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M. L. Poutsma, Division Director
L. M. Ferris, Section Head - Organic, Inorganic, and Catalytic Chemistry
O. L. Keller, Section Head - Transuranium Element Chemistry
R. E. Mesmer, Section Head - Aqueous, Separations, and Structural Chemistry

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Prepared by the
OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37831
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1. INTRODUCTION AND DIVISIONAL OVERVIEW

Performing chemical research aimed at broadening the base of fundamental understanding of materials and phenomena of relevance to future energy technologies is the dominant objective of the Chemistry Division. Except for analytical chemistry which is institutionally separate at ORNL, a broad range of chemical subdisciplines is covered, as often as possible in an interdisciplinary fashion. This Report briefly summarizes progress during the last year. Some selected capsule highlights are listed here:

(1) New insights into the quantitative nature of the ^{13}C CP/MAS solid-state NMR experiment applied to coal (an upper limit of 66% carbon detection in Illinois #6) have been obtained by a multispectrum analysis procedure to account for variations in relaxation and cross-polarization times and from a comparison of these ^{13}C -NMR results with ^{14}C radioassays for a coal O-alkylated with $^{13},^{14}\text{C}$ -doubly labeled CH_3I in a manner to avoid adsorbed reagents.

(2) New structural insights into coal have resulted from quantitative chemical alteration and degradation approaches. Deprotonation-methylation with carbanion bases has categorized benzylic C-H bonds on the basis of carbon acidity; a significant number of unexpectedly acidic sites found in Illinois #6 coal were attributed to fluorene-type structural units. Excision of aliphatic units by acid-catalyzed transalkylation showed that bituminous coals typically contain more alkyl sidechains than subbituminous coals whereas the inverse is true for crosslinking groups such as methine.

(3) The enthalpy of dilution of aqueous calcium chloride was measured at high temperatures to very low molalities by use of a heat and liquid flow calorimeter. This experimental capability increases the reliability of calculated values of excess thermodynamic properties by reducing the dependence of these values on the model used to represent the experimental results.

(4) An ion interaction-association model has provided an accurate representation of experimental results for heats of dilution of HCl to high temperatures and is consistent with the results of earlier conductivity studies above 400°C . However, this approach lacks uniqueness below 250°C since excellent fits are also obtained with the simple ion-interaction parameters. In both cases the temperature dependence was simplified by use of density as a variable.

(5) A concentration cell with hydrogen electrodes was used successfully to conduct potentiometric titrations of the chromate (CrO_4^{2-}) anion in 1 M NaCl up to 200°C , even though Cr(VI) is thermodynamically unstable with respect to H_2 under these conditions. Thus the protonation quotients for chromate forming the bichromate (HCrO_4^-) and the dichromate ($\text{Cr}_2\text{O}_7^{2-}$) anions could be derived as a function of temperature.

(6) Kinetic measurements of the thermal decarboxylation of acetate coupled with equilibrium measurements of iron-acetate ($(\text{FeAc})^{2-n}$) complex formation in aqueous systems at $100\text{--}300^\circ\text{C}$ suggest a key role for metal transport as acetate complexes in certain hydrothermal systems. Detailed computer modeling has quantified the role of geochemical parameters such as temperature, pH, CO_2 , and H_2S in the transport and deposition of gold and silver in geothermal brines.

(7) A two-dimensional ocean model that includes biological processes has been used to study the response of the oceans to increasing atmospheric CO_2 . The results indicate that the net rate of uptake at a given time is proportional to the excess carbon in the atmosphere less that in the oceans.

(8) Several syntheses in liquid ammonia aimed at producing aluminum triamide consistently gave polymeric aluminum amide-imides. These materials were demonstrated to be thermal precursors for preparing aluminum nitride.

(9) Gaseous SiS , prepared in situ from Si and H_2S , reacted with NH_3 at temperatures below 1100°C to give Si-S-N compositions that served as precursors to $\alpha\text{-Si}_3\text{N}_4$ on further heating to 1500°C in K_2 .

(10) It is possible to transform localized, nonbonding $5f$ orbitals in the actinide metals Am , Cm , Bk , and Cf into delocalized, bonding orbitals by the application of very high pressures that reduce the relative atomic volumes to the point where f_{spd} energy bands are created. X-ray studies of phase-pressure behavior (up to 52 GPa) thus have given a new and controlled way to study both periodic trends in these heavier actinides and the very complicated delocalized bonding configurations which occur naturally in the lighter actinides, for example, plutonium.

(11) Studies to examine the trend toward increased stability of the divalent state when progressing across the actinide series have focused on the metal hydrides. The formation of not only an fcc dihydride (AmH_{2+x}) but also a hexagonal trihydride (AmH_{3-y}) has been found to persist at least as far as Bk .

(12) In an extensive survey study, macrocyclic polyethers plus organophilic acids in toluene have been found to constitute strongly synergistic extraction systems for alkali, alkaline earth, and some transition metal cations. Equilibrium extraction studies as a function of pH and ligand concentrations have shown that the pronounced observed selectivities among cations depend not only on the match of ion size with macrocycle cavity size but also more subtly on the structure of annelated substituents on the macrocyclic ring.

(13) Knowledge of the structure of solvent extraction complexes, determined in the crystalline state by X-ray diffraction and in solution by NMR, has helped to elucidate the mechanism of extraction of alkaline earth cations by a synergistic alkylphosphoric acid--macrocyclic crown ether combination and of extraction of uranyl nitrate by a trialkylphosphate.

(14) In an application of photoacoustic spectroscopy to studies of electrochemical corrosion, the phase-lag approach was used at varying chopping frequencies to determine the composition (TiO_2) and thickness (20-30 nm) of the surface layer on a Ti electrode in $1\text{N H}_2\text{SO}_4$ maintained in the passive state by potentiostatic control.

(15) The sensitive balance between ring chlorination and aryl-aryl coupling products formed from anthracene radical cations in SbCl_3 -rich melts was shown to be directly related to the balance between excess chloride donors and acceptors in the melt.

(16) Kinetic studies of one-electron transfer in SbCl_3 -rich melts involving N-containing heteroaromatics such as phenothiazine revealed kinetic barriers resulting both from inherently slow reduction of Sb(III) and from ground-state complexing of the heteroaromatics in acidic melts.

(17) The ability to perform computer simulations of low-energy alkali-metal ion scattering from single-crystal surfaces has been improved by the observation that the potential curves for elastic scattering of Li^+ , Na^+ , and K^+ from Mo(001) in the 500-2500 eV energy range fit very well to an empirical form recently reported in the literature.

(18) The incident angle dependence for such ion scattering was shown to be sensitive to atomic scale roughness; this observation was used to characterize the surface topography of an amorphous $\text{Fe}_{80}\text{B}_{20}$ metallic glass.

(19) Computational modeling of crystal structures has shown that differences in the extent of out-of-plane distortion of the naphthalene nucleus in peri-substituted polyphenylnaphthalenes arise from differences in intermolecular packing forces rather than being inherent in the isolated molecules as suggested in the literature.

(20) Neutron scattering experiments with use of the "isotopic difference method" have shown a well-defined hydration shell of 7.4 water molecules surrounding Dy^{3+} ion in D_2O solution at a metal-oxygen distance of 237 pm. Comparison with our earlier results for Nd^{3+} (8.5 water molecules at 248 pm) gives model-free evidence for the effect of the lanthanide contraction on aquo ions.

(21) By use of synchrotron radiation coupled with angle-resolved electron spectroscopy, studies of photoelectron dynamics have been made for gaseous molecules and metal vapors. Molecular results include analyses of autoionization in N_2O , the Cooper minimum in the series $\text{CCl}_4\text{F}_{4-x}$, and shape resonances from core-shell electron ejection from SiCl_4 . The emphasis in the metal atom studies was on Ag, which gave a critical test of the difference between free atom and solid metal behavior in the region of the Cooper minimum, and on resonances in Yb.

(22) The most successful statistical mechanical technique for treating molecular fluids was used for the first time to treat directly a molecular mixture which is based on both attractive and repulsive forces, and the approach which will ultimately be used to greatly improve the accuracy of the approximate technique just mentioned was further developed by extending its application to lattice fluids.

(23) As an extension of earlier work on calculating infrared spectra, progress has been made in developing a semiclassical method for calculating neutron molecular spectra of polyatomic molecules.

(24) Both experimental and assessment studies relating to safety analysis of proposed nuclear waste repositories have been conducted. Experimental emphasis has been on interactions among basalt, ground water, and Np or Tc species in terms of oxidation state control, sorption, and solubility.

(25) Progress in development of chemical applications of artificial intelligence has taken place in several arenas: an expert system for printing ink chemistry; structure-activity relationships for trichothecene mycotoxins; reasoning by analogy in a safety engineering setting; and an expert system for organic synthesis.

(26) Identification of several reaction intermediates formed during the exhaustive photo-oxidative degradation of 2,4-dinitrotoluene in dilute aqueous solution revealed that the aromatic ring was activated for oxidative cleavage by substitution with hydroxyl groups and partial loss of nitro groups.

An overview of staff, organization, and funding sources is provided at the end of the Report. The major source of funding is the DOE Office of Basic Energy Sciences, in particular the Divisions of Nuclear Sciences, Materials Sciences, Chemical Sciences, and Engineering, Mathematical, and Geosciences. Also represented is work carried out for other parts of DOE and for other agencies such as the Nuclear Regulatory Commission, the Department of the Treasury, and the Department of Defense.

The presence of faculty guests and students from the U.S. and abroad continues to enhance the productivity of the Division. These interactions include professors on leave, postdoctoral fellows, graduate students, and undergraduate students in special training programs. These various collaborations are acknowledged individually in the text of this Report.

Additional information on any of the research programs described herein can be obtained by contacting individual staff members of the Division.

2. COAL CHEMISTRY

This research program is aimed at obtaining a better understanding of the chemical structure and reactivity of coal. The general approach involves the development and application of chemical and spectroscopic techniques to coal, with the interpretation of results aided by parallel studies with appropriate model compounds. New insights into the quantitative aspects of the CP/MAS- ^{13}C -NMR experiment applied to coal are described in 2.1 for a bituminous coal and its corresponding O-methyl derivatives, with a comparison of methods for preparing the O-methyl coals presented in 2.2. In 2.4 the technique of using carbanion bases to probe the distribution of acidic C-H groups in coals is applied to an O-methyl Anthracite. The potential of this method to selectively introduce phosphorus labels into coal has been explored with model compounds (2.3). Aliphatic substituents and linking groups excised from coal by the $\text{CF}_3\text{SO}_3\text{H}$ catalyzed transalkylation reaction are quantitatively compared for nine coals of varying rank in 2.5. Modifications in free radical reaction pathways resulting from restricted mobility are presented in 2.6 for the thermolysis of surface attached bibenzyl. The mechanism for the Na-K alloy induced C-C bond cleavage in the model compound, 1-benzyl naphthalene, is reported in 2.7.

2.1 Quantitative Analysis of Coals and Coal Derivatives by CP/MAS- ^{13}C NMR Spectroscopy

(E. W. Hagaman, R. R. Chambers)

In a previous report a general method of analysis of integrated intensity data from CP/MAS- ^{13}C -nmr spectra of coals was given. The method explicitly accounts for the ^1H $T_{1\rho}$ differences typically found for the aromatic and aliphatic resonance bands of coals and corrects intensity data for carbons which cross polarize slowly. The latter correction is an estimate made by assigning a single average cross polarization time, T_{CH} , to the non-protonated aromatic carbon fraction of the coal.

In this Section, coal structure parameters derived from this method of analysis, summarized below, are compared with the same quantities determined from single spectrum analysis with the cross polarization contact time, t_{cp} , constrained to 1 ms. The multispectrum analysis entails acquiring several (typically 5) spectra at contact times >2.0 ms and fitting the aromatic and aliphatic integrated intensity data independently to Eq. 1.

$$A(t) = KN \frac{T_{1\rho\text{H}}}{T_{1\rho\text{H}} - T_{\text{CH}}} (e^{-t/T_{1\rho\text{H}}} - e^{-t/T_{\text{CH}}}) \quad (1)$$

which is an approximation of the general expression, Eq. 2, describing the development of the carbon signal intensity in a spin-lock, CP/MAS- ^{13}C -nmr experiment with non-negligible $T_{1\rho\text{H}}$ relaxation.¹

$$A(t) = KN \frac{T_{1\rho\text{H}}}{T_{1\rho\text{H}} - T_{\text{CH}}} (e^{-t/T_{1\rho\text{H}}} - e^{-t/T_{\text{CH}}}) \quad (2)$$

In this expression $A(t)$ is ^{13}C signal intensity at $t = t_{\text{cp}}$, N represents the number of acquisitions and K is a constant proportional to the number of ^{13}C spins and spectrometer sensitivity. T_{CH} is the ^1H - ^{13}C cross polarization time constant under the Hartmann-Hahn condition, and $T_{1\rho\text{H}}$ is the proton spin-lattice relaxation time in the rotating frame.

Equation 1 is derived from Eq. 2 under the conditions $t_{\text{cp}}/T_{\text{CH}} \gg 1$ and $(e^{-t_{\text{cp}}/T_{\text{CH}}})/(e^{-t_{\text{cp}}/T_{1\rho\text{H}}}) \ll 1$. For the coals discussed here, with $T_{1\rho\text{H}}$ and $t_{\text{cp}} > 2.0$ ms and $T_{\text{CH}} < 350$ μs , errors of $\leq 1\%$ result from using the simplified expression. This is not true if data acquired using $t_{\text{cp}} = 1.0$ ms is included in the analysis. K is evaluated at $t_{\text{cp}} = 0$ as

$$K = A_0 \frac{T_{1\rho\text{H}} - T_{\text{CH}}}{T_{1\rho\text{H}}} \quad (3)$$

and f_a is given by $K(\text{arom})/[K(\text{arom}) + K(\text{aliph})]$.

The application of Eq. 3 requires estimates of T_{CH} for several carbon types in coals. Previous studies of coals indicate that T_{CH} values of 35, 65 and 350 μ s for protonated carbons (aromatic and aliphatic), methyl carbons (methylether) and non-protonated aromatic carbons, respectively, are acceptable estimates for the present analysis. The aliphatic resonance band is considered to have a negligible fraction of non-protonated carbons and 60% of the aromatic resonance band is considered to be non-protonated carbon.²

Table 2.1 summarizes f_a and $^1H T_{1\rho}$ for Illinois #6 vitrain and two O-CH₃ derivatives of this coal which differ in their extent of methylation. The f_a values labeled MSA are obtained from the fitting procedure, and those labeled SSA are computed from the uncorrected areas measured at $t_{cp} = 1.0$ ms. For each coal, the two f_a values are the same within our error limits.

The $^1H T_{1\rho}$ measured from the aromatic resonance band is ca. 10-20% longer than that found from the aliphatic resonance manifold.

Table 2.1 ^{13}C and ^{14}C Parameters for Ill. #6 Vitrain and Illinois #6-OCH₃ Derivatives

		Ill. #6 Vitrain	Ill. #6-OCH ₃ Derivatives				
			1 ^a	2 ^a	3 ^b	4 ^b	5 ^b
f_a	MSA ^e	.71 $\pm$ .01	.29 $\pm$ .01		.35 $\pm$ .01		
	SSA ^f	.70 $\pm$ .02	.30 $\pm$ .02	.30 $\pm$ .02	.34 $\pm$ .02	.33 $\pm$ .02	.34 $\pm$ .02
$T_{1\rho H}$ (ms)	aromatic	2.5	2.6		3.0		
	aliphatic	2.3	2.2		2.6		
$^{13}C_c$	MSA ^e	—	7.35		5.78		
	SSA ^f	—	6.80	7.11	5.72	5.66	5.38
$^{14}C_d$			5.129	4.99	3.7	3.66	3.55
$^{14}C/^{13}C$			.72 ^h	.70	.64	.65	.66

^aPrepared using (nBu)₄N⁺OH⁻/CH₃I.

^bPrepared using KOH/CH₃I.

^c $^{13}C_c$ = introduced methyls/100 coal carbons (nmr analysis).

^d $^{14}C_c$ = introduced carbon/100 coal carbons (^{14}C -combustion analysis).

^eMSA = multispectrum analysis.

^fSSA = single spectrum analysis, $t_{cp} = 1.0$ ms.

^gThis value could be as much as 5% high.

^hThis value is calculated using the average ^{13}C parameter.

This difference is responsible for the gradual increase in f_a (≤ 1 percentage point/ms) for these coals as t_{cp} is lengthened. The time constant ratio in Eq. 3 differs from unity significantly only for non-protonated carbons. Since this carbon type is principally confined to the aromatic fraction of the coal, the correction produces a decrease in f_a . With $T_{CH} = 350 \mu s$ for non-protonated carbons and $^1H T_{1\rho} = 2.0$ ms, the Illinois #6 vitrain derivatives incur a one percentage point reduction in f_a . It should be noted that the correction terms here are maximized since these coals have short $^1H T_{1\rho}$ ($\sim 2-3$ ms). Longer $^1H T_{1\rho}$'s (up to ca. 10 ms) are not uncommon in other coals and in extensively modified Illinois #6 derivatives.

The number of methyl carbons introduced into the coal matrix is determined by assuming that f_a of Illinois #6 vitrain is valid for the original coal carbon of the products, i.e., interconversion of sp^2 and sp^3 carbons does not occur as a consequence of the derivatization. Hence f_a of Illinois #6 vitrain and the aromatic resonance area of the product allow partitioning of the aliphatic resonance area into components representing coal carbon and introduced carbon. MSA and SSA listings of the quantity CH_3 introduced/100 coal carbons are found in Table 2.1 for five Illinois #6- OCH_3 derivatives. The degree of methylation of samples 1 and 2 is higher than for the remaining samples, reflecting their method of preparation (see Section 2.2). The MSA and SSA numbers for each derivative are the same within the estimated 10% error in this quantity.

The calculated values for the number of methyl groups introduced into Illinois #6- OCH_3 -3 using single spectrum analysis with $t_{cp} = 1.0, 2.0$ and 3.0 ms, is 5.72, 5.34 and 5.01, respectively, and indicate the magnitude of the error which is introduced by the $T_{1\rho H}$ differentials between the coal and its derivative. Clearly the value at $t_{cp} = 1.0$ ms is indistinguishable from the values obtained by the full fitting procedure.

Thus a 1.0 ms cross polarization contact time is a judicious compromise value consistent with a nearly complete cross polarization signal from all carbons including detectable non-protonated carbons and minimum error introduced by differential $T_{1\rho H}$ relaxation effects.

Section 2.2 discusses the determination of the quantity "introduced carbon/100 coal carbons" by ^{14}C -combustion analysis. This ^{14}C -parameter has a probable error of $<5\%$ in products demonstrably free of carbon containing reagent and serves as a reference point against which the ^{13}C parameter, "introduced methyl/100 coal carbons," determined from integrated intensity of the CP/MAS- ^{13}C -nmr spectrum, is measured. The ratio of these quantities, i.e., ^{14}C parameter/ ^{13}C parameter $\equiv ^{14}C/^{13}C$, will be unity in the event that the nmr technique measures both the introduced methyl carbon signal and the coal carbon signal with unit intensity response. It is assumed in our method of analysis that the signal from the introduced methyl carbons is detected with unit intensity response. The ^{14}C , ^{13}C , and $^{14}C/^{13}C$ parameters are listed for the Illinois #6- OCH_3 derivatives reported in Table 2.1. The values of the $^{14}C/^{13}C$ parameter are typical of a larger number of similar determinations for which this ratio is $0.66 \pm .06$. This number represents the fraction of carbon in the coal which yields the observable signal in the CP/MAS- ^{13}C -nmr experiment. Under the assumption that all introduced methyl carbons yield unit intensity response, the analysis provides an upper limit for the observable fraction of coal carbons.

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2.2 A Study of Various O-Alkylation Procedures for Coal

(R. R. Chambers, Jr., E. W. Hagaman, M. C. Woody)

For some time, we have been interested in determining to what degree the CP/MAS- ^{13}C -nmr experiment can be used in a quantitative fashion in the analysis of coal and coal derivatives. The quantitative capability of the experiment has been demonstrated for simple, diamagnetic organic compounds.¹ However, the question of whether the quantitative nmr experiment remains valid for paramagnetic substances such as coal has been a subject of some debate.

Our approach to this question has been to introduce into coal a known quantity of carbon in the form of a ^{13}C , ^{14}C double labeled reagent. The ^{14}C label serves to define unambiguously the number of carbons introduced into the coal derivative. A comparison of the ^{14}C number with the ^{13}C nmr integration provides a measure of the ability of nmr to detect the native carbons in coal.

With any method involving coal modification, there are several potential sources of error which can come into play. First, the removal of solvent and reagent byproducts requires that one use an exhaustive extraction during work-up. Since most coals are partially soluble in virtually every organic solvent, it is necessary to carefully design a chemical modification reaction in which reagents can be removed by a water extraction. Any loss of coal due to an organic extraction may introduce uncertainty in the calculation of introduced carbon. On the other hand, to the extent that reagents are incompletely removed, an appropriate correction must be factored into the calculation of total added carbon. Secondly, it is necessary that the chemical reaction not result in any re-hybridization of carbon during the course of reaction.

Initial efforts at defining a suitable coal reaction, subject to the aforementioned limitations, have focused on the methylation of heteroatom sites in coal with ^{13}C , ^{14}C CH_3I . It has

been reported that treatment of coal with $(n\text{-Bu})_4\text{NHO}^+$ in THF followed by alkylation with CH_3I produces an O-methylated coal derivative which can be freed from R_4NX^+ salts by water extraction.² This reaction was carried out on an Illinois No. 6 vitrain using various labeled reagents (Table 2.2) to determine whether this procedure represents an acceptable means for derivatizing coal for purposes of quantitative nmr studies.

The number of groups introduced per 100 total carbons derives from ^{14}C combustion analysis and the elemental analysis for the sample. These values are then adjusted to a per 100 coal carbons basis. (Column 3, Table 2.2). This adjustment corrects for the carbon introduced from all three reagents and amounts to a 10% correction. The total amount of carbon introduced from each reagent is obtained by multiplying column 3 by the number of carbons in that particular reagent. Summation of column 4 gives C_{int} , the total number of introduced aliphatic carbons. A significant fraction of C_{int} (~44%) derives from retained $(n\text{-Bu})_4\text{NX}^+$. This salt contaminant can be easily removed by solvent extraction with THF or CH_3OH . For example, THF and CH_3OH extraction of a coal sample containing 4.9% (w/w) $(n\text{-Bu})_4\text{NX}^+$ reduces the salt content to 0.19% (w/w) and 0.28% (w/w), respectively. But, the ^1H nmr spectrum of the CH_3OH extract shows that an aliphatic component ($\delta = 1.2$ ppm, $-(\text{CH}_2)_n-$) of coal is also removed by the extraction.

To alleviate the contamination by $(n\text{-Bu})_4\text{NX}^+$, an alternative O-alkylation procedure was tested which avoids the use of an organic base. This was accomplished using 2 M KOH suspended in THF and CH_3I as the alkylating agent (5 days reaction time). Two Illinois #6 coal samples were derivatized in this fashion (Table 2.3). The data in Table 2.3 show that THF retention is small. Only 3% of the total added carbon, C_{int} , derives from THF.

The number of methyl groups introduced into the Illinois coals are approximately 29% lower than the value previously observed with $(n\text{-Bu})_4\text{NHO}^+$. The DRIFT spectra of these O-methylated Illinois

Table 2.2 O-Alkylation of Illinois No. 6 with
 $(n\text{-Bu})_4\text{NHO}^+\text{-}/\text{CH}_3\text{I}$

Sample No.	^{14}C Reagent	No. Groups/ 100 Coal C	No. C/ 100 Coal C
1	CH_3I^*	5.12	5.12
	$(n\text{-Bu})_4\text{NHO}^+\text{-}$	0.25	4.0
	THF	0.029	0.12
			$C_{\text{int}}=9.24$
2	CH_3I^{**}	4.99	4.99
	$(n\text{-Bu})_4\text{NHO}^+\text{-}$	0.25	4.0
	THF	0.029	0.12
			$C_{\text{int}}=9.11$

*Contains 20.6% C-13

**Contains 19.9% C-13

Table 2.3 C-Alkylation of Illinois No. 6 with
 $\text{KOH}/\text{CH}_3\text{I}$

Sample No.	^{14}C Reagent	No. Groups/ 100 Coal C	No. C/ 100 Coal C
1	CH_3I^*	3.66	3.66
	THF	0.031	0.12
			$C_{\text{int}}=3.78$
2	CH_3I^*	3.55	3.55
	THF	0.031	0.12
			$C_{\text{int}}=3.67$

*Contains 21.4% C-13

coals show residual hydroxyl absorption at 3200-3600 cm^{-1} indicating that complete O-alkylation is not achieved. Presumably additional CH_3 groups could be added by a second $\text{KOH}/\text{CH}_3\text{I}$ treatment.

A detailed comparison of these ^{14}C results with the ^{13}C nmr integration data can be found in Section 2.1 of this report.

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2. R. Liotta, K. Rose, E. Hippo, *J. Org. Chem.* **46**, 277 (1981) and references therein.

2.3 Preparation and Characterization of Organophosphorus Compounds for Double CP/MAS- ^{13}C -NMR Studies

(R. R. Chambers, Jr., E. W. Hagaman, R. L. Ravnin)

To date most investigations into coal structure involving nmr have probed the ^1H or ^{13}C nuclei which are native to the sample or have been introduced by chemical modification. The capability of nmr to provide structural information would be enhanced if other nmr active nuclei such as ^{31}P could be introduced into coal. Two types of nmr analysis could be envisioned for such ^{31}P -coal derivatives. First, direct nmr detection of the phosphorus nucleus would allow one to generate ^{31}P spectra which can be analyzed for chemical shift value and coupling to neighboring nuclei. A second type of experiment involving double cross polarization from $^1\text{H} \rightarrow ^{31}\text{P} \rightarrow ^{13}\text{C}$ could be used to obtain ^{13}C spectra which reflect only the immediate carbon environment around each phosphorus.

The successful application of these techniques to coal make it necessary to develop chemical reactions for introducing phosphorus at native coal carbons. Here we briefly describe one approach to this problem. Earlier work has shown that carbanion sites on coal can be generated from strong bases. It

is known that such anions will react with dialkyl or diaryl phosphinic acid chlorides.² Thus several organophosphorus model compounds were prepared according to (Eq. 1).

$\text{R} = -\text{CH}_3, -\text{Ph}$

Each compound was analyzed by nmr (^1H , ^{13}C , ^{31}P), and it was found the spectra agree with the assigned structure. Typically, yields ranged from 42 - 67%.

Solid state nmr studies on these derivatives are currently underway.

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2. K. D. Berlin, T. H. Austin, M. Peterson, M. Nigabhushanam, in 'Topics in Phosphorus Chemistry,' M. Grayson and E. J. Griffith, eds., Interscience, New York, Volume 1, 1964, pp. 17-56.

