.08 in 800 hours, and the experiment was terminated before a stationary value could be demonstrated. The discrepancy is slightly larger than the dispersion in K' , but the result demonstrates semiquantitatively the reversibility of the reaction. Additional data, at longer times, with other samples and with specific analysis of Ni^{3+} and Li^+ would be required for definitive characterization of the composition of the phase and of the chemical diffusion coefficient.

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14. ENHANCED OIL RECOVERY

The research described in this chapter is supported by the Office of Oil, Gas and Shale, Department of Energy. Most is oriented toward the micellar flood approach to enhanced recovery. One objective is to find cheaper chemicals for the process. Emphasis has been on non-petroleum raw materials and on lower cost conversions to useful substances, for example, fermentation in the field to produce mobility-control biopolymers. Other research is directed toward fundamental understanding of the chemistry of micellar floods.

14.1 Chemicals for Enhanced Oil Recovery

14.1.1 Surfactants from Tall Oils and Tall-Oil Components

(J. S. Johnson, Jr., R. M. Jones,¹ L. J. Magid,² C. G. Westmoreland)

A. Ionic. An interest of the chemicals program since its beginning has been surfactants from non-petroleum feedstocks. Emphasis has been on the fatty-acid fraction of tall oils, a byproduct of the pulping of softwoods, on what appears to be the principal active ingredient of tall-oil fatty acids, sodium oleate, and on its derivatives. Oleates and other unsaturated C_{18} carboxylate salts are also prominent constituents of vegetable oils, such as those from soybeans, peanuts, and cotton seeds. Compositions giving optimal properties for oil recovery appear to be essentially the same with pure sodium oleate as with crude tall oils.³

Another set of derivatives to which we have given considerable attention is comprised of oleates with alkyl substituents on the carbon next to the carboxylate. Optimal salinities for a given alkane carbon number (ACN), were shown to decrease (or ACN's for a given salinity increase) in an orderly trend with increasing numbers of alkyl carbons in the substituents.³ We have been looking in more detail at a few of these systems. As an example, a map of the regions in which two and three phases are found in systems containing sodium 2,2 dimethyl oleate is given in Fig. 14.1. The contour lines in the three-phase region approximate the volume fraction of the microemul-

sion phase. It can be seen that as the compositional range of the middle phase becomes narrower, the relative volume of the middle phase becomes larger. This behavior is consistent with an apparently developing consensus,⁴ that the boundaries between two and three phases in many systems favorable for oil recovery are not far from critical end-points. The opalescence (superscript "o" in the figure) and indefinite menisci (indicated by parentheses) observed near the boundaries between two and three phase regions are qualitatively in agreement with this picture.

Interfacial tension scans, measured by the spinning drop technique, are presented in Fig. 14.2. These cover a range of alkane carbon numbers at two salinities, one (0.25 M) where the ACN range of three phases is very narrow and the other (0.375 M) where it is relatively wide. It can be seen that the narrower range corresponds to a much steeper dependence of tension on ACN and much lower values at the crossover. There is an anomalously high value for the top vs bottom at the lower salinity well outside of obedience to Widom's Rule.⁵ We are not sure about the reason for this, but suspect there may not be enough surfactant in these phases to supply the surface area of the long thin drop which the expected low interfacial tension would require. In any case, the lower tensions between the middle vs the other two phases would be consistent with proximity of critical end-points. Their presumed closer proximity where the middle-phase region is narrow is consistent with the lower values of interfacial tension observed with 0.25 M NaCl.

Fig. 14.1. Map of two- and three-phase regimes of aqueous/hydrocarbon systems containing sodium 2,2 dimethyl oleate (initial aqueous, 0.01 M surfactant; 5 v/v% *i*-butyl alcohol; NaCl plus 5 mole % sodium carbonate/bicarbonate, pH 9.9; WOR=2, 60 days equilibration, 31.5°C; contour lines approximate volume fraction of middle phase).