2.4 Selective Methylation of Coal as a Function of pK_a of C-H Bonds: A Study of O-Methyl Anthracene

(R. R. Chambers, Jr., M. C. Woody)

Earlier we reported results on the reactivity of a bituminous coal, O-methyl Illinois No. 6, towards a series of bases of varying pK_a with a $^1\text{CH}_3\text{I}$ quench. It was found that the number of methyl groups added increased with an increase in base strength. These results were interpreted in terms of a distribution of acidic C-H groups in coal which vary in pK_a value. Some surprisingly acidic C-H bonds ($\text{pK}_a < 23.4$) were found suggesting that cyclopentadiene-like rings may be important structural subunits in coal. A minor (<0.1%)

but highly radioactive impurity in the alkylating agent gave anomalously high ^{14}C assays in this previous Illinois #6 study. Thus the actual number of $^{14}\text{CH}_3$ groups introduced were overestimated. The correct values using scrupulously purified $^{14}\text{CH}_3\text{I}$ are 0.438, 1.33, and 2.75 $^{14}\text{CH}_3$ per 100 coal carbons after three serial treatments with phenylfluorenyl-, fluorenyl-, and trityl-lithium as the base, respectively. A higher rank coal, 0-methyl anthracite, has been treated similarly and the data presented here along with some results regarding base incorporation.

The 0-methyl anthracite was prepared from anthracite coal (aromaticity = 0.92) using $(n\text{-Bu})_4\text{NHO}^-$ as the base and CH_3I as the alkylating agent.² The CP/MAS- ^{13}C -nmr spectrum of the product indicated approximately 0.1 methyl ester per 100 coal carbons was formed during the alkylation. There was also a high field resonance at -30 ppm which was assigned to entrapped CH_3I .³ This methyl iodide is tightly bound to the coal since neither high temperature nor high vacuum completely removes the retained reagent. The 0-methyl coal was exhaustively extracted with hot THF and the THF-insoluble portion dried in a vacuum oven at 110°C overnight. The insoluble fraction accounts for >99% of the weight of the whole 0-methyl coal. The dried, THF-insoluble fraction was treated with phenylfluorenyl-, fluorenyl- and trityl-lithium as before and alkylated using $^{14}\text{CH}_3\text{I}$. Radioassay gave the number of methyl groups introduced. The results from three sequential alkylations with each base are presented in Table 2.4.

No distinct trends are evident from the data except in the case of fluorenyl as the base where there is a gradual increase in the number of $^{14}\text{CH}_3$ with each successive alkylation. The data does establish an upper limit of approximately 0.008 $^{14}\text{CH}_3$ per 100 carbons that can be introduced with any of the bases. This value is significantly less than that found with 0-methyl Illinois No. 6 using the strongest base trityllithium. Since alkylation under these conditions is primarily limited to the benzylic

Table 2.4 Introduction of ^{14}C -Methyl Groups Into 0-Methyl Anthracite*

Base	Step No.	No./100 C
Phenylfluorenyl (pK_a 18.5)	1	0.0172**
	2	0.0095**
	3	0.0169**
Fluorenyl (pK_a 23.4)	1	0.0036
	2	0.0055
	3	0.0086
Trityl (pK_a 30.7)	1	0.0056
	2	0.0041
	3	0.0079

*Not corrected for base incorporation.

**A repeat of the first alkylation gave 0.0057 $^{14}\text{CH}_3/100\text{C}$, indicating a high uncertainty in these values.

C-H groups in coal, this result is not surprising for the higher rank anthracite coal has a much smaller fraction of aliphatic carbon than the lower rank Illinois coal (f_a anthracite = 0.92, f_a Illinois No. 6 = 0.70).

In general, a strong base such as an alkyllithium can react with coal in one of two fashions. It can either abstract an acidic proton from carbon or a heteroatom, or it can add to an electrophilic center such as a carbonyl group (reactions 1 and 2).

To determine whether reaction 2 is significant for coal, several 0-methylated coals (THF insoluble fraction) of varying rank were treated with ^{14}C -fluorenyl- and ^{14}C -trityl-lithium and quenched with CH_3I or H_2O . The results are summarized in Table 2.5.

Table 2.5 Base Incorporation Into O-Methyl Coals During ^{14}C -RLi/CH₃I Treatment

O-Methyl Coal*	No. ^{14}C Groups/100 Carbons	
	^{14}C -Fluorenyl	^{14}C -Trityl
Anthracite	0.0077	0.0046
Illinois No. 6	0.77 0.89(H ₂ O quench)	0.30, 0.34
Wyodak	1.59 1.67(H ₂ O quench)	0.30 0.37 (H ₂ O quench)

*The THF insoluble fractions of each coal was used in this work.

Two interesting trends are observed from the data. First, the number of fluorenyl groups introduced per 100 carbons decreases in the order Wyodak (1.59) > Illinois No. 6 (0.77) > Anthracite (0.0077). This trend is consistent with a decrease in carbonyl content (ketones, quinones, esters) of the coal as one goes up in rank. And secondly, it is found that trityllithium is less reactive than fluorenyllithium towards each coal. One manifestation of this is that the bituminous Illinois coal and subbituminous Wyodak coal show comparable reactivities towards trityl anion. These data most likely reflect the reluctance with which the hindered trityllithium adds to carbonyl groups in simple compounds.⁴

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2. R. Liotta, G. Brons, *J. Am. Chem. Soc.* **103**, 1735-1742 (1981) and references therein.
3. See Section 2.5.2.
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2.5 Studies of Coal Structure by Acid Catalyzed Transalkylation

2.5.1 New Structural Features of Coal: A Comparison of Nine Coals

(B. M. Benjamin, E. C. Douglas, P. M. Hershberger¹ J. W. Gohdes²)

Introduction: Problems associated with the investigation of chemical constitution of coal were discussed in the first part of this series.^{3,4} Coal is a complicated polymeric material made up of components derived from diverse sources. It can not be dealt with in the laboratory like a conventional polymer derived from a simple monomeric source. A frustrating property of coal derives from the fact that no individual compound exists in it in sufficient quantities that can be isolated and characterized in traditional experimental fashion. Attempts to break coal into small identifiable fragments by such methods as oxidation or pyrolysis usually go too far so that reassembly of the available information in terms of a meaningful model is dubious. Nevertheless considering all sources of information, it is generally accepted that coal is composed of aromatic clusters and hydro-aromatic clusters bound together by connecting groups such as methylene, dimethylene, and ether linkages. Other details of the substance include a variety of substituents such as phenolic hydroxyls and aliphatic side chains.

In the first report of the series, we demonstrated that a large number of substituent groups could be cleaved from the coal polymer network using an adaptation of the transalkylation reaction. Our procedure employs trifluoromethanesulfonic acid (TFMSA) as catalyst to cleave aryl-alkyl bonds. Toluene is used as reaction medium and acceptor for the severed fragments. A general mechanistic scheme for the transalkylation reaction, using ethylbenzene as an example, is shown in Fig. 2.2 in the section on model com-

pounds, 2.5.3. The reaction is visualized as a chain process which is initiated by a small amount of carbonium ions derived from impurities in the substrate. There are sufficient materials in coal to provide this step. From an extrapolation of the principles outlined in Fig. 2.2, Section 2.5.3, it is expected that aliphatic groups cleaved from coal can be identified as toluene derivatives and that a collection of free aromatics should appear.

Discussion and Results: We have refined the procedure outlined in ref. 3,4 (see Section 2.5.2 of this report) for use in comparing similar structural features of different coals. A brief description follows: Four grams of dry coal were mixed with 20 ml of toluene, and 2 ml of TFMSA were added. The reaction was allowed to take place at reflux temperature for 48 hours after which it was quenched. Toluene containing solutes were recovered for analysis. The solid residue was washed with hexane and

water and returned for further reactions. The toluene fraction was qualitatively analyzed by capillary gc/ms and quantitatively analyzed by capillary gc using an internal reference. Four successive reaction cycles were run on each of nine coals to recover most of the excisable groups.

Table 2.6 contains a list of the coals along with their ultimate analyses and the ultimate analysis of the residue from the fourth reaction cycle. Fluorine analyses reflect reaction of the acid catalyst with the coal samples. The same is true of sulfur analyses except that sulfur can be removed from some samples by dissolution of iron sulfides. Carbon/hydrogen ratios reflect changes in composition from two interactions: removal of aliphatic substituents and addition of toluene groups.

Table 2.7 contains a list of the compounds identified in the products from the first transalkylation cycle of two coals, Pittsburgh

Table 2.6 Ultimate Analyses of Parent Coals and Solid Residues after 4 Reaction Cycles (a)

Coal	C	H	N	S	F	Ash
PSOC 293 Pitt (Parent)	71.65 75.56	4.57 4.14	1.15 1.34	2.89 1.66	3.47 0.009	6.99 7.37
Ill #6 (Parent)	75.56 76.00	4.49 5.39	1.30 1.59	2.85 2.14	2.49 0.01	2.20 3.04
PSOC 213 Ky #9 (Parent)	72.61 65.48	4.39 4.60	1.10 1.47	1.73 2.82	2.38 0.01	7.14 9.41
CL&C Bituminous (Parent)	75.46 79.04	4.99 5.45	1.59 1.83	2.42 0.76	3.28 0.005	2.31 2.47
Cannel (Parent)	64.24 63.40	3.70 4.64	1.03 1.26	0.49 0.51	1.38 0.04	21.92 23.01
Wyodak (Parent)(b)	72.22 64.27	4.95 4.78	0.83 0.93	1.28 0.36	1.07 —	3.46 6.82
Texas Lignite (Parent)	51.19 46.18	3.89 4.63	0.62 0.65	2.45 2.50	1.61 0.01	26.39 26.85
PSOC 246 Lignite (Parent)	70.69 58.11	4.50 4.62	0.48 0.86	0.92 0.73	1.74 —	2.87 8.52
Anthracite (Parent)	80.43 87.61	2.01 2.20	0.71 0.90	1.96 —	2.74 —	5.25 7.21

(a) Samples were dried in vacuum (0.05 mm) for 24 hrs at ambient temperature.

(b) This sample of Wyodak coal had a lower H/C ratio than that used in refs. 3 and 4.

seam PSOC-293 and Illinois #6. These two coals produced the largest variety of cleaved products. Many of the products were present in trace amounts, and their concentrations were not estimated. Successive reaction cycles produced fewer products. The lists of compounds from other coals are shorter but in some cases include different substances. For example, Texas lignite yields 1,1-disubstituted alkanes detectable to molecular weight 378, which is equivalent to a 14 carbon chain. Most other coals do not produce ditolylalkanes with chains larger than 5 or 6 carbons.

Alkyltoluenes are produced by all nine coals. The longest chain alkyltoluenes, up to 20 carbons, are derived from Illinois #6 coal, whereas PSOC-293 gave toluene substituted with up to C-14. North Dakota lignite PSOC-246 gave a shorter chain length, up to toluene C-6.

Several unsubstituted aliphatic hydrocarbons, chain lengths up to C-20, are derived from PSOC-293. These hydrocarbons are not found in detectable quantities when the same coal is treated in refluxing benzene without acid. The reason for the difference may be that the pores in the coal polymer are opened by action of the acid making extraction more efficient. Free unbranched aliphatics are not known to be a product of acid catalyzed fragmentation of substituted aromatics.

Numerous isomers of indanes, tetralins, and naphthalenes substituted with methyl or alkyl groups are abundant in the list in Table 2.7. It is not known at this time if all these compounds are derived directly from coal or from secondary reactions of materials cleaved from coal. Because model experiments have not given large amounts of these compounds, it is believed that part of them are severed from coal, having been attached by $-CH_2-$ moieties for example.

The presence of extremely low concentrations of polynuclear aromatics, 3 or more condensed rings, and their derivatives is disappointing. The list includes only phenanthrene, methyl-, dimethyl-, and trimethyl-phenanthrenes, and

pyrene. It is possible that many of the polynuclear aromatics in coal are bound directly to each other. Another possibility is that aryl-aryl bonds are formed by Scholl type reactions⁵ under acid treatment. They then remain fixed in the polymer. Experiments with model systems support this possibility.

In order to obtain a quantitative comparison of structural features of the nine coals used in this research, we selected for critical examination the twenty most abundant compounds from the list in Table 2.7. The concentrations were estimated by comparing their peak areas in the capillary gc traces with an internal reference. Concentrations were calculated by assuming that each carbon in any compound produces an equal response from the flame ionization detector. This method was necessary because it was impossible to obtain all isomers or compounds to establish response factors. For example, there are six positional isomers of ditolylmethane and five of them appear as resolved peaks in the gc. There are forty-two isomers of methyltolylanthracene. Compounds tested by the analytical method produced errors no greater than 10%. The data are recorded in Table 2.8. Concentrations are given in numbers of each compound per 100 carbon atoms in the original coal. Concentrations in the first reaction cycle were generally one half to two thirds of the total in four cycles.

Most of the compounds listed in Table 2.8 are toluene derivatives of the groups excised from coal. Thus ethyl groups originally attached to a coal aromatic cluster appear as ethyl toluene. The same is true for propyl, butyl, etc. Methylenes and methines excised from between coal aromatics appear as ditolylmethane and tritolylmethane, respectively. Special attention is given to 1,1-ditolyl- derivatives. Work with model systems has shown that ethyl groups originally attached to single polynuclear aromatics, such as in ethylphenanthrene and ethylpyrene, appear in the final product as ethyltoluene and 1,1-ditolyethane. The reactions involved are discussed in Section 2.5.3. In other experiments, it was shown that

Table 2.7 Compounds Found in the First Transalkylation Cycle^{a,b}

Compound	Pitt Seam PSOC-293	Ill #6	Compound	Pitt Seam PSOC-293	Ill #6
Nonane	+	-	Indane-C-6	+	+
Ethyltoluene	+	+	Trimethylnaphthalene	+	+
Octane	+	-	Phenyltolylmethane	+	+
Isopropyltoluene	+	+	Trimethylnaphthalene	+	+
Indane	+	-	Indane-C-6	-	+
n-propyltoluene	+	+	Trimethylnaphthalene	+	+
Methylindane	+	+	Trimethylnaphthalene	+	+
iso-Butyltoluene	+	+	Indane-C-5	+	-
sec-Butyltoluene	+	+	Indane-C-6	+	-
Methylindane	+	+	Fluorene	+	-
Methylindane	+	+	Indane-C-6	+	-
n-Butyltoluene	+	+	Trimethylnaphthalene	+	-
2-Methyl-1-tolylbutane	-	+	Indane-C-6	+	-
Naphthalene	+	+	Indane-C-7	+	+
Methyltetralin	+	-	Ditolylmethane	+	+
Methyltetralin	+	-	1,1-Ditolylethane	+	+
3-Methyl-1-tolylbutane	+	+	Nonyltoluene	+	-
Methyltetralin	+	+	1,2-Ditolylethane	+	+
Dimethylindane	+	+	1,2-Ditolylpropane	+	+
Dimethylindane	+	-	2,2-Ditolylpropane	+	-
n-Pentyltoluene	+	+	1,1-Ditolylpropane	+	+
Dimethyltetralin	+	-	Phenanthrene	+	-
Dimethyltetralin	+	+	1,1-Ditolylbutane	+	+
Dimethyltetralin	+	-	Aliphatic Hydrocarbon	-	+
Dimethylindane	+	-	Aliphatic Hydrocarbon-C-20	+	-
Methylnaphthalene	+	+	1,1-Ditolylpentane	+	+
Methylnaphthalene	+	+	Undecyltoluene	+	-
Dihethyltetralin	-	+	Methylphenanthrene	+	+
Hexyltoluene (Branched)	-	+	Methylphenanthrene	+	-
Indane-C-3	+	+	Dimethylphenanthrene	+	-
Indane-C-3	+	+	1,1-Ditolylhexane	-	+
Indane-C-3	+	-	Tolyl-C-13	+	+
Indane-C-4	+	+	Dimethylphenanthrene	+	-
Indane-C-4	+	+	Dimethylphenanthrene	+	-
n-Hexyltoluene	+	-	Trimethylphenanthrene	+	-
Indane-C-4	+	+	Tolyl-C-14	+	-
Indane-C-4	+	+	Tolylindane-C-3	+	-
Heptyltoluene	+	+	Tolylindane-C-4	+	-
Methylpropyltetralin	+	-	Tolylindane-C-5	+	-
Hydrocarbon, Aliphatic	+	-	Tolylidiphenylmethane	-	+
Octyltoluene	+	-	Pyrene	+	-
Dimethylnaphthalene	+	+	Tritolylmethane	+	+
Dimethylnaphthalene	+	+	Methyltolylindane	+	+
Propyltetralin	+	-	Methyltolylindane	+	-
Propyltetralin	+	-	Methyltolylindane	+	-
Dimethylnaphthalene	+	+	1,1,2-Tritolylethane	+	+
Dimethylnaphthalene	+	+	Tolyl-C-16	-	+
Indane-C-5	+	+	1,1,3-Tritolylpropene	+	+
Indane-C-5	+	+	1,1,3-Tritolylbutene	-	+
Indane-C-6	+	-	Tolyl-C-19	-	+
Octyltoluene	-	+	Tolyl-C-20	-	+
Nonyltoluene	-	+			

^a Multiple listings of compounds occur when two or more isomers were detected.

^b The minus sign (-) indicates the compound was not present in sufficient quantity to be detected and characterized by our gc/ms technique.

TABLE 2.8 Numbers of Groups per 100 Carbon Atoms in Four Cycles of Transalkylation

Compound Isolated	Pitt PSOC293	Ill #6	KY #9 PSOC213	CL&C Bituminous	Cannel	Wyodak	Texas Lignite	PSOC246 Lignite	Anthracite
Ethyltoluene	0.337	0.321	0.226	0.287	0.271	0.0346	0.150	0.0677	0.0391
Propyltoluene	0.143	0.167	0.119	0.122	0.110	0.0507	0.0858	0.0297	0.0164
Butyltoluene	0.0402	0.0395	0.0301	0.0365	0.0433	0.0145	0.0326	0.0105	—
Pentyltoluene	0.0124	tr	0.0087	0.0138	tr	0.0025	0.0118	0.0034	—
Phenyltolylmethane	0.0156	0.0191	0.0352	0.0167	0.0221	0.0361	0.0542	0.0606	tr
Ditolylmethane	0.761	0.865	0.975	0.741	0.606	0.660	0.998	0.463	0.175
1,1-Ditolylethane	0.0216	0.0565	0.131	0.0434	0.0281	0.199	0.155	0.182	0.0039
1,2-Ditolylethane	0.0559	0.0512	0.0356	0.0418	0.0446	0.0103	0.0458	0.0042	0.0078
1,1-Ditolylpropane	—	0.0125	0.0370	0.0178	0.0030	0.0303	0.0202	0.0241	—
1,2-Ditolylpropane	0.0124	0.0035	0.0133	0.0005	—	—	0.0280	—	tr
1,1-Ditolylpropene	0.0350	0.0379	0.0261	0.0277	0.0215	tr	0.0165	—	—
1,1-Ditolylbutane	—	—	—	—	—	0.0045	0.0018	0.0033	—
Tritolylmethane	0.0076	0.0226	0.0609	0.0164	0.0223	0.221	0.104	0.379	0.0096
1,1,2-Tritolylethane	0.0131	0.0170	0.0406	0.0112	0.0060	0.0791	0.0793	0.0757	—
1,1,3-Tritolylpropene	0.0095	0.0174	0.0283	0.0139	0.0137	0.0219	0.0283	—	—
Naphthalene	0.0070	tr	tr	—	0.0168	—	0.0015	—	—
Methylnaphthalene	0.0667	0.0560	0.0737	0.0810	0.166	0.0438	0.141	0.0311	—
Dimethylnaphthalene	0.0324	0.0299	0.0262	0.0300	0.0419	0.0160	0.0401	0.0115	—
Trimethylnaphthalene	0.0070	0.0082	0.0052	0.0057	0.0009	0.0058	0.0108	0.0023	—
Methyltolyl naphthalene	0.0271	0.0106	0.0352	0.0165	0.0215	0.0112	0.0210	—	—

1-substituted aliphatics undergo transalkylation many times slower than their 1,1-disubstituted counterpart. For this reason, we believe that part of the 1,1-diarylalkanes represent a similar structural feature in coal. The same reasoning applies to 1,2-diarylalkanes.

1,2-Diphenanthrylethane undergoes reaction at a finite rate whereas 1,2-diphenylethane reacts very slowly. A second source of 1,2-ditolylalkanes may be from rearrangement of 1,1-diaryl systems with chain lengths longer than two, especially certain branched chain species. Even in these compounds, 1,2-migration takes place at a much slower rate than aryl interchange. 1,2-Diphenylethane does not rearrange at all. Therefore these 1,2-diaryl systems must be present to a small extent in coal.

Naphthalene derivatives are abundant in the coal transalkylation products. As pointed out earlier, the presence of these compounds is interpreted as a consequence of their cleavage from the periphery of the coal polymer network as well as from positions between aromatic clusters. Methyltolynaphthalene is somewhat of a puzzle. Several isomers of the compound are derived in varying amounts from most of the coals. The mechanism through which toluene becomes attached to naphthalene is not understood. Similar compounds have not been observed as products from any model system tested. We are equally uncertain about the origin of 1,1,3-tritolylpropene. An explanation of the formation of these two latter compounds is deferred for later work. Their presence appears to be diagnostic of the reactivity of specific features of coals since their concentrations are different in the several coal types.

Analysis of the data in Table 2.8 reveals several trends. Aliphatic substituents such as ethyl, propyl, etc. are more abundant in bituminous coals and drop to low concentrations in subbituminous coals and lignites. The connecting group, methylene, represented by ditolylmethane, shows nearly the same con-

centration in nearly all the coals except anthracite and North Dakota lignite PSOC-246. In contrast the cross-linking group, methine, represented by tritolylmethane, shows a wide concentration difference, varying from 0.0076 per 100 carbons in a bituminous coal to 0.38 in a lignite. The abundance of cross-linking groups like methine and 1,1,2-trisubstituted ethane are expected to be related to solubility of the corresponding coal. This conjecture is borne out roughly since PSOC-293 and Illinois #6 are 15% and 14% soluble in tetrahydrofuran, whereas PSOC-246 and Wyodak are about 8% soluble.

Texas lignite does not fit the patterns just discussed. It differs from the other coals in several respects. It contains more long chain aliphatic substituents and has a higher ash content. It also produces more toluene soluble material after transalkylation, see Table 2.9. The original Texas lignite is 9.8% soluble in pyridine, 13% soluble on a daf basis.

It is possible to obtain the n-propyl/iso-propyl substituent ratio from the gc traces. n-Propyl and iso-propyl are not interconverted⁶ at a rate competitive with transalkylation. Our work with pure model compounds shows no detectable interconversion under the experimental conditions. Therefore, those ratios listed in Table 2.10 represent the isomer ratios derived from coal. The bituminous coals had nearly equal numbers of n- and iso-propyl. It is tempting to speculate that these findings are related to the relative stabilities of the two isomers associated with conditions during coalification. It is also conceivable that sources of material from which the coal is derived are responsible; that is, refuse from some vegetation may have principally iso-propyl side chains. A similar treatment of the longer chain aliphatic substituents is not fruitful because their concentrations are low and errors in analyses may be larger. In most of the coals, three butyl isomers were apparent. Two pentyl isomers were observed and only one hexyl, heptyl, and octyl isomer

Table 2.9 Total Product Yields From Transalkylation
Reactions Based on 4 g Starting Coal

	Weight of Solid Residue(a)	% Change	Weight of Toluene Solubles(b)	% of Starting Coal(c)
PSOC 293 Pitt	4.38	9.6	1.11	27.7
Ill #6	4.27	6.7	.820	20.5
PSOC 293 Ky #9	4.37	9.2	.725	18.1
CL&C Bituminous	4.44	11.1	.969	24.2
Cannel	4.01	0.31	.567	14.2
Wyodak	4.21	5.3	.879	22.0
Texas Lignite	3.42	-14.5	1.12	28.1
PSOC 246 Lignite	3.96	-1.0	.377	9.4
Anthracite	4.28	7.0	.144	3.6

(a) Weight of the solid residue recovered after the fourth transalkylation cycle. The value does not include small losses encountered during transfers. Losses of 30 to 100 mg are possible due to material clinging to filter paper and equipment.

(b) These values were obtained by combining all toluene and hexane solutions and allowing them to evaporate at ambient temperature to minimize losses of volatile coal derivatives such as ethyltoluene.

(c) Based on dry whole coal. Some of the material did not pass through the capillary gc column. These values include the weights of toluene substituents.

Table 2.10 n-Propyl/isoPropyl Substituent
Ratio for 9 Coals

PSOC 293, Pitt.	1.0
Ill. #6	1.24
PSOC 213, Ky. #9	0.62
CL&C Bituminous	0.69
Cannel	0.86
Wyodak	0.057
Texas Lignite	0.35
PSOC 246 Lignite	0.059
Anthracite	0.44

was found. It has been shown⁷ that sec-butylbenzene and iso-butylbenzene interconvert when treated with Friedel-Crafts catalyst. No n-butylbenzene is formed, and n-butylbenzene does not isomerize.

Table 2.9 illustrates two aspects of the reaction. The first consideration is the change in weight of the solid residue after four reaction cycles. For most samples, the solid residue gained weight, a fact which reflects reactions of the coals with the solvent and the acid catalyst. It was shown earlier⁴ that Kentucky #9 coal adds 2.4 tolyl

groups per 100 carbon atoms in the first cycle.

Although it was not the objective of this work to solubilize or liquefy coal, some solubility data were available. Approximately one third of the original weight of the coals appeared in the toluene soluble part. PSOC-246 lignite and anthracite gave the lowest toluene solubility. Toluene substituents and heavy nonvolatiles are included in this fraction. The solid residue from Illinois #6 was 4.2% soluble in THF, a lower value than the starting coal. The present reaction conditions are not suitable for liquefaction.

Conclusions: More than 115 compounds have been identified in the products from the transalkylation of coals. Some of the compounds are common to all of the coals, but the composition of the product mixture varies depending on the type and rank of the individual coal. A comparison of nine coals has been made from a quantitative estimate of the twenty most abundant substituents and connecting groups. It is apparent that the more soluble coals have the greater number of substituents and connecting groups, and the less soluble coals have the greater number of cross-linking groups. Several substances of unknown origin appear in the product list, and some of these substances are major products. Therefore, it will be necessary in future work to determine how they are related to coal structure.

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2.5.2 New Structural Features of Coal: Anomalous Results Caused by Adsorption of Reagents

(B. M. Benjamin, E. W. Hagaman, R. R. Chambers
E. C. Douglas)

In the previous report,¹ we showed that the acid catalyzed transalkylation reaction is useful for examining a variety of structural aspects of coal. In our procedure, trifluoromethanesulfonic acid is used as catalyst for the cleavage of aryl-alkyl bonds. Toluene is used as reaction medium and acceptor for the severed fragments. The present method has an advantage over former procedures² in which phenol was used as acceptor. Phenol and its derivatives are more susceptible to secondary reactions such as cyclization and degradation.