Fig. 14.2. Interfacial tensions between normal alkanes and aqueous 0.01 M sodium 2,2-dimethyl-oleate (5 v/v% iso-butyl alcohol, pH 9.9 buffered with 10 mole % salt as carbonate-bicarbonate, WOR=2, 31.5°C).

B. Non-ionic. The investigation of ethoxylated tall oils and of mixtures of them with ionic petroleum sulfonate surfactant was completed. Papers have been submitted on both subjects.^{6,7}

In the systems containing only non-ionic surfactants, the range of salinities over which a large number of multicomponent systems containing ethoxylated tall oils or tall oil derivatives form middle phase microemulsions was determined. *n*-Octane and *n*-decane were the hydrocarbons; 2-methyl-1-propanol and 2-butanol, the cosurfactants. It is possible, with an appropriate choice of surfactant, to produce systems with optimal salinities from 0 wt. % to ca. 17 wt. % NaCl. Phase volume diagrams were obtained for 24 of the systems investigated. An example is given in Fig. 14.3. Interfacial tension (IFT) measurements for selected systems showed tensions in the millidyne/cm range at the optimal salinities (the salinity at approximately the midpoint of the three-phase region).

Fig. 14.3. Phase volume diagrams for the Trydet OA-7/sec-butyl alcohol/n-octane system at surfactant/cosurfactant ratios (wt/wt) or 5:2 (●); 3:2 (■); and 2:3 (▲).

The petroleum sulfonate used in the study of mixed ionic and non-ionic surfactants was the Stepan Chemical Company commercial product, Petrostep 465. In multicomponent systems containing this surfactant alone, there were apparent three phase regions over a wide range of salinities; the middle phases in these systems are probably macro- rather than microemulsions and their existence depends upon the mode of sample preparation (and apparently upon variations in P-465 composition).

Hydrophilic non-ionic surfactants which are tall oil derivatives increased the range of existence (with respect to salinity) of true middle phase microemulsions in these P-465 systems. These middle phase microemulsions were observed at salinities considerably below those required for the non-ionics alone to show three phase behavior. Modest increases in optimal salinity and broadening of the low IFT region with respect to salinity (without marked increases in minimum IFT) were caused by the non-ionics when 2-butanol is the cosurfactant and *n*-decane is the hydrocarbon. Examples of IFT results are presented in Fig. 14.4.

Fig. 14.4. Interfacial tension measurements for P-465/2-butanol/aqueous NaCl/*n*-decane systems without nonionic present (●); with Trydet OA-7 (■); with Ethofat 0-20 (▲). IFT's for the microemulsion phase vs. the hydrocarbon phase are shown with filled points, IFT's for the microemulsion phase vs. the aqueous phase with open points.

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14.1.2 Biopolymers

(A. L. Compere, W. L. Griffith, S. V. Greene,¹ J. M. Crenshaw,¹ R. A. Gracey²)

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2. Faculty of Department of Chemistry, University of Tennessee, Knoxville. Part-time ORNL employee.

As mentioned in the previous report,³ polymers which increase solution viscosity are a necessary constituent of the aqueous solutions used to drive a micellar flood oil bank, to decrease fingering of the drive solution into the oil bank itself.

Fingering of the aqueous drive solution into the surfactant bank is likely to cause breakthrough of the drive solution to the producing well prior to the oil bank. The resulting high-mobility path would cause bypassing of the oil. Current technology often uses polyacrylamide polymers as viscosifiers; there is however, increasing use of xanthan, a microbially produced gum. We have been interested in scleroglucan, a water-soluble fungal gum, because it appears more amenable to field production and purification, practices which should result in substantial cost savings.⁴ Current investigations also indicate that chemical and other properties of scleroglucan make it more attractive than xanthan for some uses.⁵

Where a fungal fermentation to produce scleroglucan is performed in the field, it may be desirable to use available local water for process make-up. These waters may be brines and may additionally contain trace elements. We have tested the sensitivity of a scleroglucan production organism, which was kindly given us by Ceca, S.A., to these materials. Bench tests⁶ indicated that 2% w/v of either NaCl or Instant Ocean, a synthetic seawater, were well tolerated by this strain of *Sclerotium rolfsii*. Ten-liter fermenter tests confirmed this result, yielding, respectively, 1.5% and 1.3% w/v recoverable polymer, measured as volatile suspended solids. This is comparable to the yield from a normal fermentation on standard medium. The time required and the fermentation oxygen and pH profiles, as well as broth viscosity, were also well within the normal range expected of the organism. Although use of field brines could, especially if seawater could be added, provide major advantages, it is necessary to remember that sterilization and handling of these saline solutions could result in both corrosion and scaling problems.

Because of the high content of trace metal ions in some brines, we were interested in the effect of trace metal addition to fermentation broth used for biopolymer production. Small shake flask tests to measure growth in the presence of the selected trace elements were performed at ambient temperature (~26°C). Bio-

mass production was not adversely affected at or below the concentrations: 8 mM Mn; 4 mM B, Co, and Zn; 2 mM Ba, Cu, and Fe; and 0.4 mM Cd and Ni. Biomass production in one-liter fermenter tests at 18°C was not adversely affected at 0.3 mM Mn and 0.1 mM Zn. However, it was lowered, relative to controls, in the cases of 0.2 mM B, 0.1 mM Ba, 0.4 mM Fe, and 0.1 mM Ni. Broth viscosity at a shear rate of 11.25 sec⁻¹ was decreased in the cases of 0.1 mM Cd and 0.4 mM Fe, relative to controls. Based on both small flask growth tolerance tests at 27°C and one-liter fermenter tests at 18°C, it appears that the strain of *Sclerotium rolfsii* used will tolerate the levels of many trace elements which might reasonably be expected in groundwaters. However, the interactions which might occur where trace metals are present at the salinity level of natural brines have not been evaluated.

1. Department of Chemistry, University of Tennessee. Part-time employee.
2. Oak Ridge Associated Universities student trainee; Centre College, Ohio.
3. Chem. Div. Annu. Prog. Rep. February 29, 1980, ORNL-5665 (July 1980), p. 96.
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14.1.3 Cosurfactants

(A. L. Compere, W. L. Griffith, J. M. Googin,¹
R. A. Hulseman²)

As mentioned in previous reports^{3,4} the 3 and 4 carbon alcohols added to modify properties of micellar floods surfactant solutions can be produced by fermentation.⁵ Some of these materials, notably 1-butanol, are currently in short supply. Their availability could be a major barrier to large-scale micellar flood operations. Other uses for the mixtures of solvents, generally called neutral solvents, produced by bacterial anaerobic fermentation, include fuel extension

and in a variety of industrial solvent applications. These mixtures, principally 1-butanol, with lesser amounts of any of acetone, ethanol, or 2-propanol, are produced from the same kind of feedstocks which are used for ethanol production, in the same kind of equipment, and require roughly the same fermentation time.

With the help of MIT School of Chemical Engineering Practice Teams^{6,7} we have been analyzing the separations of neutral solvent mixtures. The high volatility of 1-butanol and the miscibility gap between 1-butanol and water permit development of innovative separations methods. However, as shown in Table 14.1, developed in a recent study,⁸ even classical separations schemes have a markedly higher overall process energy efficiency and a lower net solvents production cost for neutral solvents than for ethanol. The bacteria, *Clostridia*, used for neutral solvents production, has an added advantage in being able to ferment small fragments of hemicellulose and cellulose chains, typical of hydrolysis products from biomass.