We have developed the method further for use in making a qualitative and quantitative comparison of similar chemical features of several coals. While carrying out this work, we encountered an experimental problem which can cause anomalous results. Our procedure¹ calls for four separate reaction cycles for each coal sample. The four cycles are necessary to recover most of the excisable substituents because in any single reaction, the acid catalyst is slowly consumed by reaction with both coal and solvent. Evidence for these reactions is found in the increased sulfur and fluorine content of the recovered solid coal (see Table 2.6, Section 2.5.1) and in the occurrence of cresol in the recovered solvent fraction. Following each reaction cycle in the reaction sequence, the residual solid coal is recovered on a filter and washed until free of organic and inorganic solubles. In the original procedure, after the reaction was quenched by the addition of sodium bicarbonate and water, the coal slurry was poured on a fritted glass funnel protected by filter

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2. GLCA/Science Semester Student from Carleton College, Northfield, Minnesota.
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paper, and the toluene filtrate was collected for analysis. The solid residue was prepared for the next reaction cycle by washing it with ether followed by hot water, and the washing process with ether and hot water was repeated. The solid coal was then dried in vacuum before further treatment or analysis. Ether was chosen to remove the soluble organics because it renders the coal flocculent and easily filterable while, on the other hand, a more conventional hydrocarbon wash solvent, such as hexane, renders the reaction mixture difficult to handle and extremely slow to filter.

The consequence of the practice of washing coal with ether results in small amounts of ether being adsorbed on the coal. Some of this ether, but not all of it, is removed after washing the coal with hot water and evacuating it. A small amount of ether clings tenaciously to the coal. It is introduced into the next reaction cycle and, under transalkylation conditions, suffers carbon-oxygen bond cleavage,

and the ethyl group becomes bound to the acceptor, in this case toluene. Through these means, the ethyl group bound to coal is overestimated. When hexane is used as wash solvent, the residual adsorbed hexane is unreactive under the reaction conditions, and it produces no anomalous result.

Table 2.11 presents a comparison of results for the ethyl substituent determined by using both ether wash and hexane wash on two coals, Wyodak and anthracite. It is not expected that large amounts of any substituent can be found on anthracite. Therefore, the numbers listed for cycles 2 and 3 following ether washes are suspect, and the correct numbers of ethyl substituents are found opposite the lines labeled hexane wash. The same problem is seen to exist for Wyodak coal. The data listed for ethyl groups in Wyodak coal opposite the lines labeled hexane wash are a correction to that recorded in the previous report.¹ Recorded values of other substituents are not effected.

Table 2.11 Concentrations of Ethyl Groups Found in Anthracite and Wyodak Coals

	Cycle 1(a)	Cycle 2(a)	Cycle 3(a)	Cycle 4(a)	Total No./100 Carbons
Anthracite					
Ether Wash					
Ethyltoluene	0.026	0.060	0.19	(b)	0.094(c)
Ditolylethane	0.0039	0.0038	0.0065	(b)	0.0049(c)
Hexane Wash					
Ethyltoluene	0.081	0.031	0.028	0.024	0.039
Ditolylethane	0.0045	0.0025	0.0029	0.0016	0.0039
Wyodak					
Ether Wash					
Ethyltoluene	0.078	0.48	0.57	0.64	0.80
Ditolylethane	0.23	0.41	0.39	0.30	0.62
Hexane Wash					
Ethyltoluene	0.12	0.026	0.015	0.0065	0.079
Ditolylethane	0.11	0.054	0.042	0.024	0.11

(a) values for the individual cycles are recorded in mmoles found in 4g coal. The values in the totals column are recorded in numbers of ethyl groups per 100 carbon atoms in the starting coal.

(b) The fourth cycle was not completed.

(c) Summed over three cycles only.

The occurrence of ditolyl substituted ethane will be dealt with in a subsequent paper.

The adsorption of solvents and reagents subsequent to performing extractions and reactions upon coal has been a subject of previous frustrations.³ Perhaps the widest recognized example is found in the extraction of coal with pyridine. Variable amounts of pyridine adhere persistently to the extract and the residue. Collins,⁴ et al, studied the problem using carbon-14 labeled pyridine. They found that most of the radio-labeled pyridine could be replaced by exchange with unlabeled pyridine, but between 0.2-1.7% of the labeled reagent remained. Chambers⁵ showed that some pyridine could be washed out of the coal using 5% v/v tetrahydrofuran in water but that some pyridine remained, 0.29% even in *O*-methylated coal. In a similar way, Chambers⁶ showed that tetrahydrofuran cannot be removed completely from coal by washing it with water and evacuating it.

A dramatic example of adsorbed reagent is revealed in the CP/MAS-¹³C-nmr spectrum of an anthracite-*O*-CH₃ coal shown in Fig. 2.1. This derivative was prepared by treating a suspension of the coal in THF with 91.2% ¹³CH₃I and 2 molar KOH. After stirring at room temperature 5 days, the solution was neutralized (HCl), the solvent removed under vacuum and the product washed with hot water and dried overnight at 0.05 mm and 110°C. The spectrum of this material, Fig. 2.1a, expectedly differs from that of the anthracite from which it was prepared by the appearance of a new low intensity resonance band (50-52 ppm) representing ester methoxyl carbons and, unexpectedly, by a more intense resonance at -30 ppm which partly overlaps the first upper aromatic sideband. The narrow half-width of the peak suggests that the resonance arises from a single entity. The unusual chemical shift is strong evidence that the resonance is due to methyl iodide, whose solution chemical shift at infinite dilution in benzene is -25 ppm.

To support this assignment, an exchange experiment was performed. The anthracite-*O*-CH₃

Fig. 2.1. CP/MAS-¹³C-nmr spectrum of anthracite *O*-CH₃ coal: (a) original *O*-methylated coal, (b) *O*-methylated coal exchanged with normal CH₃I, and (c) difference spectrum.

derivative was stirred at room temperature for 5 days in a THF solution containing 50 molar equivalents of natural abundance methyl iodide (based on estimated methyl iodide incorporation in the coal from nmr integration). Solvent and excess halide were removed, and the sample was dried overnight as before. The spectrum of the product, Fig. 2.1b, differs from that of its precursor only by a diminution in the intensity of the methyl iodide resonance as is most clearly seen in the difference spectrum C, (=a-b), in Fig. 2.1.

The loss in intensity is in accord with expectation for partial exchange of enriched methyl iodide. If the isotope dilution had occurred statistically, the -30 ppm resonance

would have been effectively eliminated from the spectrum of the product (Fig. 2.1b). That ca. one half of the enriched methyl iodide did not exchange under the reaction conditions but did survive the drying procedure suggests the existence of very strong adsorption, perhaps through intercalation of the methyl iodide in the coal.

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2.5.3 Reactions of Selected Model Systems Related to the Transalkylation of Coal (B. M. Benjamin, J. W. Gohdes¹)

Introduction: Use of the phrase "Models for Coal" seems ostentatious. It is an oversimplification which ignores the fact that more than one hundred years of research has revealed little about the chemical constitution of coal. It presumes that a simple compound will exhibit a chemical behavior similar to coal. We prefer the phrase "models for coal partial structures" or "models for structures thought to be present in coal." Regardless of the choice of words, if the behavior of coal toward any chemical reaction is investigated, it is necessary to know how a series of simpler systems behave toward the same reaction conditions. Some of the information can be found in the literature, but

usually certain critical definitive experiments are lacking. This is true for the transalkylation reaction. Although the literature is replete with mechanistic studies of the transalkylation reaction, the examples are limited to the most simple structural entities like ethylbenzene and other mono-substituted alkyl benzenes. Sparse information is found on more highly substituted systems, and virtually no work has appeared on polycyclic aromatics.

We have reported our work on the transalkylation of several different structural types related to those obtained from coals.² The choice of those compounds was intended to reveal how the simpler substituted aromatics behave under our experimental conditions. Also two more complex compounds 1,1-diphenylethane and 1,1-diphenylpropane were investigated to assess the reactivity of the 1,1-disubstituted system and the stability of the reaction products. In this report, we consider the reactivity of alkyl substituted polynuclear aromatics, how they compare with the simpler systems and how they influence product yields in mixtures. This approach is more closely related to reactions with coal.

It is appropriate to review the currently accepted mechanism³ of the transalkylation reaction. Figure 2.2 shows a reaction scheme modified to conform to our reaction conditions. Ethylbenzene serves as an example of reactant, but the phenyl ring may be visualized as any larger aromatic. The reaction is a chain process which is initiated by carbenium ions formed from impurities in the reagents. Hydride is abstracted from the α position of the reactant. The resulting benzylic carbenium ion is attacked by solvent, toluene, and after deprotonation of the intermediate, 1-phenyl-1-tolyethane is formed. Reprotonation at the ipso position of the phenyl ring produces an intermediate from which benzene and ethyltoluene are products. Continuation of the chain process (not shown in Fig. 2.2) in the presence of excess toluene gives a product mixture consisting of ethyltoluene, 1,1-ditoly-

Fig. 2.2. Mechanism of the transalkylation of ethylbenzene in the presence of toluene as solvent.

ethane and benzene. Inspection of Fig. 2.2 reveals that product distribution may depend on acid catalyst strength and the presence of hydride donors or acceptors. This possibility has been recognized, but the experiments were not definitive.⁴

Results and Discussion: Transalkylation procedures were similar to those reported earlier.² Reactants were purchased or were synthesized by methods found in the literature, and they were purified before use.

Ethylbenzene transalkylates at a very slow rate. Only 1.2% of product is formed in 48 hours under the experimental conditions. The product consists of 0.19% ethyltoluene, 0.66% 1,1-ditolylethane, and 0.35% of other compounds. *n*-Propylbenzene gives about the same results. *iso*-Propylbenzene reacts 10^2 times faster, and no 1,1-diarylpropane is formed. The mechanism is different, probably involving free secondary cationic intermediates. Ethyl substituted polycyclic aromatics react faster than the monocyclic counterparts. 9-Ethylphenanthrene gives 3.2% product in 48 hours, and 2/3 of the product is 1,1-ditolylethane.

In sharp contrast, 1-ethylpyrene undergoes 33.6% conversion in only 6 hours. Approximately half of the product is 1,1-ditolylethane. 9-Ethylanthracene gives 40% conversion in 6 hours. Again, half of the product is ethyltoluene, and half is 1,1-ditolylethane. All three of the ethyl substituted polynuclear aromatics give small amounts of other products. The reactions produce the expected amounts of free aromatics.

Attempts to transalkylate 1,2-di-(9-phenanthryl)-ethane produced only trace amounts of products, ditolylethane and phenanthrene in 48 hours. The result is comparable to that found earlier² for 1,2-diphenylethane for which no products were found. In contrast with the above results, 1,2-di-(9-anthryl)-ethane gave 40% conversion in 6 hours. The main product was ditolylmethane, 16%. Between 5% and 7% of methylanthracene, methyltetrahydroanthracene and tolylanthracene were formed. Only 6% free anthracene was found. Small amounts of many other products were identified including numerous hydroanthracenes and more highly condensed ring compounds. Clearly, the substituted anthracene reacts by a different mechanism, probably radical cations.⁵

An attempt was made to determine relative reaction rates by running competitive reactions using, for example, *iso*-propylbenzene as reference in a mixture with 9-ethylphenanthrene or 2-ethylanthracene. In each of these reactions transalkylation took place 2 to 5 times faster, but the product distribution was quantitatively different. Similar observations were made when the 1,2-diarylethanes were reacted with *iso*-propylbenzene present. It is presumed that the presence of other aromatics, particularly polynuclear aromatics increases the rate of transalkylation. These results were confirmed by reacting ethylbenzene in the presence of phenanthrene. Within 48 hours, 9.3% ethyltoluene and 1.8% 1,1-ditolylethane were formed. In the presence of anthracene, ethylbenzene gave 11% ethyltoluene and 1.9% 1,1-ditolylethane. Probably protonation of the polynuclear system gives a cation resembling

a good hydride abstractor, which accelerates the reaction by increasing the number of chain initiation steps.

Conclusion: The following summary consists of general statements to be used in rationalizing the coal transalkylation reaction in comparison with model compound reactions:

Simple alkylsubstituted monocyclic aromatics transalkylate at a very slow rate.

Alkylsubstituted polynuclear aromatics transalkylate 10-100 times faster than their monocyclic counterpart.

An alkylsubstituted aromatic transalkylates 2-5 times faster when mixed with a polynuclear aromatic.

Based on the generally accepted structure of coal as substituted polynuclear aromatic clusters, we believe that the above observations account for the rapid production of many of the products during the transalkylation of coal.

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2.6 Effects of Surface Immobilization on the Thermolysis of Model Coal Structures: Surface Attached Bibenzyl

(T. D. J. Dunstan,¹ A. C. Buchanan, III, M. L. Poutsma)

The α,ω -diphenylalkanes, $C_6H_5(CH_2)_n C_6H_5$, represent models for the aliphatic bridging

groups between aromatic clusters in coal, and the free radical mechanisms for the thermolyses of these compounds in the fluid phase have received considerable attention.²

However, the initially formed reactive intermediates in coal will remain covalently attached to the cross-linked macromolecular framework; hence their reactivities may be subject to restraints in mobility. We are exploring this complication by studies of the thermolysis of model compounds immobilized on inert solids.

Preliminary results for the thermolysis of several diphenylalkanes attached to a silica surface have been presented.³ This report presents detailed studies of the initial products formed by thermolysis of bibenzyl (1,2-diphenylethane) immobilized on a silica surface and the preliminary results on the effect of changes in the degree of surface coverage on the product distribution.

Experimental: Attachment of p-Hydroxybibenzyl to the Silica Surface-Preparation of a High Surface Coverage Batch. Cab-O-Sil (a fumed silica; $200 \pm 25 \text{ m}^2\text{g}^{-1}$) was dried in an open air oven at 210°C for 4.5 h. A slurry of 8 g of the dried Cab-O-Sil in dry benzene was mixed well with 4.8 g of p-hydroxybibenzyl in benzene. The solvent was removed on a rotary evaporator at 80°C and 0.025 torr. The resulting powder was transferred into a sealing tube, evacuated, and degassed thoroughly by 8 freeze-pump-thaw cycles with intermittent purging using purified argon. The tube was sealed under vacuum (4×10^{-3} torr) and heated at 225°C for 1 h. The reaction of the phenol 1 with surface hydroxyl groups⁴ produced the surface attached bibenzyl 2.

Unreacted 1 was sublimed off at 300°C (5×10^{-3} torr) for 0.5 h, and the resulting powder was thoroughly mixed with a mini-mill.

Assay of the Bibenzyl Attached Cab-O-Sil.

About 0.1 g of the above sample was stirred overnight in 10 ml of 1 N NaOH. Into the clear solution, 1.0 ml of solution containing an internal standard (p-hydroxybiphenyl) in NaOH was added. The solution was acidified and extracted with dichloromethane. The CH_2Cl_2 fraction was dried over anhydrous sodium sulphate and the solvent evaporated to leave a white residue of phenols. About 0.2 ml of silylating reagent (BSTFA:pyridine = 3:1 (v/v)) was added to the residue, and this solution was heated on a steam bath for 0.5 h. The silylated phenols were analyzed by GC (12 m x 0.25 mm id column coated with OV-101), and the amount of silylated p-hydroxybibenzyl was calculated using peak areas and experimental molar response factors. The maximum surface coverage that could be obtained using the experimental procedures described above was found to be 0.465 ($\pm 2\%$) mmol of 1 per gram of derivatized silica.

Preparation of Derivatized Cab-O-Sil With

Lower Surface Coverages. Two batches with lower surface coverages were prepared using smaller proportions of 1 to Cab-O-Sil. A batch with 0.158 mmol of 1 per gram of the sample was prepared using 1.0 g of the phenol to 23 g of Cab-O-Sil, and a surface coverage of 0.045 mmol g^{-1} was obtained using 0.5 g of 1 to 45 g of Cab-O-Sil.

Thermolysis of Bibenzyl Immobilized on

Cab-O-Sil. Thermolyses were carried out in evacuated sealed Pyrex tubes with the heated end containing the solid (0.25 to 0.50 g) and the other end held at 77 K to collect volatile products as formed. The volatile products were analyzed by GC using p-xylene and 2,2-diphenylpropane as internal standards. The p-hydroxybibenzyl in the trap was determined by GC after silylation with p-hydroxybiphenyl as internal standard. Products attached to the silica after thermolysis were liberated as phenols for analysis using 1 N

NaOH as described above. They were analyzed by GC after silylation using 2,5-dimethylphenol and p-hydroxybiphenyl as internal standards. Products were identified by GC/MS and with the aid of authentic standards.

Results and Discussion: DRIFT Spectra.

Diffuse reflectance FT-IR (DRIFT) spectra were obtained for samples of Cab-O-Sil (10 wt% in KBr) that were untreated (Fig. 2.3a) and that had a high coverage of attached bibenzyl (Fig. 2.3b). The spectra below 1400 cm^{-1} were dominated by the very intense Si-O stretching modes. To facilitate comparison, the intensity of the Si-O lattice mode at 1867 cm^{-1} in each spectrum was normalized to an absorbance value of unity.

Adsorbed water on the silica surface is evident from the broad band at $\sim 3400\text{--}3000\text{ cm}^{-1}$ in the untreated Cab-O-Sil (Fig. 2.3a). This water is removed by the drying procedures associated with the attachment of the bibenzyl on the surface (Fig. 2.3b). The surface hydroxyls of the untreated silica fall into two general categories: (1) isolated hydroxyls that give rise to the sharp peak at 3741 cm^{-1} , and (2) a variety of hydrogen bonded hydroxyls that produce the broad band at $\sim 3700\text{--}3400\text{ cm}^{-1}$. In Fig. 2.3b, the isolated hydroxyl band at 3741 cm^{-1} is missing, suggesting complete reaction has occurred at these sites during the bibenzyl attachment. In addition the band for the hydrogen bonded hydroxyls has narrowed and also diminished in intensity. As expected, some surface hydroxyls remain after the attachment reaction because of steric restraints that do not allow derivatization of all surface hydroxyl sites. The new IR peaks in Fig. 2.3b at 3066-2858 and 1609-1450 cm^{-1} are all consistent with peaks expected for the bibenzyl moiety.

Thermolysis of Surface Attached Bibenzyl at High Surface Coverage (0.465 mmol g^{-1}). Product distributions were examined at low conversions ($< 5\%$) in order to determine primary products, and the results are given in Table 2.12. Studies at 375 and 400°C have shown that small temperature differences have

Fig. 2.3. DRIFT spectra of Cab-O-Sil silica: (a) untreated; (b) with surface attached bibenzyl.

only a small effect on the product distribution. Conversions were determined from a summation of the products detected on a milliequivalent basis. During the initial stages of the thermolyses, 5 to 6% of phenol 1 was evolved into the vapor phase, probably resulting from a surface dehydroxylation type of reaction.⁵

The product distribution is consistent with the initial thermolysis event being the homolytic cleavage of the central $sp^3 \rightarrow p^3$ bond in 2

leading to surface attached benzyl radical 3 and free benzyl radical 4 (Eq. 2). The surface attached radical 3 has enough conformational mobility to be able to abstract hydrogen from a neighboring 2 to form surface attached bibenzyl radical 5 (and probably $\equiv SiOC_6H_4CH_2\dot{C}HC_6H_5$) and surface attached toluene (gives cresol on workup) as shown in Eq. 3.

These steps are analogous to those observed in the thermolysis of liquid phase bibenzyl.^{2a,c,d} Free benzyl radicals produced in Eq. 2 can also abstract hydrogen from 2 to form toluene (Eq. 4), or they can couple to form bibenzyl (Eq. 5).

At all conversions shown in Table 2.12, comparable amounts of products are obtained from surface attached benzyl radicals (cresol) and from free benzyl radicals (toluene + 2 bibenzyl) indicating that Eqs. 2-5 adequately describe the fate of these primary radicals.

Moreover, based on the amounts of cresol, toluene, and bibenzyl formed in the four runs at 375°C, a first order rate constant of $1.1 \times 10^{-6} s^{-1}$ can be calculated for the initial bond homolysis (Eq. 2), which is identical to the value measured for the analogous process in the thermolysis of liquid bibenzyl in tetralin at 375°C.^{2d} This indicates that sur-

Table 2.12 Product Distribution for Thermolysis of Surface Attached Bibenzyl
(0.465 mmol g⁻¹) As a Function of Conversion

Reaction Temperature (°C)	350	375	375	375	375
Reaction Time (min)	20	10	20	40	60
Conversion (%)	0.18	0.51	1.6	3.3	5.1
Composition (mmol/100 mmol p-hydroxybibenzyl)					
p-hydroxybibenzyl					
(i) Vapor phase	5.0	6.1	5.68	5.0	5.4
(ii) Surface attached	94.4	94.9	93.7	92.1	89.8
Cresol	0.021	0.057	0.12	0.23	0.39
Toluene	0.020	0.055	0.096	0.20	0.28
Bibenzyl	—	0.003	0.010	0.031	0.048
Hydroxy-1,1-diphenylethane	0.034	0.27	1.16	2.39	3.67
Hydroxydiphenylmethane	—	—	0.005	0.014	0.037
3-Hydroxy-9,10-dihydrophenanthrene	0.010	0.032	0.11	0.17	0.20
3-Hydroxyphenanthrene	—	0.004	0.037	0.13	0.27
Benzene	0.007	0.010	0.021	0.077	0.12
Ethylphenol	0.003	0.009	0.028	0.11	0.19
Ethylbenzene	0.003	0.010	0.020	0.096	0.14
Styrene	—	0.002	0.005	0.024	0.034
Phenol	0.003	0.010	0.024	0.085	0.16
t-Stilbene	—	0.002	0.003	0.008	0.012
p-Hydroxy-t-stilbene	0.018	0.04	0.07	0.12	0.17
Surface Dimers	—	0.002	0.01	0.024	0.03

face immobilization has had little effect on the initial unimolecular bond homolysis.

A dramatic change in the thermolysis reaction that can be attributed to surface immobilization is observed in the fate of the surface attached bibenzyl radical **5**. In the liquid phase, the analogous radical, $\text{C}_6\text{H}_5\dot{\text{C}}\text{HCH}_2\text{C}_6\text{H}_5$, decays primarily by bimolecular coupling to produce dimers (~21 mol% of the products at comparable conversions) and by disproportionation to produce stilbene (~10

mol%) as major products.^{2a,c,d} However for surface attached radical **5**, very little coupling (<1 mol% surface attached dimers) is detected. Furthermore the principal bimolecular decay path for **5**, loss of hydrogen to another radical to produce surface attached stilbene (~3 mol%) is also a minor reaction path. The dominant decay path observed for radical **5** is a rearrangement path involving a reversible 1,2-phenyl shift followed by hydrogen abstraction from a neighboring **2** to form

surface attached 1,1-diphenylethane and regenerating radical 5.

This radical chain path produces isomerized product 6 as the major product (~60 mol% at low conversions), whereas in the liquid phase thermolysis, 1,1-diphenylethane accounts for only ~10 mol% of the initial products. The chain length [6/1/2(cresol + toluene + 2 bibenzyl)] for the surface isomerization process is 9.7 after 20, 40, or 60 min at 375°C; however, at lower conversions, the chain length is only 4.6 possibly due to inhibition by underivatized hydroxyls on the silica.

A second reaction path observed for 5 (whose counterpart is negligible in the liquid phase thermolysis) is an intramolecular cyclization to form surface attached 9,10-dihydrophenanthrene (gives 3-hydroxy-9,10-dihydrophenanthrene on workup). Further loss of hydrogen produces surface attached phenanthrene, which is not detected until after ~20 min of thermolysis at 375°C. As the conversion increases, the amount of surface attached 9,10-dihydrophenanthrene reaches an apparent steady state value of ~0.20 mmol/100 mmol 1. Even after 26% conversion (10 h at 375°C), the yield of the 9,10-dihydrophenanthrene is 0.22 mmol/100 mmol 1, while the yield of phenanthrene has increased to 3.1 mmol/100 mmol 1.

The results in Table 2.12 show that the isomerization path is clearly favored over the cyclization path for the reaction of 5. The ratio of 6 to cyclized products is 7.8 ± 0.2 throughout the conversion range studied at 375°C. This ratio decreases to 6.8 at 400°C and increases to 9.4 at 350°C indicating a higher activation energy for the cyclization reaction, which requires loss of aromaticity in

both phenyl rings during the process of forming the dihydrophenanthrene.

The main side reaction observed in the thermolysis of 2 is an asymmetrical cleavage that produces benzene plus ethylphenol and ethylbenzene plus phenol. These products most likely result from aromatic dealkylation involving hydrogen atoms⁶ that could be released during dihydrophenanthrene and phenanthrene formation.

Effect of Surface Coverage on Product

Distribution. We have begun to examine the effect of decreasing the surface coverage of 2 on the thermolysis product distribution to gain further insight into the effect of substrate immobilization on thermolysis pathways. Preliminary results are given in Table 2.13 for experiments performed at 375°C for 60 min. The first order rate constant for the unimolecular bond homolysis is not affected by changes in the surface coverage, indicating that no mechanistic complexity is involved in this step. It does appear that as the surface coverage is lowered, reaction of the free benzyl radicals by coupling to form bibenzyl becomes less favored compared with hydrogen abstraction to form toluene. When the surface coverage of 2 is lowered to 0.158 mmol g⁻¹, the surface attached benzyl radical can still abstract hydrogen from neighboring bibenzyl molecules on the surface (cresol = toluene + 2 bibenzyl). At a surface coverage of 0.045 mmol g⁻¹, current experimental difficulties in determining the extremely small quantities of cresol formed do not permit further comparison at this time.

Another feature to emerge from this study is the decrease in conversion as the surface coverage is lowered. The primary cause is the decrease in the rate of the isomerization process (to produce 6) whose chain length [6/(toluene + 2 bibenzyl)] decreases from 9.8 to 3.1 to 0.66 as the surface coverage is lowered. This presumably reflects the importance of the hydrogen transfer step to the overall rate of the isomerization process on the surface (Eq. 6), which is apparently impeded by lower surface coverages.

Table 2.13 Effect of Surface Coverage on the Distribution of Main Products From the Thermolysis (375°C/60 min) of Surface Attached Bibenzyl

Surface Coverage (mmol g ⁻¹)	0.465	0.158	0.045
Conversion (%)	5.1	2.2	1.2
Composition of Main Products (mmol/100 mmol p-hydroxybibenzyl)			
p-hydroxybibenzyl			
(i) Vapor phase	5.4	7.3	3.4
(ii) Surface attached	89.8	94.7	94
Cresol	0.39	0.41	^a
Toluene	0.28	0.33	0.42
Bibenzyl	0.048	0.024	0.01
Hydroxy-1,1-diphenylethane	3.67	1.18	0.29
3-Hydroxy-9,10-dihydrophenanthrene	0.20	0.21	0.13
3-Hydroxyphenanthrene	0.27	0.04	0.01
p-Hydroxystilbene	0.17	0.15	0.3

^a Not detected; see text.