1. Union Carbide Corporation Nuclear Division Central Management Staff.

2. Assistant Director, MIT School of Chemical Engineering Practice.

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14.1.4 Sacrificial Agents

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

In the previous report,¹ we presented results showing that pretreatment of minerals with several waste or low-valued organic chemicals from the pulping of wood lowered the loss from solution of a typical petroleum sulfonate surfactant

Table 14.1

Ethanol and neutral solvents production from corn
(150×10^6 kg anhydrous product/year)

Item	Cost, million dollars	
	Ethanol	Neutral solvents
<i>Capital Investment</i>		
Total investment	63.10	53.87
Working Capital	12.70	10.77
Total	75.80	64.64
<i>Fixed charges</i>		
Depreciation	5.30	5.39
License fees	0.05	0.05
Maintenance	2.50	2.15
Taxes and insurance	1.30	1.08
Total	10.15	8.67
<i>Raw materials</i>		
Corn	60.00	60.00
Other	0.05	0.05
Total	60.05	60.05
<i>Operating Expenses</i>		
Utilities	13.90	12.16
Labor	2.30	2.30
Sales, freight	5.00	5.00
Total	21.20	19.46
<i>By-product credits</i>		
Dried grains	(20.00)	(33.40)
Hydrogen		(2.04)
Total	(20.00)	(35.44)
<i>Other charges</i>		
Taxes	11.40	9.70
Profit, 15% ROI	11.40	9.70
Total	22.80	19.40
<i>Annual production cost</i>		
	94.20	72.13

Energy recovery, including corn production

Efficiency	0.62	0.91
	* * * * *	
Cost, per gallon	\$ 1.89	\$ 1.44

Source: Strobel, M. K. and Bader, J. B., 1981. *Economic evaluation of neutral solvent fermentation product separation*, M.I.T. School of Chemical Engineering Practice Report ORNL/MIT-330.

to a tenth to one-half what it was in absence of these substances. Because the value of the surfactant saved should be several times the costs for the amounts of competitive adsorbates needed and because preventing the loss of surfactant components should make easier the maintenance of compositions optimal for oil recovery as the banks move through the formation, there may be considerable benefits in micellar flooding.

We have continued to evaluate these possibilities with other minerals likely to be encountered

in oil recovery, as well as with crushed sandstones from actual oil-bearing formations, provided by the Amoco Production Company. There appears to be a qualitative pattern visible through a number of quantitative exceptions, that the relative lowering by sacrificial agents of surfactant loss is greater with those minerals which adsorb surfactant most strongly. With montmorillonite, for example, which adsorbed 0.15 to 0.25 equivalents of surfactant per kg clay at equilibrium solution concentrations high enough to reach the plateau region, pretreatment with the caustic extract from the bleaching of kraft pulp reduced loss by a much larger factor than with sandstone, on which adsorption was almost two orders of magnitude lower. The same pattern is seen with oil-field sandstones. In Fig. 14.5, in which the sandstone adsorbs little more than berea, it is seen that there is no benefit from pretreatment with weak black liquor (digester blowdown), caustic extract, or sodium saccharinate. With another sandstone (Fig. 14.6), on which surfactant loss is an order of magnitude

Fig. 14.5. Effect of sacrificial agents on adsorption of petroleum sulfonate on oil-field sandstone (Amoco #1) at pH 8 (TRS 10-80 from 0.25 M NaCl).

Fig. 14.6. Effect of sacrificial agents on adsorption of petroleum sulfonate on oil-field sandstone (Amoco #3) at pH (TRS 10-80 from 0.25 M NaCl).

higher, surfactant loss is substantially less after pretreatment.

1. Chem. Div. Annu. Prog. Rep. Feb. 29, 1980, ORNL-5655 (July 1980), p. 98.

14.2 Chemistry of Micellar Floods

14.2.1 Phase and Interfacial Behavior of Aqueous/Hydrocarbon Systems

(P. C. Ho, T. M. Bender,¹)

One of our approaches to elucidate the complex chemistry of micellar floods has been to investigate simplified model systems comprised of pure components and in many cases fewer classes of components than the five normally in real systems—hydrocarbon, surfactant, alcohol, inorganic salt, and water. In addition, the organic salt component (protosurfactant) in many of these studies has been of lower degree of alkylation than is usually thought necessary for micelle formation. As the systems have become more complex, the properties have been found to fol-

low a general trend toward the properties of systems containing organic salts recognized as surfactants, such as the formation of third phases, with low, if not ultralow, interfacial tensions between them under some conditions. Here we present examples from recent work.