It is also interesting to note in Table 2.13 that as the surface coverage is lowered, the cyclization process to form the dihydrophenanthrene on the surface remains approximately constant, while there is a precipitous decrease in the dehydrogenation process to form surface attached phenanthrene. This suggests the possibility that phenanthrene formation is not a unimolecular dehydrogenation, and that it requires hydrogen abstraction by a neighboring radical.

These studies clearly show that immobilizing free radicals on a surface can lead to an enhancement of unimolecular decay paths relative to bimolecular ones. We are also beginning to see that the isomerization and cyclization-dehydrogenation paths are very sensitive to the coverage of bibenzyl units on the surface. Future investigations should provide further insights into the effects of surface immobilization on thermolysis mechanisms.

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2.7 Reductive Debenzylation of 1-Benzyl-naphthalene by Sodium-Potassium Alloy

(R. R. Chambers, Jr., C. J. Collins,
B. E. Maxwell)

It has been reported that a Na-K alloy when dissolved in a mixture of glyme-triglyme at 0°C represents an excellent reagent for cleaving carbon-carbon bonds under mild conditions.^{1,2} When applied to coal, this blue solution of 'solvated electrons' offers an ideal reducing medium for converting coal to a pyridine soluble product.³

Under appropriate conditions (Na-K, 50/50 (v/v) glyme-triglyme, 0°C, 15 min), the sp³-sp³ carbon-carbon bond in 1,2-diphenyl-ethane is readily cleaved to PhCH₂ (91% conversion) which upon a methyl iodide quench yields ethylbenzene and toluene (ratio, 2.7:1.0). A secondary product, 1,2-diphenyl-propane^{1a} (3% yield), is also formed indicating that competitive carbon-hydrogen cleavage (or metalation) occurs under these conditions.

The observation of PhCH₃ as a major side product from the methyl quench suggests that PhCH₂ is unstable in glymes at this temperature, undergoing protonation by the solvent.

This reductive C-C cleavage reaction finds direct analogy to the observations of Lagendijk and Swarc⁴ where 1,2-dinaphthyl-ethane undergoes bond fission upon exposure to Na (in THF, THP, DME, etc.), and the more recent report of Grovenstein, et al.⁵

describing the cleavages of 1,2-diphenylethanes by Cs-K-Na alloy (THF, -75°C). These previous studies all point towards a common mechanism for sp³-sp³ C-C bond fission in which a dianion is the reactive intermediate producing the cleavage products.

There are indications that the reductive cleavages of sp³-sp² C-C bonds may follow distinctly different pathways depending upon the substrate and the reducing conditions. For example, the aryl cleavage of 9,9-diaryl-fluorenes⁶ by K in DME proceeds according to a rate law consistent with the mechanism of (Eq. 2). On the other hand, using a Na-K alloy in glymes, diphenylmethane ruptures at the aliphatic-aromatic C-C bond by a process possibly involving an ipso-aromatic attack of (PhCH₂Ph)²⁻ on PhCH₂Ph followed by loss of a benzyl anion.^{1b} This apparent variation in reaction pathway may be a general property of diarylmethane cleavages as a whole.

For this reason, we investigated the reductive debenzylolation of 1-benzyl-naphthalene by a Na-K alloy (0°C) in a mixture of glymes. All of the experimental evidence is consistent with a novel mechanism involving initial Birch reduction of the substituted naphthalene ring to give a 1,2-diarylalkane unit which then fragments by fission of an sp³-sp³ C-C bond.

When 1-benzyl-naphthalene is subjected to Na-K reduction followed by an ethanol quench, the cleavage products (19% conversion) are PhCH₃/dihydrotoluene and tetralin/dihydro-tetralin in a ratio of 1.1:1.0, respectively. In addition, there are numerous Birch reduction products derived from the 1-benzyl-naphthalene. The presence of 1-benzyltetralin (14% yield) among these was confirmed by independent synthesis and comparison of GC retention time and mass spectral properties. Analogous reduction of methylene-¹⁴C-1-benzyl-naphthalene produces Ph-¹⁴CH₃ as the sole carbon-14

labeled cleavage product thus precluding the alternative mode of reaction depicted in (Eq. 3).

There are two reasonable pathways which can account for these observations (Scheme I).

In path a, direct $\text{sp}^3\text{-sp}^2$ C-C cleavage produces a naphthalene and benzyl fragment which for simplicity are shown as their respective anions. Subsequent protonation and Birch reduction of the naphthalene anion to tetralin/dihydrotetralin and protonation/reduction of PhCH_2^- to PhCH_3 /dihydrotoluene account for the products. The alternative route, path b, proceeds by initial Birch reduction to 1-benzyltetralin followed by a facile $\text{sp}^3\text{-sp}^3$ C-C cleavage to tetralin anion and PhCH_2^- . Protonation and reduction results in the same tetralin and toluene products. Independently, it is found that the reaction of 1-benzyltetralin under similar conditions does yield PhCH_3 /dihydrotoluene and tetralin/dihydrotetralin products (71% conversion) in the expected 1:1 ratio. Both pathways are consistent with the product distribution; the major difference is the timing of events. In a, $\text{sp}^3\text{-sp}^2$ C-C cleavage occurs initially followed by Birch reduction whereas in b, Birch reduction is a prerequisite to bond cleavage.

To probe which pathway is operative, 1,5-dibenzyl-naphthalene was reduced (ethanol quench) and the product mixture analyzed by GC/MS. If dibenzyl-naphthalene cleaves according to path a, then the initial products will be PhCH_2^- and 1-benzyl-naphthalene anion 8 (Scheme II).

Protonation of 8 (by solvent or ArCH_2Ar^-) followed by a second bond cleavage reaction ultimately produces with a protic quench a naphthalene fragment 10 and two equivalents of toluene. Conversely, with path b, dibenzyl-tetralin 11 is formed initially. In 11, there is only one weak $\text{sp}^3\text{-sp}^3$ C-C bond for reductive cleavage. Thus the expected product from an ethanol quench is a 1:1 mixture of benzyl-tetralin 13 and PhCH_3 . Experimentally, reduction of 1,5-dibenzyl-naphthalene gives PhCH_3 /dihydrotoluene and a mixture of hydrogenated benzylnaphthalenes in a 1.0:1.1 ratio. This result and the notable absence of hydrogenated naphthalenes as major products confirm that path b is more appropriate.

In conclusion, this study has identified a novel mechanism by which ArCH_2Ar^- can undergo reductive C-C bond fission under dissolving metal conditions. This involves initial Birch reduction of the substrate to unmask a weak $\text{sp}^3\text{-sp}^3$ C-C bond which then cleaves readily in the presence of a Na-K alloy.

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3. AQUEOUS CHEMISTRY AT HIGH TEMPERATURES AND PRESSURES

Studies on chemical and thermodynamic properties in aqueous systems at high temperatures and pressures are of interest in this program. Results have broad basic implications regarding the factors that control solution processes of charged and uncharged species. Recent emphasis has been on the application of the isopiestic (3.1.1-3) and the calorimetric methods (3.1.4 and 3.1.6) to the study of excess thermodynamic properties and has led to major advances in this field. Modeling in the near-critical region is being advanced to include association behavior of electrolytes as previously derived from this program in dilute media using the conductance approach. Also, an extension of the complete constant approach is being applied to the modeling of electrolyte behavior (3.1.7-8). Emf techniques are continuing to be applied to unravel complex speciation and recently for Cr(VI) (see 3.2.1), a system metastable with respect to hydrogen. The redox reactions of halogens and the thermodynamics for their equilibria are being extended (3.2.3). Previous results are being analyzed in terms of a model for the decomposition of acetic acid (3.2.2).

Broadening of this program is planned as time permits to include emphasis on measurements of molal volumes to high temperatures and pressures as well as Raman spectroscopic and neutron scattering studies to provide more detailed pictures of the processes and species that occur. Results are continuing to be applied widely in steam generation, waste disposal, decontamination, geochemistry, geothermal energy extraction and chemical processing.

3.1 Thermodynamics of Electrolyte Solutions

3.1.1 Thermodynamics of Aqueous Hydrogen

Chloride to 523 K

(H. F. Holmes, R. H. Busey, D. G. Archer, J. M. Simonson, R. E. Mesmer)

The enthalpy of dilution of HCl(aq) has been measured, in this laboratory, for temperatures to 648 K, initial molalities to 15.66 mol·kg⁻¹, and pressures to 40 MPa.¹ Given a suitable reference value, the enthalpy results can be integrated to give the excess Gibbs functions (activity and osmotic coefficients) over the same range of temperature, pressure, and molality. As a general rule more reliable values for the various thermodynamic quantities can be obtained if one includes various types of thermodynamic results in an overall least-squares analysis using basic thermodynamic relationships. Since other types of thermodynamic results are very limited in this temperature range (the only other significant data in this range are the heat capacities of Tremaine² and the activity coefficients of Lietzke et al.³), calculated values of the high-temperature thermodynamic properties of HCl(aq) will depend primarily on the ORNL enthalpy of dilution results.

A complicating factor is the fact that HCl becomes an associated electrolyte (i.e., a weak acid) at high temperatures. Thus the experimentally measured heat contains a contribution from the enthalpy of ionization of hydrochloric acid. In addition, it is necessary to model the system as a mixture of solutes rather than as a pure electrolyte. However, the effects of association become important only at temperatures above about 523 K. At the lower temperatures HCl(aq) can be modeled quite accurately in terms of the relatively simple ion-interaction model for pure electrolytes.⁵ An ion association model for HCl(aq) at higher temperatures is discussed in another section of this report.

Literature data for HCl(aq) consisting of excess Gibbs energies, enthalpies of dilution, and heat capacities were coupled with the ORNL enthalpy of dilution results to give a data base to which the ion-interaction model could be fitted by a simultaneous least-squares analysis of all the data. From a thermodynamic viewpoint the analysis is essentially the same as for the alkali metal chlorides.⁶ In this model the thermodynamic properties of an aqueous solution of a pure electrolyte is given in terms of three temperature-dependent ionic interaction param-

ters, $\beta(0)$, $\beta(1)$, and C^ϕ . The problem is then reduced to finding a satisfactory, but arbitrary, expression for the temperature (and pressure in the case of HCl(aq)) dependence of these three parameters. Fortunately it was found that a relatively simple function, $f(T, \rho^\circ)$, of the temperature, T , and the density, ρ° , of pure water (at the temperature and pressure of interest) was quite adequate for both the temperature and pressure dependence of the ionic interaction parameters with

$$f(T, \rho^\circ) = a_1 + a_2 \ln(\rho^\circ/\rho_R^\circ) + a_3 (\rho^\circ/\rho_R^\circ) + a_4(T - T_R) \quad (1)$$

where T_R is 298.15 K, ρ_R° is $997 \text{ kg}\cdot\text{m}^{-3}$, and the a 's are temperature and pressure independent parameters whose values are fixed by a least-squares fit to the experimental results. The simple three-parameter ion-interaction model gave a satisfactory fit through an ionic strength of $7 \text{ mol}\cdot\text{kg}^{-1}$. Higher concentrations required an additional term, $QM^{3/2}$, where M is the molality and Q is given by a function identical to (1).

Since we are also treating heat capacity results, it is necessary to have an expression for the temperature dependence of the apparent molal heat capacity at infinite dilution, $C_{p,\phi}^\infty$. We have chosen the Helgeson, Kirkman, and Flowers model⁷ for this quantity primarily because Tremaine² has successfully applied it to their heat capacity results for HCl(aq) to 413 K. The above model gives

$$C_{p,\phi}^\infty = p_1 + p_2 T/(T-240) + p_3 T x_D, \quad (2)$$

$$\text{with } x_D = [(\partial^2 \ln D_c / \partial T^2)_p - (\partial \ln D_c / \partial T)_p^2] / D_c \quad (3)$$

where D_c is the dielectric constant of pure water at the conditions of interest and the p 's are temperature and pressure independent adjustable parameters.

A total of eleven adjustable parameters was sufficient to describe all of the results through 523 K. If the molality is limited to $7 \text{ mol}\cdot\text{kg}^{-1}$ only eight adjustable parameters are

required. Excess Gibbs quantities were fit to better than one percent, enthalpies to two to four percent, and heat capacities to better than four $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$. At 573 K HCl(aq) is too associated to be described by the simple ion-interaction model for pure electrolytes.

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3.1.2 Isopiestic Results for Aqueous Solutions of the Alkaline Earth Metal Chlorides to 523 K (H. F. Holmes, R. E. Mesmer)

We have previously published isopiestic results for aqueous solutions of the alkaline earth metal chlorides at temperatures to 473 K.^{1,2} Since that time, the ORNL isopiestic facility has been modified to permit operation to 523 K.³ Previous experience has shown that the excess Gibbs functions become more temperature dependent with increasing temperature, a characteristic which contributes significantly to the uncertainty involved in the extrapolation of results beyond the highest experimental temperature. Our enthalpy of dilution results for $\text{CaCl}_2(\text{aq})$ ⁴ can be used to extend the excess Gibbs energy data (for $\text{CaCl}_2(\text{aq})$) above the highest experimental temperature provided suitable reference values are available. High temperature reference data are desirable in order to reduce the contribution of the integration of enthalpy results to an acceptable fraction of the Gibbs functions. Simultaneous and successful analysis of the calorimetric and isopiestic

results would provide one with a high temperature isopiestic standard for concentrated solutions. The above factors are excellent reasons for extending the isopiestic results for the alkaline earth chlorides to 523 K.

These measurements have now been completed although a detailed analysis of the results has not been done at the present time. Nevertheless several qualitative observations are apparent. X-ray analysis of a residue at the conclusion of the experiment indicates that some hydrolysis of $\text{MgCl}_2(\text{aq})$ may have occurred above 200°C. The hydrolysis may not have been sufficient or taken place at the time to have a deleterious effect on the results. The osmotic coefficients for $\text{MgCl}_2(\text{aq})$ from the experiment are not obviously erroneous. The osmotic coefficients for all four of the alkaline earth chlorides at 225 and 250°C appear to be a smooth extrapolation of the results from 110 to 200°C. There was no change in the relative position of the results for these four salts. The order of increasing osmotic coefficients continues to be $\text{BaCl}_2(\text{aq})$, $\text{SrCl}_2(\text{aq})$, $\text{CaCl}_2(\text{aq})$, and $\text{MgCl}_2(\text{aq})$ at any given molality and temperature. The dependence of the osmotic coefficient on molality continues to decrease with increasing temperature. An extreme example of this is the osmotic coefficient of $\text{BaCl}_2(\text{aq})$ at 250°C, which did not vary more than 2 percent from 0.5 mol·kg⁻¹ to saturation. These results are to be incorporated in a model whose parameters will be determined from an analysis of all the available thermodynamic results for these four electrolytes.

3.1.3 The Activity Coefficient of Aqueous Sodium Sulfate at Saturation to 553 K

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

Rogers and Pitzer¹ have calculated the activity coefficient of $\text{Na}_2\text{SO}_4(\text{aq})$ to 473 K and 2.5 mol·kg⁻¹ (1.5 mol·kg⁻¹ above 393 K) by a double integration of their heat capacity results. Subsequently, Pitzer and Murdzek² have calculated the activity coefficient of saturated $\text{Na}_2\text{SO}_4(\text{aq})$ to 553 K. Their calculations were based on the same heat capacity data of Rogers and Pitzer¹ and represent an extrapolation of the experimental results in both temperature and molality. None of these calculations had access to our high temperature isopiestic results (a direct measure of the activity coefficient) for $\text{Na}_2\text{SO}_4(\text{aq})$ ³ which extend the experimental temperature range to 498 K. These isopiestic results have been subjected to a thermodynamic analysis⁴ in conjunction with the other available data for $\text{Na}_2\text{SO}_4(\text{aq})$. (Contrary to the previous report⁴ the final analysis sets the ionic interaction parameter $\beta^{(2)}$ to zero as this quantity cannot be well defined from our isopiestic results.) It is of considerable interest to compare the calculations of Pitzer and Murdzek² with our more direct determination of the excess Gibbs energy for this system.

Activity coefficients, γ , can be calculated from the measured saturation molalities, m , provided that the standard Gibbs energy change, ΔG° , for the solution process is known. For the present case the pertinent equation is

$$\Delta G^\circ/T = -R \ln (4m^3\gamma^3), \quad (1)$$

where T and R are the temperature and the gas constant, respectively. The solubility of $\text{Na}_2\text{SO}_4(\text{s})$ has been measured by Schroeder et al.⁵ ΔG° can be obtained from the appropriate literature data^{6,7} plus a double integration of the apparent molal heat capacity at infinite dilution, ϕ_C° .

1. H. F. Holmes, C. F. Baes, Jr., and R. E. Mesmer, *J. Chem. Thermodyn.* **10**, 983 (1978).
2. H. F. Holmes and R. E. Mesmer, *J. Chem. Thermodyn.* **13**, 1025 (1981).
3. H. F. Holmes and R. E. Mesmer, *J. Phys. Chem.* **87**, 1242 (1983).
4. *Chem. Div. Annu. Prog. Rep.* January 31, 1984, ORNL-6037, p. 28.

Rogers and Pitzer¹ used an empirical equation to describe ϕ_C° as a function of temperature. This equation is

$$\phi_C^\circ = a_1 + a_2T + a_3T^2 + a_4/(T-263), \quad (2)$$

where the a 's are temperature independent adjustable parameters. We adopted the same equation in our analysis of the thermodynamic data for $\text{Na}_2\text{SO}_4(\text{aq})$. However, Rogers and Pitzer¹ considered only their heat capacity results and the ϕ_C° values given by Gardner et al⁸ in fixing the parameters of equation (2) while our a 's were obtained from a simultaneous least-squares fit of all data. Differences in the two models can be seen in Fig. 3.1 which shows ϕ_C° as a function of temperature. The two models are in essentially perfect agreement below 323 K but at higher temperatures the discrepancy amounts to about $40 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$. Literature data³⁻¹² shown in Fig. 3.1 were derived by the various investigators from their own experimental results.

Despite the seemingly large differences in the two sets of ϕ_C° our activity coefficients for saturated $\text{Na}_2\text{SO}_4(\text{aq})$ and those obtained by Pitzer and Murdzek for the same conditions agree quite well. (Compare columns three and five in Table 3.1). A difference of 0.002 in γ is equivalent to an uncertainty of about $1 \text{ kJ}\cdot\text{mol}^{-1}$ (approximately 4 percent) in ΔG° for the solution process. The activity coefficient of $\text{Na}_2\text{SO}_4(\text{aq})$ as a function of molality can be obtained from a double integration (with temperature) of the apparent molal heat capacity provided one has suitable integration constants (Rogers and Pitzer¹) or from an overall least-squares analysis of all types of data (ORNL). The activity coefficient of $\text{Na}_2\text{SO}_4(\text{aq})$ at saturation is then easily calculated from the appropriate equation. These activity coefficients are listed in columns 4 and 6 of Table 3.1. One can see there is reasonable agreement among the four different activity coefficients even for an 80 K extrapolation of the heat capacity data and a 55 K extrapolation of the isopiestic results.

Fig. 3.1. The apparent molal heat capacity of $\text{Na}_2\text{SO}_4(\text{aq})$ at infinite dilution. The points are extrapolations to zero molality by the various investigators.

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3. *Chem. Div. Annu. Prog. Rep. January 31, 1983*, ORNL-5954, p. 24.
4. *Chem. Div. Annu. Prog. Rep. January 31, 1984*, ORNL-6037, p. 24.
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Table 3.1. The Activity Coefficient, γ , of Saturated $\text{Na}_2\text{SO}_4(\text{aq})$

T/K	m/(mol·kg ⁻¹)	$\gamma^a(\text{PMC})$	$\gamma^b(\text{RPd})$	$\gamma^a(\text{ORNL})$	$\gamma^b(\text{ORNL})$
303	3.518	0.139 ₄	0.137 ₈	0.139 ₄	0.139 ₅
313	3.366	0.142 ₄	0.140 ₆	0.142 ₄	0.142 ₀
333	3.148	0.141 ₇	0.140 ₄	0.141 ₆	0.141 ₈
353	3.020	0.133 ₁	0.133 ₅	0.133 ₇	0.134 ₅
373	2.970	0.120 ₂	0.120 ₀	0.120 ₆	0.122 ₁
393	2.952	0.104 ₉	0.104 ₈	0.105 ₇	0.107 ₂
413	2.957	0.089 ₁	0.088 ₈	0.090 ₄	0.091 ₉
433	2.999	0.073 ₃	0.072 ₅	0.075 ₁	0.077 ₂
453	3.062	0.058 ₇	0.057 ₅	0.060 ₉	0.063 ₅
473	3.133	0.045 ₉	0.044 ₃	0.048 ₃	0.051 ₅
493	3.203	0.035 ₀	0.033 ₄	0.037 ₅	0.040 ₈
513	3.203	0.026 ₆	0.025 ₀	0.029 ₂	0.031 ₅
533	2.964	0.020 ₈	0.019 ₉	0.023 ₂	0.024 ₃
553	2.415	0.017 ₉	0.018 ₁	0.020 ₄	0.020 ₉

^aFrom ϕ_c° and solubility.^bFrom solution data only.CPM = Pitzer and Mardzek¹.dRP = Rodgers and Pitzer².

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3.1.4 Semiempirical Modeling of the Thermodynamic Properties of Associating Solutes (J. M. Simonson, R. E. Mesmer)

Experimental studies of the enthalpy of dilution of aqueous electrolytes to high temperature (673 K) carried out using the heat and liquid flow microcalorimeter developed in this laboratory indicate significant ion association in solution at elevated temperatures.¹⁻³ The ion-interaction model of Pitzer,⁴ which has been applied successfully to a large body of electrolyte thermodynamic data, is not directly applicable to systems in which a significant fraction of the solute is present as ion pairs. This

model has been extended by other investigators⁵⁻⁷ to remove this limitation by including interactions between associated and dissociated solute species. These treatments have been limited to specific cases, extending over limited temperature and pressure ranges. The work described here was undertaken to develop a complete, consistent set of modeling equations for the excess thermodynamic properties of associating electrolytes.

The ion interaction expression for the excess Gibbs free energy per kilogram of solvent n_w is

$$\frac{G^{\text{Ex}}}{n_w RT} = -A_\phi \left(\frac{4I}{b} \right) \ln (1 + bI^{1/2}) +$$

$$2v_M v_X [m^2 B_{MX} + m^3 v_M z_M c_{MX}] \quad (1)$$

The second virial coefficient B_{MX} is a function of ionic strength given by

$$B_{MX} = B_{MX}^{(0)} + 2B_{MX}^{(1)} [1 - (1 + \alpha I)^{1/2} \exp(-\alpha I^{1/2})] / (\alpha^2 I). \quad (2)$$

In eqs. (1) and (2) I and m are the ionic strength and solute molality, ν_M and ν_X are the numbers of cations and anions resulting from complete solute dissociation, z_M is the cation charge, and A_ϕ is the Debye-Huckel limiting slope for the osmotic coefficient. The parameters b and α have fixed values of 1.2 and 2.0, respectively. Parametric expressions for other excess properties (e.g. activity and osmotic coefficients, relative enthalpies) may be derived from eq. (1).

The ion-interaction treatment assumes complete dissociation of the solute into its constituent ions. To remove this limitation we consider explicitly the ion association equilibrium. For a 1-1 electrolyte, the equilibrium constant for this reaction is

$$K_A = \frac{m_N \gamma_N}{m_M \gamma_M m_X \gamma_X} = \frac{m_N \gamma_N}{m_i^2 g_{\pm}^2} \quad (3)$$

Here m_N and γ_N are the molality and activity coefficient of the neutral species (ion pair) formed; m_i and $g_{\pm}$ represent corresponding quantities for the ions. Equation (1) is extended to include interactions involving neutral species; considering terms through the second virial coefficient for the ion pair the excess Gibbs free energy expression takes the form

$$G^{Ex} = -A_\phi \left(\frac{4I}{b} \right) \ln (1 + bI^{1/2}) + 2m_i^2 B_{MX} + 2m_i^3 C_{MX} + m_N^2 \lambda_{NN} + m_i m_N \Delta_{MXN} \quad (4)$$

In eq. (4) I represents the real ionic strength based on the fraction of the solute dissociated; λ_{NN} and Δ_{MXN} are second virial coefficients representing binary neutral-neutral and neutral-ion interactions.

The expression for the apparent relative enthalpy ϕ_L has been derived from eq. (4) and applied to the measured enthalpies of dilution of HCl(aq).² This application is complicated by the interdependence of m_i and m_N expressed in eq. (3) and by the dependence of m_i and m_N on

temperature. In addition, there is a redundancy between the equilibrium constant K_A and the second virial coefficient B_{MX} which precludes determination of both quantities from a single set of results. The redundancy has been removed by adopting a set of K_A values extrapolated from those determined from 673 to 973 K by Frantz and Marshall.³ The interdependence of m_i and m_N is accounted for by iteration of the fitting equation for each new set of parameters chosen until convergence of the molality values is attained.

The dilution enthalpy results for HCl(aq) have been fitted to the ϕ_L expression derived from eq. (4) over the ranges $298 < T < 648$ K, $70 < P < 400$ bars and $0 < m < 2$ mol·kg⁻¹ to better than 4% average absolute deviation in $\Delta \phi_L$. The parameters of eq. (4) have been given simple temperature and pressure dependence forms; a total of 11 adjustable parameters are determined in the nonlinear least-squares fit. The fit deviation (4%) is slightly larger than the estimated experimental uncertainty (~2%), and the empirical temperature and pressure forms have not yet been optimized. However, comparison of this fit to those obtained from the ion-interaction model when association is not considered shows that the association model is applicable at $T > 573$ K, where the fit of the usual ion-interaction model to the results is unacceptably poor. With the applicability of the association-interaction model demonstrated through fits of the dilution enthalpy results for HCl(aq), extension of the model to treat other types of data and other charge-type electrolytes (e.g. CaCl₂) is expected to represent quantitatively the thermodynamic properties of electrolyte solutions to temperatures well above 573 K.

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3.1.5 Volumetric Properties of Aqueous Sodium Hydroxide to High Concentrations (J. M. Simonson, R. J. Ryther¹)

The volumetric properties of aqueous electrolyte solutions near ambient temperature are of importance both in providing additional information on the thermodynamic properties of the system studied and to provide data necessary for volume-to-mass conversions required in the analysis of flow calorimetric results. Aqueous sodium hydroxide was chosen for study to support flow calorimetric work currently in progress. In addition, the high solubility of sodium hydroxide and the high viscosity of the concentrated solutions make this system especially useful as a test of the pressure derivative form of the ion-interaction model to high ionic strengths and as an indication of the applicability of vibrating-tube densimetry to very viscous solutions.

Thirteen stock solutions of NaOH(aq) ranging in concentration from 0.06 to 25.2 mol·kg⁻¹ were prepared by dilution of reagent grade 50 wt. pct. NaOH(aq). All dilutions were carried out under argon to prevent carbonate contamination. Solutions were stored under argon to prevent contamination after preparation.

Relative densities of the solutions were measured at 5, 15, 25, 35, and 45°C and 100, 3000, 5000 psi applied pressure using a Mettler-Paar vibrating tube densimeter. The apparatus was calibrated using water and 5.0 m NaCl(aq) as known density standards. The density of water at experimental conditions was calculated from the equations of Haar, Gallagher, and Kell;² NaCl(aq) densities were calculated using the equation of Rogers and

Pitzer.³ Apparent molal volumes ϕ_V were calculated from solution densities for use in further analysis of the data. The results are estimated to have an experimental uncertainty of ± 100 ppm in the solution density. Typical experimental results are illustrated in Fig. 3.2.

Our analysis of these results follows the work of Rogers and Pitzer³ on NaCl(aq). The parametric expression for the apparent molal volume

$$\phi_V = \bar{V}_2^\circ + \frac{A_V}{2b} \ln(1+bI^{1/2}) + 2RT[mB_{MX}^V + m^2C_{MX}^V], \quad (1)$$

including empirical temperature and pressure dependence forms for the quantities $\bar{V}_2^\circ$, B_{MX}^V , and C_{MX}^V was fitted to the volume data. Fitted curves are shown in Fig. 3.2 as solid lines. In all, 14 parameters were used to fit 165 data-points with a standard error of 0.19 in ϕ_V .

Fig. 3.2. Apparent molal volumes of aqueous sodium hydroxide at 5-45°C, 100 psi. Curves shown are fits of Eq. (1) to measured ϕ_V values.

This standard error is about ten times that expected on the basis of estimated experimental error. It is expected that the fit will be improved substantially through refinement of the empirical pressure and temperature dependences chosen for the parameters of eq. (1). Isothermal, isobaric fits of eq. (1) to the ϕ_V values indicate that the ion-interaction model represents well the concentration dependence of these results to high molalities.

1. Student from Earlham College participating in ORNL-GLCA/ACM Science Semester.
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3.1.6 Enthalpies of Dilution of Aqueous Calcium Chloride to Low Molalities at High Temperatures¹

(J. M. Simonson, R. H. Busey, R. E. Mesmer)

Measurements of enthalpies of dilution of electrolyte solutions yield directly the difference in apparent relative molal enthalpy between the initial and diluted solutions. An important application of calorimetric data is the calculation of solute activity coefficients through the relation

$$\ln \gamma/\gamma^* = \frac{1}{\nu R} \int_{T^*}^T [\phi_L + (m^{1/2}/2)(\partial \phi_L / \partial m^{1/2})] d(1/T), \quad (1)$$

where γ^* is the activity coefficient at the reference temperature T^* and ν is the number of ions produced on complete dissociation of the solute. The form of eq. (1) requires that the relative enthalpy ϕ_L be known; thus the dilution enthalpy results must be extrapolated to infi-

nite dilution in order to calculate activity coefficients. This extrapolation is dependent on the model used to represent the dilution results. To minimize the error which may be introduced through the extrapolation, it is important to extend the experimental study to the lowest concentrations at which dilution heats may be measured reliably. In this study we have measured enthalpies of dilution of $\text{CaCl}_2(\text{aq})$ to 623 K and 40 MPa to minimum molalities of $1.7 \times 10^{-3} \text{ mol}\cdot\text{kg}^{-1}$. These results indicate that measurements to low concentrations are especially valuable at temperatures above 523 K.

The apparatus and procedures developed in this laboratory for microcalorimetric dilution enthalpy measurements have been described in detail.² Minimum salt concentrations for which dilution heats could be measured precisely were determined by calorimeter sensitivity and the heat of dilution per mole of solute at the temperature of the experiment. Minimum molalities attained at various temperatures are listed in Table 3.2.

Table 3.2. Minimum Final Molalities $m_{\min}$ for Dilution Experiments at Temperature T

$m_{\min}$	T
0.0333	298-423
0.00833	473-573
0.00167	598-673

The enthalpies of dilution of $\text{CaCl}_2(\text{aq})$ based on a reference molality of $7.26 \text{ mol}\cdot\text{kg}^{-1}$ obtained at temperatures to 673 K are illustrated in Fig. 3.3. The results shown in Fig. 3.4 are the low concentration regions of the dilution curves above 473 K based on a reference molality of $0.1 \text{ mol}\cdot\text{kg}^{-1}$. Limiting law slopes taken from Bradley and Pitzer³ are shown as light lines in each figure. The importance of precise determination of high-temperature enthalpies of dilution to very low

Fig. 3.3. Enthalpies of dilution of aqueous CaCl_2 to 673 K plotted as differences in apparent relative molal enthalpies of the diluted and 7.2589 m solutions. Limiting slopes are shown as light lines.

Fig. 3.4. Enthalpies of dilution of aqueous CaCl_2 from 473 to 673 K plotted as differences in apparent relative molal enthalpies of the diluted and 0.1 m solutions. Limiting slopes are shown as light lines.

molalities is apparent from inspection of Fig. 3.4. Dilution results extending only to 0.1 $\text{mol}\cdot\text{kg}^{-1}$ minimum molality might be extrapolated to infinite dilution by assuming the usual smooth increase in the slope of ΔL with decreasing $m^{1/2}$ to the Debye-Hückel limit. However, the results shown in Fig. 3.4 indicate that this procedure yields ΔL values which differ from the true values by a constant at high molalities and may be incorrect in both magnitude and composition dependence at the lowest concentrations. Activity coefficients calculated from such incorrect ΔL values may be expected to be significantly in error.

The high sensitivity and precision of the heat and liquid flow microcalorimeter used in this work has enabled us to obtain enthalpies of dilution to low molalities at high temperatures. Analysis of these results using the ion association-interaction model is expected to

make available an accurate set of values of the excess thermodynamic properties of $\text{CaCl}_2(\text{aq})$ to 673 K.

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3.1.7 Solvation-Ionization Equilibria for Describing Concentrated Aqueous Electrolyte Behavior, 25-300°C¹

(W. L. Marshall)

Previously, application of a complete equilibrium constant (K°), which includes the solvent as a reactant of variable concentration, has described ionization behavior of many

electrolytes over wide ranges of temperature, pressure, and concentration of water^{2,3}. This constant was applied only where the concentration of electrolyte approached zero, and therefore the concentration or density of pure water was always used. A similar model was applied to describe the vaporization of water where the molar concentration of solution free water $[C'(H_2O)]$, defined here to be nonsolvating water, was equated to its activity $[a(H_2O)]$ through a vaporization or structural constant (B) postulated to represent the number of "bonds" per molecule destroyed upon vaporization⁴.

In the present study, dissolved electrolytes are considered both through their solvation behavior and through $a(H_2O)$ related to $C'(H_2O)$ in the solution. At a given molarity (M) of electrolyte, $C'(H_2O)$ should equal the analytical concentration of total water ($C(H_2O)$) minus the concentrations removed by solvating each of the electrolyte species. Thus for NaCl,

$$C'(H_2O) = C(H_2O) - j \cdot C(NaCl^+ \cdot jH_2O) - p \cdot C(Na^+ \cdot pH_2O) - q \cdot C(Cl^- \cdot qH_2O) \quad (1)$$

where j , p , and q are average solvation numbers and C is the molarity of the designated species. For each electrolyte, a conventional ionization constant (K), a value c' j , and a term n (which equals $p + q - j$, the average increase in solvation number in the ionization process) are applied to a description of $a(H_2O)$ as a function of $C'(H_2O)$. The structural constant B , taken to be a property of the solvent and essentially independent of temperature and of the nature of the electrolyte up to moderate concentrations, was included also.

For the ionization of an electrolyte (AB), the equation and complete ionization constant may be represented by:

$$K^0 = \frac{[A^+ \cdot pH_2O][B^- \cdot qH_2O]y_{\pm}^2}{[AB^+ \cdot jH_2O][H_2O]^n} \quad (3)$$

$$= Qy_{\pm}^2/[H_2O]^n \quad (4)$$

$$= K/[H_2O]^n \quad (5)$$

where the brackets signify absolute concentration (moles/volume), K^0 is a complete constant, Q is the conventional ionization quotient, $y_{\pm}^2$ is the product of the ionic molar activity coefficients, and K (which equals $Qy_{\pm}^2$) is the conventional ionization constant²⁻³ in this study always in units of molarity. Customarily for a stoichiometric equivalent electrolyte, x is taken to equal the fraction of electrolyte ionized in the equilibrium expression:

$$K = \frac{x^2 y_{\pm}^2 M}{(1-x)} \quad (6)$$

from which x may be calculated. Substitutions into eq 1 and rearrangement yield the following expression for $C'(H_2O)$ for a univalent electrolyte incompletely ionized,

$$C'(H_2O) = C(H_2O) - M \cdot (nx + j) \quad (7)$$

where M is the molarity of electrolyte. From the preceding Report⁴ an equation that appears to represent $\log a(H_2O)$ up to moderate solute concentrations may be written:

$$\log a(H_2O) = (1/B) \cdot [\log C'(H_2O) - \log C(H_2O\text{-pure})] \quad (8)$$

where $\log C(H_2O\text{-pure})$ equals 1.7430 at 25°C and atmospheric pressure, and B is believed to equal 6.67 for water and to be essentially independent of temperature.

Activities and vapor pressures of NaCl solutions up to 300°C have been summarized recently⁵. By using published values of n (25-800°C), simultaneously determined best fit values of K , j , and B were obtained with eqs. 6-8 for describing the activities of water over aqueous NaCl solutions at temperatures from 25 to 300°C.

Figure 3.5 shows separate plots of the several values against temperature. We observe that (1) values of $\log K$ make a relatively smooth curve,

Fig. 3.5. Simultaneously determined values of (a) $\log K$ (based on molarity), (b) j_{2m} , (c) B , and (d) the sum $(n + j_{2m})$; aqueous sodium chloride, 0-2 m, 25-300°C.

(2) j_{2m} decreases with increasing temperature and approaches the constant value of 1.8 at 400-800°C, observed previously⁶, (3) B is essentially a constant, with the average value of 6.60 slightly lower than the proposed value of 6.67 for pure water, and (4) the sum, $(n + j_{2m})$ [representing the total solvation number of Na^+ plus Cl^- over the 0-2 m range], is almost constant with an average value of 11.3, which is near the constant value of 12.0 given earlier for the range, 400-800°C⁶. Fig. 3.6 shows a plot of the presently calculated values of $\log K^\circ$ and those from the literature at temperatures from 0 to 800°C.

In addition to the above observations, activities of water [$a(\text{H}_2\text{O})$] were described at 25°C for seventeen electrolyte solutions. Some calculated concentrations at 25°C of free (nonsolvating) water extrapolated to values near zero at the solubility points for several salts (NaCl , RbCl , CsCl , RbBr , RbI). Relative solva-

Fig. 3.6. Log complete equilibrium constant (K°) for aqueous sodium chloride versus $1/T$ (K), 0-800°C.

tion numbers obtained for univalent ions decreased with increasing size of the ions as expected. The evaluations indicate that electrolyte species approaching high concentrations destroy some bonding in water, with H^+ , Li^+ , and ion-pairs having the least effect. Earlier descriptions by solute-solvent mass action equilibria at the limit of infinite dilution are now applied with reasonable success to concentrated electrolytes.

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3.1.8 On Raoult's Law and Solvation Equilibria¹ (W. L. Marshall)

Raoult's Law may be expressed,

where $a(\text{solvent})$ is the activity of solvent and N_1 is the mole fraction, $s_1/(s_1 + s_2)$, expressed by the number of moles of solvent (s_1) and solute (s_2) in a given weight of solution. N_2 is the corresponding mole fraction of solute. Generally s_1 is calculated without assumption of polymerization of solvent species. For a strong electrolyte the number of moles of ions formed upon complete ionization may be used for calculating s_2 .

A modified Raoult's Law expression for electrolyte behavior in aqueous solution may be written,

$$N'_1 = \frac{[55.506/B - (nx + j)/B \cdot m]}{55.506/B - (nx + j)/B \cdot m + (x + 1) \cdot m} \quad (2)$$

which may be simplified to,

$$N'_1 = \frac{[55.506 - (nx + j) \cdot m]}{[55.506 - (nx + j) \cdot m + (x + 1) \cdot B \cdot m]} \quad (3)$$

From the previous Report² B represents the average polymerization number for the solvent (water in these studies), j is the average solvation number of the neutral solute species, n is the net increase in (average) solvation number when a (neutral) solute species ionizes to form two ions, x is the fraction of ionization at equilibrium for a given solute concentration, $55.506/B$ is the molality of "polymeric" units of solvent, m represents the formal molality of solute, and N'_1 is the mole fraction of free (nonsolvating) water. The value, $(nx + j)/B$, is the number of polymeric moles of solvent required for solvation shells. The value, $(x + 1) \cdot m$, is the total number of moles (s_2) of solute species. It is equal to m or $2m$ when x equals zero or 1, respectively.

As a close approximation for a strong electrolyte, $(nx + j)$ can be replaced by an average

solvation number (G) and $(x + 1)$ by 2 to give,

$$N''_1 = \frac{[55.506 - G \cdot m]}{[55.506 - G \cdot m + 2Bm]} \quad (4)$$

By applying the structural constant (B) and mass action equilibria to vaporization behavior² together with N''_1 instead of absolute concentration, the following relationship is written,

$$\ln a(\text{H}_2\text{O}) = (1/B) \cdot \ln [N''_1] \quad (5)$$

where N''_1 may be substituted for N'_1 to produce the simpler equation.

The compilations for NaCl of Pitzer,³ et al., at 25, 100, 200, and 300°C to 6 molal and the experimental values of Liu and Lindsey⁴ at molalities greater than 6 were used with eq 5 to obtain either the solvation number G_f or j_f where the subscript refers to the full range of molality. Examples of fits for NaCl-H₂O at 25-300°C are shown in Fig. 3.7b and are compared to those using Raoult's Law in Fig. 3.7a. [Over the widest range of molality, an average value of 5.50 for B provides the best

Fig. 3.7. Comparisons of fits $[\ln a(\text{H}_2\text{O})_{\text{CALCD}} - \ln a(\text{H}_2\text{O})_{\text{OBS}}]$ for activities of water over NaCl-H₂O solutions, 25-300°C, by (a) Raoult's law and (b) the modified Raoult's law (MRL), 0-maximum molality NaCl.

fit, and this decrease from 6.67 at low concentrations may indicate some decrease in solvent structure caused by the high concentrations of electrolyte.] With mass-action equilibria, the use of absolute concentration with the respective ionization constants (always based on molarity) as described in the previous Report², together with the addition of a Debye-Hückel term, still would appear to be the preferred description. Application of the modified Raoult's Law, however, is a simpler approach.

The relative contribution of the addition of a Debye-Hückel term to eq 5 was evaluated also in this study. The added Debye-Hückel term was divided by a quadratic expression (with parameters a and b) and the best fit (solving for a, b, and a solvation number) to observed activity provided values of a and b that made the Debye-Hückel term strongly significant only at molalities up to about 2. The overall fit was not greatly improved except at the low molalities.

Figure 3.8 shows the calculated average solvation number (G_F) and the solvation number (j_F) for the neutral NaCl° ion-pair. The values decreasing with increasing temperature are to be

Fig. 3.8. Best fit values for G_F and j_F for aqueous NaCl solutions from the modified Raoult's law (MRL) and concentration (CONC) equations; 0-300°C.

expected in view of increasing association and kinetic energy.

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3.2 Equilibrium, Kinetics, and Speciation Studies

3.2.1 Hydrolysis of Chromium(VI) in Aqueous NaCl Solutions from 25 to 200°C

(D. A. Palmer, D. Wesolowski, R. E. Mesmer)

The chemistry of Cr(VI) in solution has application in corrosion inhibition and control. It is also encountered in steel systems as a corrosion product, particularly in oxidizing environments.

Formation constants for the bichromate ion, HCrO_4^- , have been measured at 25° intervals from

25 to 200°C in a 1 m NaCl solution. These experiments were carried out in the hydrogen electrode concentration cell¹ at relatively low hydrogen pressures (i.e. equivalent to < 2 bar of H_2 at room temperature compared to > 30 bar in previous studies²). The low H_2 pressure was maintained to minimize the reduction of chromate(VI) to the chromic(III) ion, which is the thermodynamically stable form in this reducing environment. Nevertheless, reduction was apparently the cause of unstable readings at very low pH values (< 3), at low Cr(VI) concentrations (e.g. 0.001 m), and at temperatures above 200°C, so that these became the boundary conditions for the experiments. The hydrolysis was studied at 0.01 and 0.03 m Cr(VI) concentrations by titrating basic CrO_4^{2-} solutions with

standardized HCl, thereby avoiding the low pH region.

As the dichromate ion, $\text{Cr}_2\text{O}_7^{2-}$, represents a small, but significant fraction of the total Cr(VI) content, at temperatures up to 150°C, these emf data were treated on the assumption that three species were present, viz. CrO_4^{2-} (1:0), HCrO_4^- (1:1), and $\text{Cr}_2\text{O}_7^{2-}$ (2:2). However, the (2:2) species never became a major component of the system and hence the assigned $Q_{2,2}$ values are not precise enough to warrant further discussion at this time.

The results are presented in Fig. 3.9 in the form of a plot of the $\log Q_{1,1}$ (equation (1)) values versus the reciprocal Kelvin temperature, where the smooth curve was fitted according to the equation (based on constant ΔC_p),

$$\log Q_{1,1} = 1788.6/T - 36.179 + 14.538 \log T \quad (2)$$

which gave an average absolute deviation in the experimental $\log Q_{1,1}$ values of 0.012. The thermodynamic parameters at 25°C derived from this preliminary equation³ are: $\log Q_{1,1} = 5.794 \pm 0.015$, $\Delta H = 1.8 \pm 0.9 \text{ kJ mol}^{-1}$, $\Delta S = 117 \pm 3 \text{ J K}^{-1} \text{ mol}^{-1}$, and $\Delta C_p = 121 \pm 12 \text{ J K}^{-1} \text{ mol}^{-1}$.

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Fig. 3.9. The dependence of the logarithm of the formation quotient for bichromate in 1 M NaCl on the reciprocal temperature in degrees Kelvin.

These values are consistent with the numerous other studies conducted at 25°C in other media,⁴ (C. f. at zero ionic strength the following parameters have been reported:⁵ $\log K_{1,1} = 6.500$, $\Delta H^\circ = 5.4 \text{ kJ mol}^{-1}$, $\Delta S^\circ = 142 \text{ J K}^{-1} \text{ mol}^{-1}$, and $\Delta C_p^\circ = -146 \text{ J K}^{-1} \text{ mol}^{-1}$ at 25°C) except for the heat capacity term which experience shows should be positive.

This study establishes that the capabilities of the concentration cell can be expanded to possibly include other highly oxidizing systems, as well as help demonstrate that hydrolysis equilibria can be readily measured using Pt electrodes at lower temperatures (25°C) and H_2 pressures (1 bar). The investigation is continuing and will include a range of sodium chloride concentrations from 0.2 to 5 M.

Because of the strong and distinctive absorption spectra of the hydrolyzed Cr(VI) species, the potential exists for the use of chromate as a spectrophotometric pH sensor in oxidizing media once the equilibrium speciation has been determined.

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3.2.2 Chemical Model for the Effect of Acetate on the Transport Properties of Hydrothermal Solutions

(D. A. Palmer, S. E. Drummond)

Acetate is now being recognized from field studies as an important product of the thermal degradation of organic matter, kerogen, trapped in sedimentary rocks. We recently reported¹ the kinetics of decarboxylation of acetic acid and

were able to establish a series of boundary conditions for the migration of natural gas via the precursor carboxylic acid solutions in natural hydrothermal systems. Activation energies for this process, namely,

varied markedly from 8 to 57 kcal mol⁻¹, depending on the material, and/or vessel surface, present. Thus a thermal window, or a limited range of depths, could be proposed in which decomposition was sufficiently slow to allow for significant vertical movement of the released acetate solution, but at the same time, fast enough to be virtually complete within a reasonable geological time frame, say 50 million years. However, the effect of variations in the pH of these solutions was not addressed and the mechanism of reaction was not understood.

We have now completed a series of complementary experiments with solutions of sodium acetate, and acetic acid/acetate mixtures in titanium, stainless steel and gold containers. It was found that the entire data set can be represented by a single straight line on an isokinetic plot, as illustrated in Figure 3.10.

In terms of the natural gas migration model, this simplifies the interpretation as it obviates the need to consider the pH dependence explicitly. However, on the mechanistic level, this relationship appears to be an over-simplification, and is perhaps therefore fortuitous, because it embraces both first- and zero-order processes. It does at least immediately establish that within these two subsets, common mechanisms prevail. Moreover, for all these experiments the reaction is believed to be surface catalyzed. The lowest activation enthalpies, coupled with the most negative activation entropies, reflect the greatest degree of catalysis. Catalysis apparently occurs at specific "active sites" on the surface which are generated early in the reaction sequence in direct proportion to the acetic acid concentration, and/or the concentration of acetate ion. The

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Fig. 3.10. Isokinetic plot for the decarboxylation of acetate. Legend: Acetic acid in magnetite (a), 1 M in silica (b) 18 M HAc in silica, (d) stainless steel (e), titanium (f), titanium at supercritical conditions (g), and passivated titanium (k), acetate in stainless steel (i), enlarged surface area of stainless steel (c), titanium (h), and gold (j).

acid dependence is presumed due to the dissolution, or oxidation, of the metal surface by protons, as observed for example in stainless steel and titanium vessels. Whereas acetate ions promote the solubility of the metal oxide by complexation, as in the case of titanium. The acetic acid molecules and acetate ions are able to diffuse to these sites and undergo reaction. Within this general framework, the reactions which manifest first-order behavior predominate where a sufficient (or equilibrium) number of sites are available to satisfy the initial given acid or acetate concentrations, and hence no surface area dependence is observed. A typical example of this behavior would be the reaction of acetic acid in stainless steel, where a large amount of iron is initially observed in solution, presumably giving rise early to a large number of active sites. Conversely, zero-order reactions predominate when the number of

available sites is limited either due to a restricted surface area or to a low density of active sites per unit surface area. Naturally in this case the rate of reaction should be proportional to surface area. We were unable to observe any of these reactions change their order from first to zero as the surface area was decreased because, before this transition could occur, the vessel walls invariably became the dominant catalyst. In other words, a totally inert container for studying these reactions has not been found. Thus, because both the first- and zero-order reactions probably involve the same activation step at the surface (i.e. the rate in both cases is proportional to the number of adsorbed species), it is not surprising that they both share the same isokinetic relationship shown in Fig. 3.10, indicating one overall mechanism with the same rate-limiting step - presumably the cleavage of the C-C bond of the adsorbed acetate species.

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3.2.3 The Thermodynamics of Formation of Polynuclear Bromine Species in Aqueous Solution and the Hydrolysis of Bromine
(R. W. Ramette,¹ D. A. Palmer)

The partitioning of iodine between a solution containing iodide ions and another iodide-free solution at the same acidity and ionic strength proved to be an excellent method for determining the formation constant for the triiodide anion over a wide temperature range.^{2,3} This technique has now been applied to the tribromide analog, as well as to determining the formation constant of pentabromide species. These equilibria are described by the following equations,

In addition, it was found necessary to take the hydrolysis of bromine into account, especially in the "bromide free" solution. This hydrolysis reaction is represented by equation (3),

The thermodynamic data were taken from Liebhafsky⁴ and corrected using the Davies equation⁵ to approximate the activity coefficients of the bromide ions and protons. Hydrolysis led to the formation of some tribromide, which was taken into account but never represented more than 0.35% of the free bromine in solution, even at the higher temperatures where the degree of hydrolysis is greater. The ionic strength, total bromide and proton concentrations were maintained at 0.1 M. A total of 16 experiments were conducted over the temperature range 5 to 80°C. These experiments were divided into two sets, namely, one at ca. 0.002 M free bromine where the presence of the pentabromide ion was minimal, and the other at ca. 0.15 M where it represents as much as 24% of the total bromide at low temperatures. The results were treated simultaneously using the Busing and Levy nonlinear least-squares program⁶ which was adapted to allow for iteration within the CALC subroutine in order to make the corrections for hydrolysis as described above.

The following thermodynamic parameters at 25°C were derived from this treatment: $K_3 = 16.7 \pm 0.3$, $\Delta H = -5.86 \pm 0.06 \text{ kJ mol}^{-1}$, $\Delta S = 3.7 \pm 0.4 \text{ J K}^{-1} \text{ mol}^{-1}$, and $\Delta C_p = -17.0 \pm 3.9 \text{ J K}^{-1} \text{ mol}^{-1}$; while $K_5 = 37.8 \pm 0.4$, $\Delta H = -12.9 \pm 0.4 \text{ kJ mol}^{-1}$, $\Delta S = -13.1 \pm 0.9 \text{ J K}^{-1} \text{ mol}^{-1}$, and $\Delta C_p = -2 \pm 33 \text{ J K}^{-1} \text{ mol}^{-1}$. The value of K_3 at 25°C and the associated enthalpy term are in close agreement with the recommended NBS values (viz. $K_3 = 17.1$, $\Delta H = -6.28 \text{ kJ mol}^{-1}$, and $\Delta S = 2.6 \text{ J K}^{-1} \text{ mol}^{-1}$). The heat capacity term is reported here for the first time and is very similar to that calculated in our earlier study of the triiodide ion, e.g. $-21 \text{ J K}^{-1} \text{ mol}^{-1}$. The corresponding NBS values for the pentabromide ion show a greater disparity with the parameters

reported above, viz. $K_5 = 21.8$, $\Delta H = -15.57$ kJ mol⁻¹, and $\Delta S = -26.7$ J K⁻¹ mol⁻¹ at 25°C. The heat capacity change is zero within the accuracy of both data sets.

Note that due to the high bromine vapor pressures encountered, the upper temperature limit for the Teflon vessel used was ca. 80°C. Attempts to reach higher temperatures using a Teflon-lined titanium pressure vessel were thwarted by the attack of bromine vapor on the vessel walls.

Preliminary emf measurements were made of the hydrolysis equilibrium,

using the same cell arrangement described previously^{2,3} for the analogous iodine reaction. These results at 25°C are in close agreement with the only previously reported findings,⁷ and are potentially more reliable as they: (1) involve only the two half equations which

make up equation (4), rather than an indirect comparison of the $\text{Br}_2/\text{BrO}_3^-$ and Br_2/Br^- couples versus a Calomel electrode; and (2) the current study requires much smaller corrections for the liquid junction potential, i.e. <1 mV compared with 31 mV. The temperature dependence of the equilibrium is currently under investigation.