Figure 14.7 summarizes a salinity scan of phase volumes in a system containing also *n*-octane, 1-butanol, sodium 3,5-diisopropyl salicylate, and water. The compositions are given on the figure; that of NaCl in the abscissa refers to percent in the initial aqueous phase, rather than to the whole system. Analyses of the different phases are in progress, and values presently available are given.

The pattern is similar to that of micellar-flood systems. At low salinities, there are two phases, the organic salt being mainly in the lower. At about 3.5% NaCl, there is a rather abrupt transition into a three-phase regime, in which the protosurfactant is concentrated in the middle phase. Sodium chloride is found mainly in the lower aqueous phase, but there are appreciable amounts in the middle.

Fig. 14.7. Phase volume diagrams on *n*-octane/1-butanol/aqueous NaCl/Na 3,5-diisopropylsalicylate systems (28°C): salinity scan. Salicylate, 2 wt % of total system; alcohol, 2 wt % of total system; water/hydrocarbon weight ratio, 1:1.

Figure 14.8 summarizes interfacial tensions between phases in a scan of protosurfactant concentration, in this case, 2,5 diisopropyl benzene sulfonate. Largely because of uncertainties in densities, the values are not considered highly accurate, and violations of Widom's rule are probably not significant. However, even allowing for this, some of the values are low enough to

Fig. 14.8. Phase volume diagram of *n*-octane/1-butanol/aqueous NaCl/Na 2,5-diisopropylbenzene-sulfonate systems (28°C): effect of sulfonate concentrations. Alcohol, 6 wt % of total system; NaCl, 5 wt % NaCl in water; water/hydrocarbon weight ratio, 1:1.

suggest proximity of critical end points (see Section 14.1.1A).

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14.2.2 Osmotic Coefficients of Solutions of Organic Salts

(P. C. Ho, M. A. Kahlow,¹ T. M. Bender,² J. S. Johnson, Jr.)

A primary motive for studies of aqueous/hydrocarbon systems with low equivalent-weight organic salts, such as those described in the preceding subsection, is to differentiate between properties peculiar to surfactants and those ascribable to what might be called the chemical nature of the system. Although the number of alkyl carbons on the protosurfactants is too small for the formation of micelles and other aggregates typical of surfactants to be expected, it is not

clear that these salts do not associate to some degree. One indication of complexing is gross non-ideality in the free energies of solutions. The activities of the solutes are also basic information useful in interpretation of solubilities and adsorption, as well as phase behavior. We are therefore measuring the osmotic coefficients (ϕ) of representative protosurfactants by the isopiestic method:

$$\phi \equiv \frac{-55.51 \ln a_w}{\nu m} = \frac{\nu_{\text{ref}} m_{\text{ref}} \phi_{\text{ref}}}{\nu m}$$

where a_w is the activity of water, ν is the number of moles of ions per mole of solute (here two in all cases), m is concentration in moles/kg water (55.51 is the number of moles of water/kg), and subscript "ref" refers to the reference salt whose solution is in vapor-pressure equilibrium with the solution of the solute under investigation. Osmotic coefficients for the reference salt, NaCl here, are obtained from the literature.

Figure 14.9 summarizes some of our results. The two sulfonates and the salicylate appears superficially to adhere to the pattern typical of simple inorganic 1,1 electrolytes. Values of ϕ decrease at low concentrations (ionic strength is the same as molality in these systems) to a minimum, after which they increase with increasing concentration. The normality may be more apparent than real however. The values at low concentration fall below those expected from Debye-Hückel theory with any plausible value of the distance-of-closest-approach parameter; inorganic salts almost invariably fall above. There is a trend in these results and in others we have obtained or found in the literature to lower values of ϕ at a given concentration for increasing numbers of alkyl carbons on the sulfonates.