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4. GEOCHEMISTRY

The principal focus of this research is on experimental studies of silicate melts (4.1) and the aqueous fluids (4.2) that promote the redistribution of elements and isotopes (4.3) in the crust. The long range goal of the program is the use of experimental results from simple analog systems to formulate physicochemical models of large scale geologic processes and cycles. A large internally heated pressure vessel is being used to study phase equilibria, and crystallization kinetics under controlled redox conditions in silicate melt-mineral systems. These results are fundamental to an understanding of the development of magmatic fractionation in crustal igneous rocks and the evolution of magmatic/hydrothermal fluids. Unique hydrothermal experimental facilities, including electrochemical cells, electrical conductivity cells and gold-lined pressure vessels, are used to examine acid dissociation, hydrolysis of metal ions, speciation in supercritical aqueous fluids and chloride brines, hydrothermal solubilities of minerals and decarboxylation kinetics of organic acids. Modelling of CO_2 fluxes in the oceans (4.4) is conducted in collaboration with the Environmental Sciences Division.

4.1 High Temperature Silicate Studies

4.1.1 Iron Redox Kinetics in Silicate Melts

(M. T. Naney and S. E. Swanson¹)

Redox kinetics of high and intermediate SiO_2 melt compositions were investigated in hyperliquidus experiments with natural rhyolite (U.S.G.S. standard rock RGM-1, Glass Mtn., CA; wt % $\text{SiO}_2 = 73.4$), pantellerite and pantelleritic trachyte (P-27 and P-231, Pantelleria, Italy; wt % $\text{SiO}_2 = 69.0$ and 62.4 respectively), and andesite (K28, Dennison Volcano, AK; wt % $\text{SiO}_2 = 62.0$). Experiments were performed at 100 kPa (1 atm), $\log f_{\text{O}_2} = -7.83$ and $T = 1243$ or 1343°C . After heating in a CO_2/CO furnace atmosphere for periods ranging from 1 to 8520 min, samples were withdrawn from the furnace and quenched in a filtered H_2/Ar gas jet. Wet-chemical analysis for FeO and FeO(tot) were performed using a colorimetric technique.

The observed variations of FeO/FeO(tot) as a function of time were modeled assuming that the profiles result from diffusion of oxygen in a spherical silicate liquid drop. The simple diffusion model used has the following boundary conditions: (1) samples have a uniform initial concentration of the diffusing species; (2) concentration of the diffusing component [reflected in FeO/FeO(tot) values] at the surface of a spherical liquid drop remains constant and is in equilibrium with the f_{O_2} of the CO_2/CO furnace atmosphere; (3) the diffusion coefficient (D) at

constant temperature is independent of the concentration of the diffusing component. This analysis permits the use of simple calculations and graphical inspection to test the initial assumption that the observed profiles can be modeled by a process having a significant diffusion component and to extract mass transfer coefficients (D) from the experimental data. Mass transport processes in addition to diffusion operate in these experiments. This is evident from changes in the modal volume of vapor bubbles with time. The vesiculation and subsequent migration of bubbles inferred from observations of several silicate drops held at temperature for increasing periods of time suggest a mechanism to stir the liquid and transport exsolved or trapped volatiles out of the melt. Therefore, the values obtained are not true diffusion coefficients. However, if these values are viewed as "effective diffusion coefficients" they can provide useful information for experimentalists and for the interpretation of redox equilibration controls at the surface of lava flows.

Estimates of D were made using the diffusion model previously described and the constraint that the concentration-time profile for the appropriate D must reach a "constant" value as observed (Fig. 4.1). The minimum equilibrium time was assumed to be the experiment of shortest duration among those that had attained a

Fig. 4.1. Variation of the ratio $\text{FeO}/\text{Fe}(\text{tot})$ as a function of time. The ratio $\text{FeO}/\text{Fe}(\text{tot})$ represents the fraction of the total iron (calculated as FeO) present as ferrous iron (calculated as FeO) in glasses produced by heating 100 mg aliquots of natural pantellerite sample P-27 to 1343°C at log oxygen fugacity = -7.83 . Experimental data points are represented by filled squares. Curves are concentration-time profiles calculated assuming three different effective diffusion coefficients (D). Bold line represents the profile meeting criteria discussed in text.

constant $\text{FeO}/\text{Fe}(\text{tot})$ ratio maximum (reduction) or minimum (oxidation) value. Concentration changes of 5% cannot be resolved by the analytical methods used, therefore a 95% change is indistinguishable from 100% change. It was also arbitrarily assumed that this minimum time represented a change of 99.99%. The resulting coefficients are significantly greater than diffusion coefficients measured by oxygen isotope diffusion in silicate melts of similar composition.

The "effective diffusion coefficients" obtained from this exercise, when plotted as a function of calculated non-bridging oxygen/tetrahedral cation ratios (NBO/T - a composition dependent measure of silicate melt polymerization), are useful for predicting melt equilibration times. Linear least squares fits to the data obtained at 1243 and 1343°C provide relationships between NBO/T and D that may be used to estimate an effective D (Fig. 4.2). The estimated diffusion coefficients can be used to estimate the time needed to reach redox equilibrium for melts of other compositions. The diffusion model requires that the quantity $Dt/a^2 = 1$ at equilibrium (D = diffusion coefficient, cm^2/sec ; t = time, sec; a = radius of

Fig. 4.2. Variation of the effective diffusion coefficient (D) as a function of NBO/T (non-bridging oxygen/tetrahedral cation ratio - a calculated bulk composition dependent parameter describing the extent of polymerization in a silicate melt). Effective diffusion coefficients were determined as described in the text and illustrated in Fig. 4.1. Linear trends are least squares fits of isothermal data. Open squares - 1343°C , closed squares - 1243°C .

sphere, cm). With the estimate of an effective D and the known diameter of the liquid droplets used in an experiment, the time to reach redox equilibrium within selected limits can be calculated. Equilibrium times estimated by this method are typically on the order of 300 minutes longer than equilibrium times observed during experiments. Although far from precise, such estimates are a useful guide for conducting experiments with new bulk compositions.

1. S. E. Swanson, ORAU visiting scientist, University of Alaska.

4.1.2 Redox Kinetics and Estimates of f_{O_2} in Volcanic Systems

(S. E. Swanson¹ and M. T. Nanay)

Estimates of oxygen fugacity (f_{O_2}) in glassy siliceous lavas based on coexisting Fe-Ti oxides pairs² and bulk rock composition³ yield different results for a large number of cases reported in the literature. For a given temperature, f_{O_2} calculated from bulk composition is 1×10^8 log units higher (more oxidized) than the value derived from coexisting Fe-Ti oxides contained in the rock (Fig. 4.3). The magnitude of this difference (Δ = rock composition f_{O_2} minus Fe-Ti oxide f_{O_2}) increases with increasing

Fig. 4.3. Variation of $\Delta = \text{Calc-Obs}$, the difference between magmatic oxygen fugacity (f_{O_2}) values estimated by glass redox state and Fe-Ti oxide mineral pairs [$f_{O_2}(\text{glass})$ minus $f_{O_2}(\text{Fe-Ti oxide})$] as a function of temperature (estimated from the compositions of coexisting Fe-Ti oxide pairs). Closed diamonds represent data from volcanic rocks containing >70 wt % SiO_2 , open squares represent volcanic rocks containing <70 wt % SiO_2 . All data shown is from the open geologic literature.

silica content (Fig. 4.4), degree of oxidation and crystallinity (Fig. 4.5); but shows no correlation with eruptive style (Fig. 4.4). Lower temperatures recorded by Fe-Ti oxides correlate with larger Δ values (Fig. 4.3).

Subsolidus changes in rock chemistry related to hydration or devitrification of volcanic glass account for the existence of a Δ value in many of the samples. Glassy rhyolites with 2-3 wt % H_2O yield $\Delta = 3$ to 5 log units, similar rocks with 0.4 to 0.8 wt % H_2O yield $\Delta = 1$ to 2 log units (Fig. 4.6). The effects of devitrification are more difficult to quantify because of

Fig. 4.4. Variation of $\Delta = \text{Calc-Obs}$ as a function of the wt % SiO_2 content of natural volcanic rocks. The style of volcanic eruption is differentiated by symbols. Same data set as used in Fig. 4.3.

Fig. 4.5. Variation of $\Delta = \text{Calc-Obs}$ as a function of the iron redox state of the rock. Rocks having different groundmass matrix texture are indicated by the symbols shown in the legend.

a common association with hydration. However, devitrified samples tend to have the largest Δ values within a given suite of samples (Fig. 4.5). Experimental studies of silica-rich melts⁴ indicate that iron redox kinetics in rhyolitic melts are very sluggish when compared with other silica-rich melts (pantelleritic and andesitic melts) and with the kinetics of Fe-Ti oxide equilibration.⁵ Oxide phases included

Fig. 4.6. Log oxygen fugacity (f_{O_2}) as a function of temperature for a suite of glassy rhyolites. Oxygen fugacity estimates calculated from glass redox state are shown by open circles. The labels indicate the wt % H_2O contained in the glasses. The solid circles represent f_{O_2} estimates determined from the compositions of coexisting Fe-Ti oxide mineral pairs. Temperature is estimated from the Fe-Ti oxides.

within a silica-rich melt are not expected to record equilibrium changes in the magmatic system during cooling because of the sluggish kinetics of the host melt. Instead, oxide phases may change composition in response to a buffer imposed upon them by the host melt. This suggests that unaltered quenched silicate liquid (volcanic glass) may record higher (pre-eruptive?) temperature and oxygen fugacity. The Δ values of 1 to 2 log units observed in relatively dry, glassy rhyolites may provide a measure of the effect of different "blocking" temperatures for the Fe-Ti oxides and the silicate liquid in natural systems.

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4.1.3 A Mössbauer Study of the Influence of Melt Quenching on Iron Site Occupancy in Silicate Glasses

(M. D. Dyar,¹ M. T. Naney, S. E. Swanson²)

A recent Mössbauer spectroscopy study of lunar analog glasses³ has shown that the different quenching methods commonly used in high-temperature experiments can produce significant changes in the ratio of octahedrally and tetrahedrally coordinated iron structural sites, together with changes in the ratio of ferrous and ferric iron in silicate glasses of the same composition. The implication of this finding is that it may be difficult or impossible to preserve the iron structural site partitioning and ferrous/ferric ratios of silicate melts during the quenching process. The nature and magnitude of such structural and chemical changes is important to both experimentalists studying the physiochemical properties of simu-

lated magmas produced in the laboratory and to geochemists attempting to infer the properties of magmas from the study of natural volcanic glasses. In both cases the materials studied are glasses produced by the rapid cooling (quenching) of silicate melts.

To evaluate the potential of different quenching methods for influencing iron site partitioning and redox state in silicate liquids spanning the compositional range of terrestrial magmas, a cooperative study was conducted with the Massachusetts Institute of Technology. The primary goal of this study was to ascertain if the structural and chemical changes ascribed to quenching in simulated lunar glasses could be observed in any or all of three glass compositions produced by quenching melts derived by heating natural basaltic, andesitic, and rhyolitic volcanic rocks.

All quenching experiments were conducted at 1343°C, and $\log f_{O_2} = -7.83$. Starting materials consisted of crushed basalt (U.S.G.S. standard rock BCR-1) andesite (K2B, Dennison Volcano, Alaska) and rhyolite (U.S.G.S. standard rock RGM-1). Approximately 100 mg of powdered rock were pressed into a pellet 5 mm in diameter and 3 mm thick. Samples were attached to loops of platinum wire (0.20 mm dia.) using a filament wire heater, before being suspended in the hot zone of a CO₂-CO gas mixing, vertical tube furnace. Each silicate melt composition was subjected to three quenching methods: (1) withdrawal of the silicate liquid sample droplet from the furnace into the path of a filtered air jet; (2) withdrawal from the furnace into a filtered H₂-Ar jet; and (3) dropping the sample (without exposure to air) into a NaCl-ice brine. Sample cooling rate is slowest during an air quench and fastest in an NaCl-ice brine quench.

Mössbauer spectra were recorded on a constant acceleration Austin Science Associates spectrometer using a 70-80 mCi ⁵⁷Co in Pd matrix source. Velocity was calibrated relative to the spectrum of iron foil. Mössbauer spectra were fit to a sum of Lorentzian/Gaussian combined line shapes³ by means of a Gauss non-linear regression procedure, using a facility to constrain any set of

parameters or linear combination of parameters as provided by the program STONE.⁴

Mössbauer parameters for the basalt, andesite, and rhyolite glasses are shown in Table 4.1. For this suite of samples no significant variation in values of isomer shift and quadrupole splitting were observed among spectra from glasses of the same composition, with one exception. This indicates that no changes in ferrous/ferric ratio can be detected for samples quenched by the three methods used in this study. The exception is most probably the

result of a sample configuration change during the melting experiment that fused two samples together. The resulting sample experienced a different cooling history during the quench because of the larger mass.

Although the relative peak positions in the different spectra remain generally constant within the resolution of the technique, there is significant variation in peak areas, for the basalt glasses in particular. The ratio of octahedral Fe^{2+} /tetrahedral Fe^{2+} becomes larger as the quench medium changes from ice-brine to

Table 4.1. Mössbauer parameters for basalt, andesite, and rhyolite glasses quenched into different media

Sample	Quench Medium	$\sim\text{Fe}^{2+}_{\text{oct}}$			$\sim\text{Fe}^{2+}_{\text{tet}}$			χ^2	% Misfit
		I.S.1	Q.S.1	% Area	I.S.2	Q.S.2	% Area		
Basalt glass	Brine/Ice	1.16	2.00	54	0.99	1.77	46	906	0.29
		(0.007)*	(0.009)	(1.6)	(0.008)	(0.010)	(1.6)		(0.29)
	H_2 -Ar Jet	1.14	1.99	59	0.86	1.75	41	1047	0.47
		(0.006)	(0.008)	(1.5)	(0.009)	(0.011)	(1.5)		(0.04)
	Air Jet	1.13	1.98	64	0.84	1.76	36	1013	0.25
		(0.004)	(0.005)	(1.1)	(0.007)	(0.009)	(1.1)		(0.02)
Andesite Glass**	Brine/Ice	1.11	1.97	27	0.94	1.63	73	391	-0.17
		(0.007)	(0.013)	(2.5)	(0.019)	(0.037)	(2.2)		(-0.03)
	H_2 -Ar Jet	1.08	1.92	10	0.80	1.35	90	667	0.41
		(0.007)	(0.016)	(2.6)	(0.031)	(0.064)	(2.2)		(0.07)
	Air Jet	1.09	1.97	29	0.96	1.706	71	404	-0.15
		(0.009)	(0.016)	(2.2)	(0.014)	(0.029)	(2.0)		(-0.03)
Rhyolite Glass	Brine/Ice	1.04	1.66	100				593	0.17
		(0.007)	(0.008)	(1.2)					(0.04)
	H_2 -Ar Jet	1.05	1.71	100				862	0.65
		(0.006)	(0.008)	(1.0)					(0.06)
	Air Jet	1.05	1.70	100				473	-0.19
		(0.008)	(0.011)	(1.7)					(-0.06)

*Standard deviations (in parentheses) refer to errors in the curve-fitting procedure (related to counting statistics). The total error in these measurements are isomer shift = 0.02 mm/sec, quadrupole splitting = 0.06 mm/sec, % area = 2% I.S.1, I.S.2 = isomer shift of peak doublets 1 and 2 respectively. Q.S.1, Q.S.2 = quadrupole splitting of peak doublets 1 and 2 respectively. % area = % fraction of total Fe^{2+} . % Misfit = a measure of the "uncertainty" of fit.

**Due to poor statistics on four peak fits, three peak fits are tabulated. Doublet 1 pairs peaks 1 and 2; doublet 2 pairs peaks 1 and 3.

H₂-Ar to air. The ice-brine bath is the most efficient quenching medium tested, yielding samples with up to 46% of the Fe⁺² in the tetrahedral sites. The H₂-Ar jet is slightly less efficient, with 3-10% less Fe⁺² in tetrahedral sites. The air jet is the least efficient quench medium used, producing glasses with the majority of Fe⁺² in octahedral sites. These trends may be predicted from the known relationship between temperature, cooling rate, and molar volume: rapidly (ice-brine) cooled glasses are most random and least dense, while more slowly (air) quenched samples are relatively more ordered and dense. Changes in site size and geometries in the densest glasses may cause Fe⁺² to preferentially occupy more spacious octahedral sites.

The correlation between quench medium and Fe site occupancy is not observed in the rhyolite and andesite glasses. The rhyolite samples were too Fe-poor to enable detailed Mössbauer spectra to be measured; however the basic fits showed no changes among the samples. If measurable structural and chemical changes of iron do occur during the quenching of natural magmas it is unlikely that any natural glass cools rapidly enough to preserve the iron site occupancy and valence state of the magma completely.

1. M. D. Dyar, Department of Earth, Atmospheric, and Planetary Sciences, Massachusetts Institute of Technology, Cambridge.
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4.2 Hydrothermal Geochemistry

4.2.1 Chemical Model for the Effect of Acetate on the Transport Properties of Hydrothermal Solutions

(D. A. Palmer, S. E. Drummond)

Acetate is now being recognized from field studies as an important product of the thermal

degradation of organic matter, kerogen, trapped in sedimentary rocks. We recently reported¹ the kinetics of decarboxylation of acetic acid and were able to establish a series of boundary conditions for the migration of natural gas via the precursor carboxylic acid solutions in natural hydrothermal systems. Activation energies for this process, namely,

varied markedly, from 8 to 57 kcal/mol, depending on the material, and/or vessel surface, present. Thus a thermal window, or a limited range of depths, could be proposed in which decomposition was sufficiently slow to allow for significant vertical movement of the released acetate solution, but at the same time fast enough to be virtually complete within a reasonable geological time frame, say 50 million years. However, the effect of variations in the pH of these solutions was not addressed and the intimate mechanism of reaction was not understood.

We have now completed a series of complementary experiments with solutions of sodium acetate, and acetic acid/acetate mixtures in titanium, stainless steel and gold containers. It was found that the entire data set can be represented by a single straight line on an isokinetic plot, as illustrated in Fig. 4.7.

In terms of the natural gas migration model, this simplifies the interpretation as it obviates the need to consider the pH dependence explicitly. However, on the mechanistic level, this relationship appears to be an oversimplification, and is perhaps therefore fortuitous, because it embraces both first- and zero-order processes. It does at least immediately establish that within these two subsets, common mechanisms prevail. Moreover, all these reactions are believed to be surface catalyzed with the lowest activation enthalpies, coupled with the most negative activation entropies, reflecting the greatest degree of catalysis. Catalysis apparently occurs at specific "active sites" on the surface. These sites are generated in direct proportion to the free acid con-

ORNL-DWG 84-16221

Fig. 4.7. Isokinetic Plot for the Decarboxylation of Acetate. Legend: Acetic acid in magnetite (a), silica (b) 18 M HAc, (d) 1 M HAc stainless steel (e), titanium (f), titanium at supercritical conditions (g), and passivated titanium (k), acetate in stainless steel (i), enlarged surface area of stainless steel (c), titanium (h), and gold (j).

centration, and/or the concentration of acetate ion. The acid dependence is due to the dissolution, or oxidation, of the metal surface by protons, as observed for example in stainless steel and titanium vessels; whereas the number of available sites can also be enhanced when the metal ion forms stable complexes with acetate in solution thereby promoting the solubility of the metal, as in the case of titanium. The acetic acid molecules and acetate ions are then able to diffuse to these sites and undergo reaction. Within this general framework, the reactions which manifest first-order behavior predominate where an excess of potential sites are available, such that for a given acid or acetate concentration, no surface area dependence is observed. A typical example of this behavior would be the reaction of acetic acid in stainless steel, where a large amount of iron is initially observed in solution, presumably giving rise early to a large number of active

sites. Conversely, zero-order reactions predominate when the number of available sites is limited and hence they are all occupied. Naturally in this case the rate of reaction should be proportional to surface area. We were unable to observe any of these reactions change their order from first to zero as the surface area was decreased because, before this transition could occur, the vessel walls invariably became the dominant catalyst. In other words, a totally inert container for studying these reactions has not been found. Thus, because both the first- and zero-order reactions probably involve the same activation step at the surface, it is not surprising that they both share the same isokinetic relationship shown in Fig. 4.7, indicating one overall mechanism with the same rate-limiting step - presumably the cleavage of the C-C bond of the adsorbed acetate species.

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4.2.2 Determination of the Formation Quotients for Iron Acetate Complexes from Magnetite Solubility Measurements from 100 to 300°C

(S. E. Drummond, D. A. Palmer, D. J. Clark¹)

Previous results (Chemistry Division Annu. Prog. Rep., 1984, Sec. 4.2.1; 1985, Sec. 3) on the kinetics of acetate decarboxylation have demonstrated that acetate is sufficiently stable to warrant its consideration as a ligand which, by enhancing the solubility of the mineral through complexation, could be effective in transporting metals in hydrothermal solutions below 300°C. Because an evaluation of the role of acetate in the migration of metals requires a knowledge of the stability constants, Q_n , that is essentially nonexistent above 25°C, we have employed a newly constructed hydrothermal apparatus to investigate mineral solubilities in acetate media. Iron was chosen for this initial effort to measure the stability of metal-acetate complexes because: iron is ubiquitous in most hydrothermal systems; iron is important in determining the mobility of other metals that

precipitate as sulfides; magnetite (Fe_3O_4) is a convenient phase for such a solubility experiment particularly since, when combined with hematite (Fe_2O_3), it constitutes both a redox buffer and a thermodynamically stable source of iron.

The experimental system consists of a gold bag which is contained inside a pressure vessel and which contains about 125 g of a 1:1 mixture of magnetite and hematite, and about 200 g of a solution of sodium acetate and acetic acid. Hence, the overall reaction being studied is expressed by the following general equation:

It follows from this expression, and the fact that the pH of the solutions were sufficiently low to allow ferrous hydroxide species to be ignored, that the total iron in solution can be accounted for as follows

$$\text{Fe} = \sum_0^n \frac{\alpha_n \cdot [\text{HAc}]^2}{[\text{Ac}^-]^{2-n}} \quad (2)$$

Accordingly the experiments involve varying the proportions and amounts of Ac^- and HAc and measuring the concentration of these species and total iron at each temperature.

Our present results have been at 0.5 m Ac^- /0.5 m HAc , 0.1 m Ac^- /0.1 m HAc and 0.1 m Ac^- /0.9 m HAc over the temperature range of 100° to 300°C. Although these results are preliminary and need further confirmation, it is apparent that over this composition range, the FeAc^+ species is predominant from 100 to 200°C while at 250°C the $\text{Fe}(\text{Ac})_2$ species appears to dominate with perhaps some $\text{Fe}(\text{Ac})_3^-$ at 250°C and above. After accounting for the ionization of acetic acid, the solubility of magnetite in the absence of acetate, and the free energies of magnetite and hematite, these results can be cast in terms of the simple iron-acetate complexing quotients. The resulting quotients (adjusted to an ionic

strength of 0.1) vary from about 10 at 100°C to 800 at 200°C for the reaction $\text{Fe}^{2+} + \text{Ac}^- \rightleftharpoons \text{FeAc}^+$, and at 250°C the quotient is about 25,000 for the reaction $\text{Fe}^{2+} + 2\text{Ac}^- \rightleftharpoons \text{Fe}(\text{Ac})_2$.

Although it is now premature to state definitely that acetate complexing accounts for a substantial portion of the iron (or perhaps other metals) in some hydrothermal solutions, these results do seem to suggest that possibility. This concept is particularly attractive in environments where neither chloride nor bisulfide complexing is sufficient to account for the metals in solution but where there are abundant potential sources of acetate. The exact role of acetate complexing in metal transport will remain speculative until more information is available on the stability of the complexes of metals with acetate and the competing ligands.

1. Student from Carleton College participating in ORNL-GLCA/ACM Science Semester.

4.2.3 Magnesium Hydrolysis to 250°C by EMF Titration

(S. E. Drummond)

The hydrolysis of magnesium in 1.0 m NaCl media has been studied from 50 to 250°C by EMF titrations using a hydrogen electrode concentration cell. Acidic solutions ($[\text{H}^+] = 10^{-3}$ to 10^{-4} m) of 0.05 m MgCl_2 were titrated with NaOH until brucite ($\text{Mg}(\text{OH})_2$) precipitation commenced. At the termination of these titrations, less than 1% of the total magnesium was hydrolyzed (i.e. $\bar{n} < 0.01$). If the hydrolysis is considered in terms of the general reaction,

then $\bar{n}$ is appropriately expressed accordingly:

$$\bar{n} = \frac{\sum y \cdot \alpha_{xy} \cdot [\text{Mg}^{2+}]^x / [\text{H}^+]^y}{\sum \text{Mg}} \quad (2)$$

Least-squares fitting of the measured values of $\bar{n}$, $[\text{H}^+]$ and $[\text{Mg}^{2+}]$ to this general form indica-

tes that a model including only the MgOH^+ species explains the hydrolysis data adequately (i.e. within about 0.0005 in $\bar{n}$). This species assignment is consistent with the results of McGee and Hostetler (1975) at similar magnesium concentrations from 0 to 90°C and is in accord with the work of Lewis (1963) who observed the $\text{Mg}_4(\text{OH})_4^{4+}$ species only at much higher magnesium levels. Over the range from 50° to 250°C the resulting data for the first hydrolysis constant of magnesium in 1.0 M NaCl, expressed in the form of equation 1, is described with a standard deviation of 0.025 log Q_{11} units by the following equation:

$$\log Q_{11} = -1.356 - 3207.2/T \quad (3)$$

This equation corresponds to a ΔH of reaction of 14.7 kcal mol⁻¹ which is in remarkable agreement with the data of McGee and Hostetler and with the predicted value of 14.9 kcal mol⁻¹ of Baes and Mesmer (1981). These data imply that for hydrothermal solutions near neutral pH and with magnesium concentrations near 0.01 M, the MgOH^+ species can represent a substantial source of alkalinity that can be released upon cooling to increase pH appreciably. For example, cooling a 250°C, 1.0 M NaCl solution with 0.01 M Mg at neutral pH (5.13) will increase the pH to 7.16 or 1.2 units alkaline at 100°C.

These experiments demonstrate that it is possible to obtain accurate hydrolysis data for magnesium notwithstanding the limited range that is accessible. As a consequence, this work will be extended over a range of NaCl media from 0.1 to 5.0 M. These results along with either isopiestic data on MgCl_2 -NaCl mixtures or brucite solubility data in NaCl media should enable the determination of the activity coefficient quotient of an ion pair (MgOH^+) with one other ion (either H^+ or OH^-). This apparently would represent the first accomplishment of its kind above 100°C.

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4.2.4 Transport and Deposition of Metals in Geothermal Systems

(D. R. Cole, S. E. Drummond)

Many shallow gold-silver ore deposits are probably "fossil equivalents" of high-temperature geothermal systems like Broadlands, New Zealand, and Steamboat Springs, Nevada. The evidence strongly suggests that the fossil and active systems are similar in their rare chemical elements (gold, silver, arsenic, antimony, lead, zinc, and mercury), ranges of temperature and pressure, fluid compositions, isotope relationships, and mineralogy of ore and altered host rocks. These similarities have prompted many geothermal companies to adopt the same exploration strategy to find economic geothermal systems as that used by mining companies in gold-silver prospecting - namely to look for specific trace element (gold, silver, lead, zinc, and mercury) and mineralogical patterns in surface rocks and shallow drill holes.