The osmotic coefficients for the two sodium benzoates are clearly abnormal, in that they exhibit a peak at moderate concentrations. The range accessible to this method does not allow definition of the minimum nor the concentrations at which the values of ϕ begin approaching unity at infinite dilution with a Debye-Hückel slope.

Fig. 14.9. Osmotic coefficients of aqueous protosurfactant solutions (25°C).

A similar maximum has been reported for sodium benzoate.³

Maxima or inflections have also been observed with the sodium salts of aliphatic organic acids. Formation of dimers has been postulated for salts of chains as short as butyrates, and higher species from sodium octanoate upwards.⁴ Aggregation of sodium benzoates having the low degree of alkyl substitution of these would be surprising, at least to us, but we have no other explanation at the moment.

Figure 14.10 summarizes results for three-component aqueous solutions of solute mixtures of sodium *p*-cymene sulfonate and NaCl. (ϕ for mixtures are computed from the cited equation, with Σm_{ions} in the denominator of the equation.) The values for NaCl are from the literature; and the mole ratios NaCl:Na *p*-cymene sulfonate investigated were 3:1, 1:1, and 1:3. It appears that the presence of NaCl is raising the activity coefficient of the organic salt. This is in agreement with inferences previously drawn from solubility measurements in NaCl solutions.⁵ The

Fig. 14.10. Osmotic coefficients of sodium *p*-cymenesulfonate/NaCl/H₂O solutions (25°C).

crossing of the curves at low ionic strength (in this case, the sum of the molalities of the two solutes) may result from a larger Debye-Hückel distance of closest approach parameter for the organic salt than for NaCl.

1. Lawrence University; Research participant in the Great Lakes College Association/Associated Colleges of the Midwest program.

2. Co-op student, University of Tennessee, Knoxville.

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14.2.3 Small Angle Neutron Scattering (SANS) of Surfactant and Protosurfactant Solutions

(R. Triolo, L. J. Magid,¹ P. C. Ho, J. S. Johnson, Jr., D. H. Smith,² W. C. Koehler³)

Micelles and microemulsions are important in many practical applications, enhanced oil recovery, catalysis and solvent extraction, for example. However, except for relatively simple surfactant, water, and salt systems there is little agreement on the structure of the solutions or size, shape and composition of aggregates. With respect to surfactant-rich middle-phase microemulsions, which form between aqueous and hydrocarbon phases under certain conditions, some even question whether discrete aggregates rich in some components exist at all. They postulate instead arrangements involving alternating layers of oil and water, with surfactant at the interfaces, or bicontinuous structures persisting over substantial distances.

In view of the complexity of the composition, confusion is not surprising, because conventional direct methods of obtaining information on sizes of species have inherent difficulties. Interpretation of ultracentrifugation results suffers from the difficulty of assigning constituents to species (not to speak of estimating degrees of ionization or activity coefficient variations) and also from the fact that the major constituents are of approximately the same density, and the buoyancy term is consequently a small difference between large numbers. Scattering of visible light avoids the latter problem, but the measuring unit (indexed inversely by the modulus of the wave vector, $k \equiv (4\pi/\lambda) \sin \theta$, where λ is wavelength and 2θ is the scattering angle) is large compared to the probable dimensions of interest. As a result, the observation is dependent on the magnitude of free energy variations associated with concentration and refractive index fluctuations in scattering elements of dimensions comparable to wave length. The difficulty of defining components consistent with the

species present remains at least with static light scattering. X-rays have wavelengths of a few Ångströms and the values of $1/k$ in scattering at small angles are comparable to the dimensions of interest. However, scattering power is a function of atomic number, and the similarity of the various components here makes the technique relatively insensitive.