Our goal is to relate quantitatively the chemical and mineralogical patterns observed in the surface rocks to physical-chemical processes occurring at depth in order to more readily discriminate between geothermal systems having great energy potential from those that do not. However, fundamental questions still remain unanswered regarding the mechanisms (e.g., boiling, mixing, and cooling) responsible for transporting and depositing gold, silver, lead, zinc, mercury, and other trace metals in geothermal solutions.

We have examined through detailed computer calculations the importance of geochemical parameters such as temperature, salinity, pH, hydrogen sulfide, and carbon dioxide on trace metal solubilities in geothermal brines. We are also quantifying the role of boiling and fluid mixing as agents of metal localization. We singled out boiling because in the majority of high-temperature geothermal systems, some of the liquid is carried off as steam. The most significant

effect of boiling on the chemistry of a geothermal solution is associated with the exsolution of carbon dioxide and hydrogen sulfide. Carbon dioxide exsolution causes dramatic increases in the solution's pH, whereas hydrogen sulfide loss to the vapor phase causes the fluid to oxidize.

Through chemical modeling we have demonstrated that significant gold transport, as $\text{Au}(\text{HS})_2^-$, can occur at low temperature ($<250^\circ\text{C}$), high total H_2S , and relatively high pH (>5). Conversely, silver concentrations in solution, as AgCl_2^- , are highest at high temperature ($>250^\circ\text{C}$), low total H_2S , and low pH (<5). The two distinct populations of silver/gold ratios (0.01 to 1 and 1 to 100) observed in both geothermal and fossil ore deposit systems can be attributed to these differences in the transport properties of gold and silver.

Under most circumstances, gold and silver concentrations decrease in solution because boiling induces mineralization. In fact, boiling is generally a favorable process for depositing most minerals, including oxides, native metals, sulfides, quartz, and, to a lesser extent, carbonates and sulfates. Interestingly, systems rich in carbon dioxide, although more effective in causing pH changes and subsequent mineralization, also tend to enlarge the areas over which deposition can occur (decreasing ore grades). The reason for this dispersed deposition is that, at higher carbon dioxide concentrations, the total fluid pressure is also higher; thus a pressure drop occurs during boiling over a greater vertical interval, resulting in a "smeared out" or enlarged mineral depositional zone. Future research efforts are focused on examining geothermal and fossil hydrothermal systems for evidence of this behavior to validate the chemical models.

4.3 Stable Isotope Geochemistry

4.3.1 Rates of Oxygen and Hydrogen Isotope Exchange in the System Basalt-Seawater

(D. R. Cole)

The existence of submarine hydrothermal systems along actively spreading mid-ocean

ridges was first suggested by Elder¹ on the basis of the high conductive heat flow measured there and by analogy with subaerial geothermal systems. Since then a large body of evidence has accumulated which indicates that convection of heated seawater through the oceanic crust, with associated submarine hot spring activity, is a very common and perhaps pervasive phenomenon along the sea floor spreading centers of the world's oceans.² This hydrothermal interaction of basalt and seawater is thought to play a major role in crustal formation and aging, including changes in chemistry, mineralogy, and physical properties; geochemical mass balances; and formation of ore deposits on and within the crust.³

A stable isotopic study was undertaken in order to quantify the influence of temperature, solution chemistry, crystallinity, surface area, water-to-rock mass ratio and time on isotopic shifts during experimental basalt-seawater interaction. Specifically, changes in the solution chemistry, mineralogy, and oxygen and hydrogen stable isotopic compositions of solutions and solids were monitored through time as interaction proceeds. This information was used to determine the mechanisms and rates of isotopic exchange reactions.

In general, oceanic tholeiitic basalts ($\delta^{18}\text{O} \approx 5.6$ ‰, $\delta\text{D} \approx -70$ ‰) were reacted with natural ($\delta^{18}\text{O}$, $\delta\text{D} \approx 0$ ‰) or artificial seawater ($\delta^{18}\text{O} \approx -5$ ‰, no Mg , SO_4^{2-} or HCO_3^-) for various durations (167 to 272 days) at temperatures and pressures ranging from 300 to 500°C and 0.5 to 1.0 kb, respectively. Most experiments were carried out in sealed capsules of gold or platinum with volumes averaging 15 cc. The water/rock mass ratios ranged from one to five. The crystallinity of the starting basalt was varied in four steps: holocrystalline (0% glass), crystalline (~20% glass), crystalline plus glass (3:1, ~40% glass), and glass. Surface areas of starting materials were determined from nitrogen and krypton BET measurements.

At 300°C it was found that Ca^{2+} , H_2S , CO_2 , SiO_2 , K^+ and H^+ were released into solution from

the rock and Mg^{2+} , SO_4^{2-} , and Na^+ were removed in varying amounts from the solution and taken up by the solid phases. The pH showed an initial drop but then gradually rose to pH ~ 5. In general, these experiments indicated that the chemistry of the solutions was controlled by the solid phases, with Mg uptake being balanced by Ca loss, and with the substitution of Na for Ca also being an essential part of the balance. Mineralogical examination showed the solid products to consist predominantly of smectites, smectite-chlorite, anhydrite and albite, which are all generally consistent with assemblages in the metabasalts recovered from the oceans.

Experiments at 400-500°C exhibited similar trends in solution chemistry as observed at 300°C, except that the magnitude of change generally increased with increasing temperature. The mineral assemblage formed at these higher temperatures consisted of smectite-chlorite, talc, actinolite, quartz, and anhydrite.

These alteration reactions are chiefly responsible for the oxygen ($^{18}\text{O}/^{16}\text{O}$) and hydrogen (D/H) isotopic changes observed in the basalt and seawater. In general, depletion of ^{18}O and enrichment of D in basalts occur at all three temperatures investigated, with the magnitudes of change being greater as temperature increases. For run durations exceeding 235 days, the $\delta^{18}\text{O}$ depletions (initial basalt minus final basalt) in basalt average approximately 0.5, 1.5, and 2.75 ‰ at 300, 400, and 500°C, respectively. The δD enrichments (final basalt minus initial basalt) average roughly 5, 15, and 30 ‰ at 300, 400, and 500°C, respectively for run times exceeding 235 days.

Isotopic shifts (i.e., ^{18}O depletion and D enrichment in basalt) observed in these low water/rock ratio experiments increase in magnitude with an increase in run duration. This trend is only true, however, for experiments conducted at 300 and 400°C. At 500°C, the basalts exhibit a nearly constant ^{18}O depletion of 2 to 3 ‰ and D enrichment of approximately 30 ‰.

The effects of crystallinity and water/rock mass ratio on the observed isotopic shifts

appear to be subordinate compared to time and temperature. Slightly greater isotopic exchange is noted for experiments in which the basalt was comprised of glass. A slight increase in the magnitude of isotope exchange was also observed as the water/rock mass ratio increased from one to five.

These isotopic data were used to calculate the fractional degree of equilibration. These calculations demonstrated that, with the exception of a few experiments at 500°C, oxygen and hydrogen isotopic fractionation departed significantly from the expected equilibrium values. Thus, the measured isotopic shifts between basalt and seawater could be evaluated on a kinetic basis. The isotopic data conform best to a pseudo-first-order rate law, and were used to calculate rate constants (shown in Fig. 4.8).

For the basalt-seawater system, the oxygen isotopic rate constants range from 10^{-10} to 10^{-8} moles $\text{O m}^{-2} \text{sec}^{-1}$ for temperatures of 300 to 500°C, respectively. These rates are very similar in magnitude to those estimated for the reactions paragonite + 3 M KCl and kaolinite + 0.04 N NaCl.⁴ Hydrogen, on the other hand, exhibits rates of exchange approximately one order of magnitude less than oxygen (e.g., $10^{-8.8}$ versus 10^{-8} at 500°C). The reason(s) for

Fig. 4.8. An Arrhenius plot of rate curves for oxygen and hydrogen isotopic exchange between basalt and seawater, compared with selected mineral-solution reactions.

this difference in rates is not readily apparent. It is possible that new phases containing only oxygen forming at the expense of the basalt nucleate (hence exchange) faster than phases consisting of both oxygen and hydrogen.

Activation energies for oxygen and hydrogen rates of exchange are very similar, 12.7 and 11 kcal mol⁻¹, respectively. These activation energies are similar to those of chemical reactions involving fluids and mineral surfaces.⁴ A diffusional isotopic-exchange component (using anorthite as an analog substance) was found to contribute only 20% to the total oxygen isotope exchange observed at 500°C. At lower temperatures, the diffusion contribution was negligible. Depending on the analog substance (e.g. muscovite vs epidote) and grain geometry (e.g. plate vs cylinder) selected, hydrogen isotope exchange through diffusion could totally dominate at 500°C or be negligible. The actual diffusion contribution probably lies somewhere in between these two extremes.

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4.3.2 Regional Oxygen Isotope Survey of Granitoids in the Southern Appalachians (D Mesolowski)

The purpose of this study is to investigate the usefulness of regional oxygen isotope analyses of granites in unraveling the petrogenesis, tectonic history, and mineral potential of a structurally complex metamorphic terrane. The ultimate goal is a better understanding of the energy resources and nuclear waste storage potential of the Southern Appalachians. The oxygen isotopic compositions of 117 whole rock samples from 83 Paleozoic plutons distributed throughout the crystalline Southern Appalachians are reported together with literature data on 20 additional plutons.^{1,2} The sample distribution is indicated in Figure 4.9. These results include nearly all of the major granitic plutons of the southeastern United States.

As can be seen in Figure 4.9, the Southern Appalachians have been divided into belts of genetically and metamorphically similar rocks separated by various structural and lithotectonic boundaries.³ Very briefly, the Blue Ridge, Ashland-Wedowee and Inner Piedmont Belts consist of strongly metamorphosed sandstones and shales, the Slate Belt rocks are predominantly weakly metamorphosed silicic to intermediate volcanics and the remaining belts contain appreciable proportions of both volcanics and clastics.

Figure 4.10 summarizes the oxygen isotope data from the granites within these belts. As can be seen, values ranging from -0.8 to 11 ‰ are

Fig. 4.9. Metamorphic belts of the Southern Appalachians and location of granitoids for which oxygen isotope data are available (▲ - this study; ● - Wenner, 1981; ○ - Casadevall and Rye, 1980).

Fig. 4.10. Distribution of oxygen isotope ratios of Southern Appalachian granites according to the metamorphic belts in which they occur (Figure 4.9).

observed (all isotopic ratios, $^{18}\text{O}/^{16}\text{O}$, are reported as per mil deviations from the SMOW standard). Since granitic magmas derived from partial melting of mantle or lower-crustal igneous rocks typically range from 6-8 ‰, explanations must be sought for isotopic enrichment or depletion beyond this range. Possibilities include: a) interaction of the subsolidus intrusives with isotopically depleted (e.g. meteoric) or enriched (e.g. magmatic, metamorphic) waters; or b) partial melting or assimilation of enriched or depleted source or host rocks. Isotopically enriched rocks include metasediments containing abundant authigenic clays and volcaniclastics which have reacted extensively with low-temperature seawater.

Depleted rocks are typically volcaniclastics which have exchanged extensively with moderate-to-high temperature meteoric water in active geothermal systems.

As the discussion above indicates, oxygen isotopic data provide a wealth of information on the origins of various rock types and the geologic processes which subsequently affect them. Obviously, correct interpretation of the data in Figure 4.10 requires substantial geological and geochemical input. However, several general observations can be made.

It is clear that the intrusives of the Blue Ridge, Ashland-Wedowee and Inner Piedmont Belts are isotopically enriched relative to those of the Raleigh, Kiokee, and Slate Belts and there is little overlap of the isotopic ranges of intrusives in these two large regions. The Charlotte and Kings Mountain Belt granites have intermediate isotopic ranges. This suggests a general west-to-east depletion in isotopic compositions (Figure 4.9) which correlates with the amount of volcanic material in the host region. However, a group of granitoids in eastern Virginia are relatively enriched in ^{18}O , and have been designated the "?" Belt in this study.

In the western belts, most of the intrusives are pre- or synmetamorphic and the isotopic results in Figure 4.10, together with recent detailed petrologic and isotopic studies in the Ashland-Wedowee Belt⁴ suggest that these intrusives were probably formed by partial melting of isotopically enriched metasediments similar to their present host rocks.

Many of the larger plutons of the Slate Belt postdate the regional metamorphic age. Also, the grade of metamorphism is not sufficient for the immediately adjacent host rocks to have been the source of these intrusives. Their source region must have lain at a much greater depth than the present surface. Therefore, in order to explain the strongly depleted isotopic values observed, either regional isotopic depletion of the Slate Belt volcanics by interaction with meteoric waters was pervasive and penetrated to great depth within the volcanic pile of which

the Slate Belt represents only an erosional remnant; or many of the intrusives underwent hydrothermal alteration by deep circulating meteoric fluids shortly after their crystallization. Additional isotopic analyses of the granites and particularly their host rocks are required in order to test these hypotheses. However, both scenarios place important constraints on the Paleoenvironment and/or tectonic evolution of the Slate Belt and adjacent terranes.

The strongly enriched granites of the "?" Belt are possibly related to continental sedimentary material like that of the Inner Piedmont rocks. If the Slate Belt represents a volcanic island arc offshore of the ancient Inner Piedmont eugeosyncline bordering the North American craton, then continental rocks further east may represent portions of the African continent rifted off during the opening of the modern Atlantic Ocean.

Table 4.2 presents some results of statistical analysis of the isotope data combined with major element analyses provided to the author by C. P. Thornton of the Pennsylvania State University. As can be seen, high ^{180} granites are enriched in potassium and depleted in sodium and calcium, or in other words, granites enriched in K-spar and muscovite relative to plagioclase. Also, the alumina saturation index (ASI) is strongly positively correlated with δ^{180} . This index is a measure of excess aluminum over that needed for the feldspar component of the rock and is typically high in S-Type granites derived from metasedimentary source rocks and low in I-Type granites derived from igneous source rocks.⁵ High ^{180} granites from the study area have low $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios and low Fe_2O_3 content. This is typical of Ilmenite-Series granitoids derived from carbonaceous sediments as compared with Magnetite-Series granites produced from more oxidized igneous source rocks.⁶

The high degree of intercorrelation among the major elements in the study area suggested factor analysis, and as shown in Table 4.2, this resulted in a small number of readily explainable master variables. Factor 1 probably

Table 4.2. Statistical analysis of oxygen isotope and major element data from the Southern Appalachian Plutons. (Major element data obtained from C. P. Thornton of The Pennsylvania State University)

Correlation Coefficient/Significance Level (%)						
	ASI*	K ₂ O	Na ₂ O	CaO	Fe ₂ O ₃	Fe ³⁺ /Fe ²⁺
δ^{180}	.47 >99	.24 >98	-.41 >99	-.24 >98	-.34 >99	-.22 >98
Rotated Factor Pattern†						
	Mafic	KSP/Plag	Quartz	Redox		
FeO	.90					
MgO	.90					
TiO ₂	.84					
CaO	.61	-.53				
P ₂ O ₅	.54					
SiO ₂	-.71		-.61			
K ₂ O		.84				
Na ₂ O		-.71				
Al ₂ O ₃	.38		.79			
Fe ₂ O ₃	.45					.69
δ^{180}		.35				-.57
% of variance explained						
	49.2	22.0	16.2	12.6		

*ASI = molar ratio $(\text{Al}_2\text{O}_3)/(\text{K}_2\text{O} + \text{Na}_2\text{O} + \text{CaO})$.

†Common factor pattern generated using the SAS computer procedures CORR and FACTOR with VARIMAX rotation (SAS Institute, Inc.). Only loadings with absolute value > 0.35 are shown.

measures the mafic content (biotite, hornblende, apatite, magnetite, etc.) of the intrusives which is apparently unrelated to their source rocks and ^{180} content. This factor most likely measures the extent of partial melting of the source rock. Factor 2 may indicate the Kspar/plagioclase ratio of the granites. This factor, which is related to the ^{180} content, probably reflects the K/Na ratio in the source rocks, which is likely to have been higher in shaley sediments than in volcanics or other igneous sources. Factor 3 most likely describes

the quartz content of the granites, this being the only major mineral in granites which contains no aluminum. Factor 4 simply measures the redox state of the granites and, as suggested above, probably reflects ^{18}O depleted, oxidized igneous source rocks versus ^{18}O enriched, carbonaceous metasediments.

Thus the $^{18}\text{O}/^{16}\text{O}$ ratios of the Southern Appalachian granitoids not only exhibit strong spatial trends (Figures 4.9 and 4.10), but also show a high degree of correlation with their major element chemistry. Space does not permit a more detailed discussion, but it is apparent that oxygen isotope analyses represent a powerful investigative tool in unlocking the secrets of Appalachian tectonic and petrogenetic history.

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4.3.3 Mineralogy and Stable Isotope

Geochemistry of Hydrothermally Altered Rocks from Selected Geothermal Systems in Iceland

(D. R. Cole)

The effect of variations in temperature, mineralogy, and fluid chemistry on isotopic fractionation has been studied in core and water samples from wells in five high ($>200^\circ\text{C}$) temperature and one low ($<200^\circ\text{C}$) temperature geothermal areas in Iceland (see Fig. 4.11).

In all areas, volcanic rocks have undergone extensive oxygen isotopic exchange with the thermal water resulting in either oxygen-18 depletions to values as low as -5.5 ‰ at temperatures greater than approximately 175°C , or oxygen-18 enrichments to values as high as $+9.5$ ‰ at temperatures equal to or less than 175°C (see Table 4.3). Vertical profiles of oxygen isotopic compositions of whole rocks generally show increased oxygen-18 depletion with increasing depth and temperature. For example, in drill hole 8 in the Reykjanes Peninsula palagonite breccia at 438 m depth has $\delta^{18}\text{O}$ values of 5.9 and 6.1 ‰, significantly enriched in oxygen-18 compared to local unaltered equivalents ($+4.6$ to 4.8 ‰). A similar palagonite breccia at 1504 m depth exhibits values of 0.5 and 0.6 ‰; a depletion of about 4 ‰.

Fig. 4.11. A simplified geological map of Iceland showing the location of the high-temperature and low-temperature geothermal areas mentioned in the text. The stippled pattern includes the active zones of rifting and volcanism. The unmarked area includes both Quaternary and Tertiary flood basalts.

Table 4.3. Summary of well data, rock types, alteration mineralogy and isotopic compositions for six Icelandic geothermal systems

Area	Well	Depth m	T°C	Rock Type	Alteration Mineralogy ^a	$\delta^{18}O$ (‰)	δD (‰)	$\Delta R-W$ (b)
Reykjanes	8	438	150	Palagonite Breccia	Mont, Qtz, Zeol, Preh, Cc, Anhy	6.1, 5.9	-53	7.2
	8	1000	200	Basalt	Chl, Qtz, Preh, Cs	3.3	-58	4.5
	8	1162	210	Tuffaceous Sed.	Chl, Qtz, Preh, Cc	2.4, 2.9	-68	3.85
	8	1220	225	Tuffaceous Sed.	Chl, Qtz, Ep, Cc	3.5	-66	4.7
	8	1280	240	Basalt	Chl, Qtz, Ep, Preh, Anhy, Cc	2.5, 2.2	-67	3.55
	8	1370	250	Tuffaceous Sed.	Chl, Qtz, Cc, Ep, Preh	3.6, 3.2	-54	4.6
	8	1504	270	Palagonite Breccia	Chl, Qtz, Ep, Preh, Anhy, Cc	0.5, 0.6	-57	1.75
Svartsengi	4	208	175	Basalt	Mont, ML Clay, Qtz, Cc, Preh	9.5		10.4
	4	612	225	Basalt Breccia	Chl, ML Clay, Qtz, Cc	3.0		3.9
	4	1108	240	Palagonite Breccia	Chl, Qtz, Cc, Ep, Py	3.1		4.0
Krusuvik	2	105	125	Palagonite	Mont, Cc, Prch, Qtz	5.2		9.6
	2	219	175	Basalt	Mont, Qtz, Cc, ML Clay-Chl	3.3		7.7
	2	612	200	Basalt	ML Clay, Chl, Qtz, Cc, Ep	2.8		7.2
	2	1023	225	Basalt	Qtz, Cc, Chl, ML Clay, Ep, Anal	2.1		6.5
Hveragerdi	4	208	195	Plagonite	Chl, Zeol, Qtz, Minor Cc, Py	1.7		9.5
	4	504	230	Basalt	Chl, Ep, Laum, Clinozo, Qtz	1.01		8.81
Reykjavik	4	1330	140	Basalt	Mont, ML Clay, Chl, Qtz, Laum	1.8		11.2
	4	2190	140	Basalt	Mont, Chl, Qtz, Laum, Ep, Cc	2.4		11.8
Krafla	4	608	270	Basalt Breccia	Chl, Qtz, Cc, Py, Ep, Preh	-5.4		1.0
	4	778-781	285	Hyaloclastite	Chl, Ep, Cc, Anal, Qtz, Woll	-5.1*		1.3

a. Abbreviations: Mont = montmorillonite, Qtz = quartz, Zeol = zeolites, Preh = prehnite, Cc = calcite, Chl = chlorite, ML Clay = mixed-layer clay, Py = pyrite, Anhy = anhydrite, Anal = analcime, Laum = laumontite, Ep = epidote, Clinozo = clinozoisite, Woll = wollastonite

b. $\Delta R-W = \delta^{18}O_{\text{Altered Rock}} - \delta^{18}O_{\text{Geothermal Fluid}}$

*Data from Hattori and Muehlenbachs²

This trend of oxygen-18 depletion with depth and temperature is a consequence of the changing intensity and style in alteration mineralogy observed with depth in each well. In general, all six geothermal areas studied exhibit a similar mineralogical zoning pattern with depth with: montmorillonite + zeolites at temperatures less than 150°C; mixed-layer clays + prehnite + minor zeolites + chlorite between 150 and 200°C; and chlorite + epidote above

200°C. Quartz and minor calcite are present in varying amounts at most depths.

Comparison of oxygen isotopic fractionation between altered rock and the thermal fluids with measured down hole temperatures (Fig. 4.12) indicate that at low temperatures (<200°C) isotopic equilibration between the fluids and bulk rock is controlled by the montmorillonite + quartz assemblage. At higher temperatures (>200°C), a combination of chlorite-water and

Fig. 4.12. Oxygen isotope fractionation between altered rocks (S) and fluids (W) for six geothermal areas in Iceland compared with selected mineral-water equilibrium isotope fractionation curves. QTZ = quartz,³ MONT = montmorillonite,⁴ EP = epidote,⁵ CHL = chlorite,⁶ WR = whole rock.⁵

montmorillonite-water fractionation dominates. These relationships have also been observed in the experimental montmorillonite- and mixed-layer clay-water oxygen isotope fractionation data obtained from various basalt-seawater hydrothermal experiments.¹

Variations in fluid chemistry appear to play a less important role in influencing isotopic variation of the altered rocks. Hydrothermal interaction of seawater with basalt at Reykjanes has produced alteration mineralogy and oxygen isotopic fractionations similar to other areas (e.g. Krisuvik, Hveragerdi, etc.) where more dilute-metamorphic waters are heated to similar temperatures. These observations suggest that the Icelandic systems studied are rock-

dominated. Water/rock ratios calculated from the isotopic shifts measured in the fluids and rocks ($W/R_{mass} \equiv [\delta^{18}O^f_R - \delta^{18}O^i_R] / 2[\delta^{18}O^f_W - \delta^{18}O^i_W]$) range from about 0.2 in the Krisuvik system to as high as 6.5 at Reykjavik. The majority of the W/R values, however, fall between 0.5 and 1.0, supporting our contention that these systems are rock-dominated.

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4.4 The Carbon Cycle

4.4.1 Uptake of CO₂ by the Oceans

(C. F. Baes, Jr., A. Bjorkstrom,² P. J. Mulholland³)

The oceans will be the ultimate sink for most of the excess carbon dioxide released to the atmosphere by humankind, a release that is currently about 5 Pg C/y and may reach several thousand Pg of carbon - many times the present atmospheric content - before the reserves of fossil carbon are exhausted. The rate at which this excess can be taken up will depend on ocean circulation, chemistry, and biology. Prediction of the uptake will require a sound knowledge of these processes and the development of models that can represent them adequately.

The partial pressure of CO₂ in surface waters (P_{CO2}) is determined by, and can be accurately calculated from, the total dissolved inorganic carbon (TC), the titration alkalinity (TA), the temperature, and the salinity. The uptake of CO₂ by photosynthesis lowers TC and the accompanying precipitation of CaCO₃ by the marine organisms lowers both TC and TA. The net effect of these biological processes is to lower

PCO_2 in the surface waters, and therefore in the atmosphere, well below what it would be if the oceans were dead and well mixed. The level of biological activity is largely determined by the rate at which limiting nutrients (phosphate and nitrate) from decomposed organic matter are returned to the surface by water circulation.

Thus upper ocean circulation plays a double role in the uptake of excess CO_2 . It not only determines the rate at which the excess CO_2 can be carried down from the surface, but also affects the steady-state value of PCO_2 through its influence on the biological processes.

Knowledge of ocean circulation and the movement of carbon has been gained largely through the use of many tracers⁴. The important naturally occurring ones include salinity, temperature, TC, TA, phosphate, nitrate, oxygen, and ^{14}C . The important transient (anthropogenic) tracers include the chlorofluorocarbons, excess carbon, ^3H , and ^{14}C . Most of the data on the distribution of these and other tracers in the oceans has come from the extensive GEOSECS survey of the early 1970's and two recently completed surveys, TTO in the North Atlantic and the Hawaii-Tahiti Shuttle Experiment.

In addition to the excess CO_2 taken up directly from the atmosphere by the oceans, excess carbon may be sequestered on the continental shelves because of anthropogenic increases in the carbon and nutrient content of river outflow. The enhanced carbon uptakes are estimated to be in the range 0.3 to 1 Pg/y.

Given the intricacies of ocean topography, circulation, chemistry, and biology, credible estimates of the response of the world's oceans can come only from models. The data on ^{14}C and ^3H have been widely applied to the calibration and testing of simple one-dimensional (depth) and two dimensional (depth x latitude) multi-box representations. The data on nutrients, TC, TA, and oxygen increasingly are being used in models that include the biological processes. As more sophisticated three-dimensional models are developed, the large amount of data on salinity and temperature can also be included in more detailed simulations of ocean circulation.

Although the arrangement of boxes and water flows in these models have a significant effect on their response to excess atmospheric CO_2 , the simulated rate of uptake has generally been substantially less than that needed to account for the anthropogenic carbon released that is not presently in the atmosphere (at least 50 Pg).