Small-angle neutron scattering avoids some of these difficulties and in principle at least should be a useful complement to the other methods. Accessible values of k are comparable to x-rays, but the scattering is dominated by hydrogen isotopes. Further, that of protons is mostly incoherent, and that of deuterons, coherent. With systems comprised of one compound in one form (e.g. a protiated surfactant) and the others deuterated, one may obtain information on the surfactant aggregates. Observations with other deuterated components may give information of the distribution of the various components in aggregates. Experiments can also be carried out on compounds selectively deuterated on a portion of the molecule to resolve details of micellar structure. We have begun studies of relatively simple solutions containing organic salts, with the long-range objective when experience warrants of applying the method to complex microemulsions. Some examples of preliminary results follow.

Sodium octanoate is near the lower end of alkyl chain length for which there is general agreement surfactant properties persist. Because its phase and other physical-chemical properties have been extensively studied and because it lies near the border between surfactants and protosurfactants, it seems a good model with which to test the technique. Its critical micelle concentration is reported to be about 0.4 M.

Figure 14.11 presents scattering intensities as a function of k for a series of concentrations. For a simple system of interacting micelles of radius R ; of which this presumably an example, the intensity scattered by the solution at a given value of k is proportional to the product of a monotonically decreasing function of k R

("self scattering") and the structure function, which is characterized by one or more peaks in k space. As a consequence, maxima in intensity can appear. The peaks disappear near (and of course below) the critical micelle concentration. When the structural function decays out or becomes constant (to the right of the maximum), the negative of the slope of a plot of $\ln I$ vs k^2 can be taken as a measure of the Guinier radius,³ R_G . For monodisperse systems, R_G is approximately R_g , the radius of gyration, and consequently is proportional to R_h , the hydrodynamic radius ($R_g = \sqrt{0.6}R_h$). For the principal peak in the figure, R_h is estimated to be 11 Å, which seems to be reasonable value. At high concentrations, a second peak is observed at higher angle. This second peak may arise from a change of structure when the concentration is greater than about one molar, or it may be caused by the second peak in the structure function. Calculations by the Mean Spherical Approximation (MSA) on model systems favor the second hypothesis, but computations specific for this system are necessary before definite conclusions can be drawn.

Sodium p(1-pentylheptyl)benzenesulfonate is an example of a surfactant with the hydrophilic group near the middle of the hydrophobic chain, a class of considerable interest at present. Its critical micelle concentration is about 0.002 M. Figure 14.12 presents scattering curves for several concentrations measured at 45°C. The maximum moves to the left with decreasing concentration, presumably because the interactions between micelles become less. The Guinier plot for the lowest concentration is shown in Fig. 14.13. Values of R_g and R_h for all concentrations are summarized in Table 14.2. The value of R_h at the lowest concentration, 17.7 Å, is in good agreement with a value obtained by dynamic light scattering, 18 Å, at 0.0089 M.⁵ Further discussion of the scattering results on this system and on a homologue, sodium p(1-heptylnonyl)benzene sulfonate (Texas #1) may be found in a recently prepared paper.⁶

With protosurfactants, one concern has been whether or not aggregates are formed, particu-

Fig. 14.11 Small angle neutron scattering of sodium octanoate solutions in D_2O , $30^\circ C$.

larly in view of the osmotic coefficient results discussed in the previous subsection. Figure 14.14 presents scattering curves for several concentrations of sodium 3,5 diisopropyl salicylate, for which the osmotic coefficients are relatively low (Fig. 14.9). It is not clear from these results that the species are monomeric, but, if aggregates are present, they do not seem to be large.

These low-equivalent-weight organic salts have strong hydrotropic properties, i.e., their aqueous solutions dissolve considerable amounts of hydrocarbons. Sodium diisopropyl salicylate is particularly effective⁷ in solubilizing toluene. A question of interest is the interaction or aggregation of the hydrocarbon with the organic salt. In Fig. 14.15 scattering results for several toluene/sodium diisopropyl salicylate ratios are presented. Although con-

siderably more data will be needed for confident conclusions concerning such water/organic salt/hydrocarbon systems, it appears tentatively that complexes between the salicylate and toluene are formed or at least that there are strong interactions.

We have obtained preliminary results on a number of other systems, including surfactant/organic salt/water and surfactant/alcohol/water. Addition of NaCl to sodium 1-(pentylheptyl) benzenesulfonate solutions moves the peak to lower k without much apparent effect on the particle dimensions. We hope that these observations may be interpreted with the help of the MSA or by alternative models. At present all our inferences from any of the results are tentative. It appears clear however that SANS will be an extremely useful method for elucidation of this class of systems.

Fig. 14.12. Scattering curves for $6\phi C_{12}SNa$ solutions at $45^\circ C$. 0.0991 M ($\square$); 0.0845 M ($\circ$); 0.0694 M ($\triangle$); 0.0547 M (+); 0.0396 M (x); 0.0247 ($\diamond$); 0.0099 (∇).

Fig. 14.13. Guinier plot for 0.0099 M $6\phi C_{12}SNa$ at $45^\circ C$.

Table 14.2 R_g and R_h values for $6\phi C_{12}SNa$ micelles in D_2O at $45^\circ C$

Concentration, M	$R_g, \text{\AA}$	$R_h, \text{\AA}$
0.0099	13.7 ± 0.1	17.7 ± 0.1
0.0247	14.5 ± 0.1	18.7 ± 0.1
0.0396	14.8 ± 0.1	19.1 ± 0.1
0.0547	15.6 ± 0.1	20.1 ± 0.1
0.0694	16.6 ± 0.1	21.4 ± 0.1
0.0845	16.6 ± 0.1	21.4 ± 0.1
0.0991	16.4 ± 0.1	21.2 ± 0.1

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Fig. 14.14. Effect of concentration of small angle neutron scattering of sodium 3,5 diisopropylsalicylate solutions in D_2O . Concentrations in moles/liter. $30^\circ C$.

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Fig. 14.15. Effect of toluene on small angle neutron scattering of sodium 3,5 diisopropyl salicylate (1.5 moles/kg D_2O , 1.2 moles/l) solutions, 30°C.

15. CHEMISTRY IN SUPPORT OF THE NUCLEAR FUEL CYCLES

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The results of studies to develop reprocessing technology for reactor fuels are not included here because regulations stipulate that such information must be distributed only under category UC-86. All work is reported under the Consolidated Fuel Reprocessing Program in topical reports and in a series of quarterly progress reports, the most recent of which is the Consolidated Fuel Reprocessing Program Quarterly Progress Report for Period Ending June 30, 1981, ORNL/TM-7914 (August 1981).

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CHEMISTRY IN SUPPORT OF THE NUCLEAR FUEL CYCLES

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DIVISIONAL PERSON-POWER AND FINANCIAL SUMMARY
FY 1981

	Funding (in thousands)	Scientific and technical person-years ^a
DOE PROGRAMS		
Fossil Energy	\$ 876	10
Fusion	100	1
Fission Energy	80	1
Basic Energy Sciences	6,910	63
Uranium Resource Assessment	50	1
Remedial Actions Program	25	—
TOTAL DOE PROGRAMS	\$8,041	76
WORK FOR OTHERS PROGRAMS		
Nuclear Regulatory Commission	\$ 100	1
Naval Research Lab — Artificial Intelligence	50	1
LBL — Molten Salt Batteries	70	1
Office of Nuclear Waste Isolation	250	2
Miscellaneous	99	1
TOTAL WORK FOR OTHERS	\$ 569	6
TOTAL FINANCIAL PLANS	\$8,610	82

^aApproximately 6 persons worked on loan to other ORNL divisions.

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CHEMISTRY DIVISION

DECEMBER 1, 1981

*DUAL CAPACITY

*ON LOAN FROM FINANCE AND MATERIALS

*ON LOAN FROM IND. SAFETY AND APPL. HP

*PART-TIME EMPLOYEE

*VISITING SCIENTIST

*STUDENT GUEST

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