Because the response times of the various processes in the oceans that affect the uptake of CO_2 differ widely, the relatively simple ocean models developed thus far cannot be expected to describe ocean uptake reliably over time periods ranging from decades to millenia. For the period of greatest interest, the next 100 or 200 years during which most of the available fossil carbon will be released to the atmosphere, more sophisticated models will be needed. They must include a more accurate representation of upper ocean circulation and of the episodic overturning of water that occurs at high latitudes in winter.

Paraphrasing H. G. Ostlund, there is a tendency, especially within that part of the community not directly involved in the technical and scientific details, to believe that modeling alone will forecast the consequences of the CO_2 release. This is definitely not the case. Nor is it true that measurements alone will suffice. Rather it will be the hand-in-hand cooperation between the experimentalists and modelers that will advance our capability to make such a forecast.

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4.4.2 Response of a 2-Dimensional Ocean Model to Increasing Atmospheric CO₂

(C. F. Baes, Jr., G. G. Killough¹)

A two-dimensional (latitude x depth) ocean model, described previously,² has been developed in which both the chemical and the biological processes affecting the distribution of carbon are represented. Steady-state calculations were performed³ to determine the dependence of the partial pressure of CO₂ in the model atmosphere on various model parameters and boundary conditions. We report here time integrations carried out to investigate how the distribution of carbon between ocean and atmosphere was affected when a steady-state condition was disturbed by changing the atmospheric partial pressure of CO₂.

The model consists of a two-dimensional array of 91 boxes, in each of which nine concentration terms were followed during the time integrations. These include carbon and radiocarbon (¹⁴C) in particulate organic, particulate inorganic, and dissolved forms, as well as alkalinity, nutrient, and oxygen. As described previously, the numerous water flows among the boxes were fixed by the geometry of the boxes and two diffusivity parameters which were not varied. The numerous simultaneous differential equations (819) were integrated on the IBM 3033 computer with available software.⁴ Absolute and relative error limits of 0.001 mmol/m³ and 10⁻⁴, respectively were found to give adequate precision. Running times were approximately 30 sec. per year of model time.

Since the pre-industrial value of atmospheric CO₂ (275 μatm) is fairly uncertain as is the course of its growth to the level (315 μatm) observed in 1958 when accurate measurements began,^{5a} the variations assumed in our model calculations prior to 1958 were chosen to represent a plausible range of possibilities. (For the period 1958-1980, all cases conformed to the observed increase to 337 μatm.) The primary purpose of these calculations was to determine the dependence of the model uptake on assumed past variations in the atmospheric content of CO₂.

The results could be fitted reasonably well by the simple differential equation

$$\frac{dX_0}{dt} = A(X_a - X_0) \quad (1)$$

in which X_0 and X_a are the amounts of carbon in the ocean and the atmosphere, respectively, in excess of the initial steady-state values, and A is an adjustable constant. (Initially X_a and X_0 on the right side of this equation were assumed to have separate coefficients, but these were found to be strongly covariant and of similar magnitude.) Upon fitting all the prescribed variations of X_a with time, A was found to be 0.0270 y⁻¹ and the average deviation of calculated X_0 values from the model results was 1.2 Pg C. A much better fit, with $A = 0.0287$ y⁻¹ and an average deviation of 0.4 Pg, was obtained when cases involving sudden changes in dX_a/dt were excluded. This equation was also found to fit quite well the previous results obtained by Killough and Emanuel⁶ from integrations of simpler one-dimensional (depth) models in which the arrangement of water flows among the boxes was varied. Depending on the arrangement, the values of A varied from 0.0275 to 0.096 y⁻¹.

The uptake rates given by all these models up to the present time are thus about proportional to the difference between the excess carbon in the atmosphere and in the ocean. By 1980, carbon released by the use of fossil fuels totaled about 160 Pg.^{5b} The net carbon released from the biosphere, mainly by the forest clearing, is very uncertain, somewhere in the range 0-300 Pg.^{5c} For the oceans to be a net sink at present, as is indicated by recent data^{5d}, the model results suggest that more than half of the total excess must still be in the atmosphere. The pre-industrial level of atmospheric CO₂ is estimated at about 275 μatm,^{5a} giving the value of X_a in 1980 as 135 Pg. If the biosphere is currently neither a net source or sink, the oceans are taking up about 2 Pg C/y. Our results suggest from this that $X_a - X_0$ is 70 Pg., that X_0 is about 65 Pg, and that the release from the biota has been about 40 Pg.

For integrations over the period 1980 to 2100, the total amount (X) of excess carbon in the ocean plus the atmosphere was specified as a function of time. Upper and lower limiting scenarios were generated from the expression

$$dX/dt = B X(t) [1 - X(t) / X(-)] \quad (2)$$

where $X = X_a + X_o$ and $X(-)$ is the maximum value of X (taken to be 5000 Pg). Values of B were chosen to give an initial (1980) rate of increase in X of 4.3%/y in one case and 2 %/y in the other. The value of X in 1980 was adjusted to give a value of dX/dt equal to the amount of fossil carbon released that year. Six integrations were run in which three past scenarios were continued according to these upper and lower limiting future scenarios. The resulting future levels of CO_2 in the atmosphere were found to depend almost entirely on the choice of the future scenarios. By the year 2100, the lower one gave about 860 μatm and the upper one gave 1740 μatm (the current value is about 350 μatm). Not surprisingly, the uptake rate fell

further and further below values predicted by Eq. 1 as X_o increased. The results (X_a to 3200 Pg and X_o to 900 Pg) can be represented approximately by

$$\frac{dX_o}{dt} = \frac{A (X_a - X_o)}{1 + B X_o^{3/2}}$$

with $A = 0.0287 \text{ y}^{-1}$ and $B = 0.00020 \text{ Pg}^{-3/2}$.

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5. HIGH-TEMPERATURE CHEMISTRY AND THERMODYNAMICS OF STRUCTURAL MATERIALS

This program focuses on the synthesis of high purity, highly dispersed covalent structural ceramic compounds of potential application to various energy-related technologies. The synthetic methods being explored range from the preparation of ceramic precursors at low temperatures in non-aqueous media to high temperature reactions which directly yield the desired products. The preparation of aluminum amides, precursors to AlN, was attempted by various methods: (1) anodic dissolution of aluminum in liquid ammonia; (2) a metathesis reaction between AlBr_3 and KNH_2 ; and, (3) the ammonolysis of aluminum hydride-etherate. Both (2) and (3) produced $[\text{Al}(\text{NH})\text{NH}_2]_n$ which converted to AlN on thermal decomposition; method (3) gave the purer product. Studies on the synthesis of TiB_2 were continued; the emphasis was on preparation of nickel-free powders for hot-pressing and sintering investigations. Gaseous HF was found to be more efficient than BCl_3 for removing the contaminant SiO_2 from SiC powders. Thermodynamically, HF should attack SiC, but the kinetics of the reaction apparently are extremely slow. Preliminary studies on the synthesis of Si_3N_4 powder using gaseous SiS as an intermediate have been conducted with success. Raman spectroscopy has been used to identify the phases present in transformation-toughened ceramic specimens containing metastable tetragonal ZrO_2 and the extent of their occurrence in the zone neighboring mechanically-induced cracks.

5.1 Synthetic Approaches to the Preparation of Aluminum Nitride

(L. Maya)

A research effort was initiated on the preparation of precursors that can be converted into non-oxide ceramic materials by pyrolytic or photolytic means. This approach offers an alternative to the more common preparation of ceramic materials by high temperature reactions. Use of precursors could result in better control of the purity of the final product and might allow some control over the morphology of the product as well.

The efforts during this report period were directed at the preparation of precursors for aluminum nitride. Initially, an electrochemical method was investigated for the preparation of $\text{KAl}(\text{NH}_2)_4$ by anodic oxidation of metallic aluminum in liquid ammonia containing KNH_2 as supporting electrolyte. The overall scheme was based on the assumption that the potassium tetra-amido aluminate, once produced, could be converted into the target compound $\text{Al}(\text{NH}_2)_3$ by partial neutralization with HBr according to the following reaction

Potassium bromide is quite soluble in liquid ammonia; thus, this property could be utilized to separate the products of the reaction.

The anodic dissolution of aluminum in liquid ammonia was found to be feasible using glassy carbon as the cathode; it became significant at approximately +2.2 V from the solvated electron couple. The dissolution efficiency was limited by the interference of solvated electrons which discharged at the anode. The generation of solvated electrons is one of the cathodic processes, and migration of the electrons to the anode could not be completely prevented even in the divided cell used. Electrodeposition of potassium at the glassy carbon cathode also took place and led eventually to catastrophic disintegration of the cathode. The presence of electroactive aluminum species produced in situ by anodic dissolution or added as $\text{LiAl}(\text{NH}_2)_4$ was detected by means of cyclic voltammetry in the form of a cathodic response at about +100 mV from the solvent decomposition limit. In summary, anodic dissolution of aluminum is feasible but not practical as a synthetic approach.

Direct chemical approaches were also examined for the preparation of the target compound $\text{Al}(\text{NH}_2)_3$. The first one is described by the following equation

The product obtained was found to have an empirical formula corresponding to $[\text{Al}(\text{NH})\text{NH}_2]_n$. Apparently, the target compound is not formed as a simple compound, but polymerizes by loss of one mole of ammonia per mole of amide to yield a white insoluble product which occludes some of the KBr by-product. The bromide impurity could be partially eliminated by repeated washings with liquid ammonia to leave a residual 4.3% Br. In an attempt to obtain a product with lower KBr content, an alternative synthetic scheme was tried. This is described by the following equations:

As in the previous case, the product turned out to be $[\text{Al}(\text{NH})\text{NH}_2]_n$ instead of the tri-amide. However, the halide contamination was limited to 1.4%.

The aluminum imide-amide products obtained by each direct chemical synthetic scheme yielded aluminum nitride on thermal decomposition. The course of the decomposition was followed by infrared spectroscopy, while also obtaining x-ray diffraction patterns at different stages. The initial materials were amorphous to x-rays. The IR showed a broad band centered at about 3200 cm^{-1} corresponding to N-H stretching vibrations; additional features included a doublet at 1550 and 1505 cm^{-1} due to bending vibrations of the NH_2 and NH moieties, respectively, and a very broad band covering the region between 600 and 1000 cm^{-1} . The N-H vibrations steadily decreased in intensity with temperature, disappearing at about 600°C . At this point, the x-ray diffraction pattern of AlN began to be evident; the conversion into a crystalline product was complete at 800°C . The weight losses were those expected for the conversion of the imide-amide into the nitride.

A metal atom reactor is being used as an additional alternative synthetic approach for the preparation of aluminum nitride. Aluminum vapors generated by resistive heating are contacted with ammonia vapors in a reactor held at -196°C . Preliminary results showed that aluminum nitride is produced directly under these conditions without the formation of an intermediate amide-imide.

5.2 Synthesis and Compaction of Submicron Titanium Diboride Powders

(J. Brynestad, C. E. Bamberger, D. E. Heatherly, J. F. Land, C. B. Finch¹, S. Baik¹)

Previous studies² on the synthesis of TiB_2 by reaction of Ti sponge with BCl_3 gas were conducted using reaction vessels constructed of nickel. The submicron TiB_2 powder produced in these studies usually contained about 0.3 wt % Ni, the result of corrosion of the vessel. We knew that the presence of some Ni was beneficial as a sintering aid in the hot-pressing of TiB_2 , but desired some Ni-free TiB_2 for use in systematic compaction studies done in collaboration with the Structural Ceramics Group of the Metals and Ceramics Division. This material was prepared by the Ti sponge- BCl_3 gas reaction either in thick-walled Ti or in SiC containers. Although SiC is thermodynamically unstable in the presence of BCl_3 , experiments had shown it to be kinetically stable up to at least 950°C . The TiB_2 powders produced in both the Ti and SiC containers had only about 0.02% Ni. However, this practically Ni-free TiB_2 could be hot-pressed to only about 83% of theoretical density (TD) as compared to the 99% of TD achieved when the powder contained about 0.3% Ni. On the other hand, pressureless sintering of the TiB_2 containing about 0.3% Ni was unsuccessful at temperatures up to 2100°C . The samples usually had low green densities (~40%) and densified to 75-85% of TD with considerable porosity and grain growth. The results were the same whether the sintering anneals were done in vacuum, argon, or argon-4% H_2 .

Because it had been found earlier that excessive oxygen and severe powder agglomeration are strong deterrents to densification of TiB_2 , an attempt was made to simultaneously deagglomerate the powder and to introduce carbon as a reducer for oxygen. The approach was a mechanical one consisting of milling a typical 650°C powder for 20 h in a polyethylene bottle using TiB_2 media and toluene. Although light scattering indicated little change in the average agglomerate size, analysis indicated a carbon increase from 0.1 to 4.1 wt % after milling. The milled powder (4.1 % C) had an as-milled oxygen content of 1.4 wt %. The powder isopressed to 47% of TD at room temperature and sintered to 96% of TD with 5-20 μ average grain size at 2050°C. Thus, it appears that incorporation of carbon provides an increase in the sinterability of submicrometer TiB_2 via the mechanism of disrupting thin oxide films on particle surfaces which inhibit unrestricted diffusive transport.

An alternative route for incorporation of carbon into the TiB_2 powder involved a chemical approach in which carbon (~4 wt %) was deposited into TiB_2 by thermal decomposition of methane which was introduced into the reactor together with the gaseous reagent BCl_3 . The compaction behavior of the resulting product has not yet been determined.

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5.3 Removal of Oxide Contamination from SiC Powders by Treatment with Gaseous HF

(J. Brynestad, C. E. Bamberger, D. E. Heatherly, J. F. Land)

We have previously reported on the removal of oxide contamination from SiC powders by treatment with $\text{BCl}_3(\text{g})$.¹ Tests using SiC powders of different particle sizes and levels of oxygen contamination showed that the oxygen content was lowered by factors up to 6; however, in

many cases the amount of residual oxygen was above the limits considered satisfactory for efficient compaction of the powders. The results obtained with BCl_3 prompted us to search for more effective gaseous reagents that reacted in a manner similar to BCl_3 (i.e., negligible kinetics of reaction with SiC despite negative free energy of reaction, but selectively reacting with the oxide). Gaseous HF appeared to be a promising candidate since the free energy changes for the following reactions were negative in the temperature range 400 to 900 K:

Thermodynamically, the decomposition reaction, Eq. (1), is favored over the oxide removal reaction, Eq. (2). However, experimentally it was shown that the rate of reaction (1) was negligible compared to that of reaction (2).

In experiments to determine the effectiveness of HF in removing oxide from SiC, typically about 15 g of SiC powder was exposed to a flowing Ar-HF mixture (~100 ml/min) in the apparatus described previously.² Completion of the reaction with HF was estimated crudely by visual observation; when liquid droplets ($\text{HF-H}_2\text{O}$) ceased to condense in the exit line, the reaction was assumed to be complete. Table 5.1 gives treatment conditions and oxide content (as oxygen weight percent) of various SiC powders before and after treatment with HF. Comparison of these data with those obtained previously¹ with BCl_3 shows that treatment with HF is more effective than BCl_3 in removing oxide from SiC powders. For example, with HF significantly higher fractions of oxide are removed at lower temperatures. The weight changes that occurred during HF treatment corresponded closely to those calculated for

Table 5.1. Oxide removal from SiC powders by treatment with gaseous HF.

SiC Batch	Temp. (K)	Time (h)	Oxygen content of SiC (wt %)	
			Initial	Final
A	923	1.5	0.5	0.1
B	473	5	6.0	0.8
B	423	13	6.0	0.7
B	473	17	6.0	0.8
B	673	4	6.0	0.5
B	673	9	6.0	0.4
C	473	14	15.0	1.2
C	673	4	15.0	0.4
C	923	1.3	15.0	0.4

the removal of the SiO₂ present based on neutron activation analysis. These results indicated that, within experimental error, no significant decomposition of SiC had occurred over the temperature range considered. However, the upper temperature limit of ~650°C (923 K) was selected because we found that, at 800°C (1073 K), the SiC was significantly attacked by HF according to reaction (1). Corrosion of the nickel reaction vessel by HF was not a problem.

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5.4 Synthesis of Silicon-Sulfur-Nitrogen Compounds and Silicon Nitride

(J. Brynestad, C. E. Bamberger, J. F. Land)

In attempts to find new routes for the preparation of Si₃N₄, we are currently studying the system Si-S-N-H; i.e., Si-H₂S-N₂-H₂ and Si-H₂S-NH₃. Boyer and Moulson¹ reported that

99.999% pure silicon powder was 90% nitrided in 20 hours at 1370°C in a N₂ + H₂ mixture, while, in pure N₂, only 30% converted. Morgan²⁻³ found that silicon was completely nitrided at 1280°C in less than 12 hours when 2% H₂S was added to a N₂-H₂ mixture (90% N₂, 8% H₂, 2% H₂S). The loss of silicon by volatile SiS_x compounds was stated to be small.² Morgan³ also did not find evidence for the formation of ternary Si-S-N compounds. Clearly, in order to prepare very pure Si₃N₄ by the reactions described above, the starting materials, mainly the silicon, must be very pure.

We speculated as to the mechanism by which H₂S speeds up the nitridation of silicon. One possibility is the reaction

immediately followed by a "regenerative" reaction like

If gaseous SiS is a reactive species, it would also be of interest to know if it would react with a N₂-H₂ mixture according to the net reaction

in the absence of solid silicon. This could lead to an attractive novel route for the synthesis of pure Si₃N₄ utilizing silicon of low purity, which is considerably less costly than pure silicon, as a source for SiS(g) by reaction (1) since impurities such as Fe do not form volatile sulfides. Although the available thermodynamic data⁴⁻⁸ are not in good agreement, they nevertheless indicate that the exothermic gas phase reaction given by Eq. (3) might run practically to completion. Preliminary experiments at 1100°C revealed that SiS(g) did not react significantly with a mixture of N₂ and H₂. However, when NH₃ was used

instead, SiS(g) reacted quantitatively at 1100°C to form a white, amorphous powder with submicron particle size distribution and containing 17.3 weight % sulfur. Upon heating to 1500°C in flowing N_2 , the powder lost ~33% in weight, and the remaining powder was white, crystalline $\alpha\text{-Si}_3\text{N}_4$. The nature of this amorphous powder precursor to Si_3N_4 has not yet been established. It may be a line compound, a mixture of compounds or a solid solution of chemically bound sulfur in a Si_xN_y matrix. As an illustration, if the powder were $\text{SiS-Si}_3\text{N}_4$ (16.0 weight % S) and it decomposed to SiS(g) and Si_3N_4 , the weight loss would be 30%. If the powder were $\text{SiS}_2\text{-Si}_3\text{N}_4$ (i.e., Si_2SN_2 analogous to Si_2ON_2), and decomposed to $\text{SiS}_2\text{(g)}$ and Si_3N_4 , the weight loss would be 39.7%.

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5.5 Raman Microprobe Characterization of the Crystallographically Transformed Zone Produced by Fracture in Partially Stabilized Zirconia

(G. M. Begun, P. F. Becher¹)

Transformation-toughened multiphase ceramics containing metastable tetragonal ZrO_2 are being widely investigated for use as technologically important structural materials. The ceramic

samples are strengthened by the presence of the metastable tetragonal ZrO_2 phase which, when subjected to a tensile stress, converts to the higher volume monoclinic phase and inhibits crack propagation. We have used Raman microprobe spectroscopy to study samples containing tetragonal zirconia. Keramidas and White² and Benner and Nagelberg³ obtained the Raman spectra of amorphous, tetragonal, monoclinic, and cubic zirconia. The tetragonal and monoclinic forms are easily characterized, and the ratio of tetragonal to monoclinic crystalline forms present in a sample can be determined by measurement of several of the non-overlapping Raman peaks assigned to the two species. The development of the Raman microprobe has made it possible to determine the microscopic state of ZrO_2 present in ceramic samples and to study its variation in the neighborhood of cracks. Clarke and Adar⁴ applied this method to the study of $\text{Al}_2\text{O}_3/\text{ZrO}_2$ and $\text{Al}_2\text{O}_3/\text{Y}_2\text{O}_3/\text{ZrO}_2$ ceramics. They established that the ratio of monoclinic ZrO_2 to tetragonal ZrO_2 was the sum of the intensities of the Raman peaks at 181 and 192 cm^{-1} divided by the sum of the peaks at 148 and 264 cm^{-1} .

We have applied the method of Clarke and Adar⁴ to several samples of MgO -partially stabilized zirconia (PSZ) (8.4 mol % MgO) obtained from the Nilsen Company of Australia (TS and MS grades) and an as-fired MgO -PSZ (7.3 mol % MgO) sample from CSIRO-Melbourne (CSIRO-AF). Cracks were propagated in thin rectangular plate-like double cantilever beam samples by wedge loading of a notch in the specimen, and Raman microscope observations were made transversely at intervals across the cracks. Excitation was with a 514.5 nm argon-ion laser with a 40X microscope objective lens and a laser spot size of ~1 μm . The instrument used was an Instruments S.A. HG-2S Raman spectrometer with microprobe attachment. Typical spectra are shown in Fig. 5.1. It can be seen that the Raman peaks at 181 and 192 cm^{-1} (monoclinic form) increase in intensity as the crack is approached (spectrum c) while the peaks at 148 and 264 cm^{-1} (tetragonal form) decrease.

Fig. 5.1. Raman spectra of Nilsen TS partially stabilized zirconia 450 μm from end of crack. Transverse distance from crack in μm (a) -190, (b) -80, (c) -5, (d) +5, and (e) +10'.

Figure 5.2 shows a plot of the % monoclinic zirconia (monoclinic + tetragonal taken as 100) as a function of lateral distance from the crack. The shape of the curve was similar for the TS and MS Nilsen samples with transformation extending to almost 100 μm and then dropping off quickly. The CSIRO-AF material gave an exponential type curve when plotted against the log of the distance. Measurements made slightly beyond the crack, at the tip

Fig. 5.2. Transformation zone size in PSZ ceramics. Upper - Nilsen TS, middle - Nilsen MS, lower - CSIRO AF.

leading edge of the crack and across the crack body in the Nilsen TS material indicate, that, at the tip, the amount of tetragonal phase is greatest but even 40 μm beyond the tip the transformation has still taken place. It is the transformation that occurs within this zone around the crack that inhibits the crack propagation.

Analysis of the tetragonal + monoclinic phase transformation behavior has provided results that yield insights into the use of microstructural and compositional tailoring to improve fracture toughness. The understanding of the physical and chemical phenomena that control particle size and spacing and the solute content of the ZrO_2 during processing and crack formation is critical in developing such ceramics.

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6. CHEMISTRY OF TRANSURANIUM ELEMENTS AND COMPOUNDS

Studies are made in this program of high-pressure and of high-temperature properties of actinide metals and compounds. High-temperature synthetic work searching for new compounds of potential relevance for long-term storage of nuclear wastes is included as well as thermodynamic studies. Also, hydrides of the actinides are being investigated with particular emphasis placed on understanding the trend toward divalency shown at the heavy end of the actinide series (but not in the lanthanides). In other experiments, transuranium metals and compounds are placed under high pressure in order to force f orbital bonding and concomitant changes in structure which are analyzed by x-ray diffraction and by uv/vis spectroscopy. Studies of magnetic properties in metals and compounds determine experimental susceptibilities for comparison with theory as part of our focus on the characterization of 5f electrons in solids. Also a new focus is the investigation of the fundamental chemistry and physics of elements at the far reaches of the periodic table. Early emphasis will be on chemical properties of elements 101-105 as an indicator of the role of relativistic effects in controlling the architecture of the periodic table at the actinide-transactinide junction. This will involve "one-atom-at-a-time" chemical methodology including solvent extraction, ion exchange, electrochemistry, and volatility studies.

6.1 Chemistry and Physics of Metals and Compounds

6.1.1 Preparation and Properties of Transplutonium Metals

(R. G. Haire)

Studies involving the metallic state of the actinides provide fundamental information about the element itself, whereas in compounds the behavior of the actinide can vary depending on the element(s) with which it has combined. The metals of the first five transplutonium elements have been prepared on multimicrogram to multimilligram scale. Normally they are prepared in conjunction with specialized experiments on the metals, with the major or entire preparation being committed to a particular study.

Although there are potentially several preparative methods for these metals, two methods have been selected for preparing the transplutonium metals in our laboratory.¹ The method of choice for a particular transplutonium metal depends on several factors, but with the quantities discussed here, the most important factor in the metal's volatility. Americium-243, californium-249, and einsteinium-253 metals are prepared by reducing the transplutonium oxide with either lanthanum or thorium metal, followed by the

volatilization and subsequent condensation of the transplutonium metal. Berkelium-249 and curium-248 metals are prepared by reduction of the transplutonium tetrafluorides with lithium metal, followed by the volatilization of the excess reductant and lithium fluoride.

During this report period both berkelium and curium metals were prepared for several research projects. The berkelium-249 metal, which decays at a significant rate (~2% per week) to californium-249 metal, was employed in X-ray diffraction studies of the metal under high pressure (see 6.1.2) and in studies of berkelium hydrides (see 6.1.6). Individual portions of the berkelium metal were also stored in order to obtain, via radioactive decay, berkelium-californium alloys which are used for additional highpressure studies. The curium-248 metal was also used for x-ray diffraction studies of the metal under high pressure, and in studies of the curium hydride system. The studies involving curium metal are also reported in sections 6.1.2 and 6.1.6.

Studies involving the transplutonium metals ranged from examining their basic physical/structural properties to specific experiments dealing with their magnetic, high-temperature thermodynamics, and metallic bonding behavior

Especially significant are the findings that high-temperature vapor pressure studies have shown that einsteinium metal is a divalent metal, and that studies of the metals under pressure have demonstrated that the 5f electrons can participate in metallic bonding.

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6.1.2 X-Ray Diffraction Studies of Actinide Metals Under Pressure¹

(R. G. Haire, J. R. Peterson,² U. Benedict,³ C. Dufour,³ and J. P. Itie³)

Two important topics in the solid state science of the actinide elements are the electron configurations and the nature of the bonding. Studies of the lanthanide and actinide metals under pressure are valuable for probing their electronic behavior and atom-atom interactions, as well as for determining equations of state for them.

The behavior of the respective 4f and 5f electrons in the lanthanide and actinide metals under pressure has been an active area of study in recent years, as modern diamond anvil pressure cells have provided a relatively convenient method of achieving high pressures. The studies of the behavior of the transplutonium metals under pressure reported here have been carried out in collaborative efforts with the European Institute for Transuranium Elements, Karlsruhe, Federal Republic of Germany. The studies employed a Syassen-Holzapfel type diamond anvil pressure cell, and the metals were analyzed as a function of pressure using energy dispersive X-ray diffraction analysis. All measurements were made at ambient temperature, and the pressures on the samples were determined using a ruby fluorescence technique (fluorescence of rubies placed in the pressure cell).

A report on the studies of berkelium and californium metals under pressure was given in

the last Annual Report⁴ and some details of these studies have been recently published.^{5,6,7} The behavior of americium, berkelium, and californium metals under pressure is summarized in the following text. Applying pressure to americium, berkelium, or californium metals first transforms their double hexagonal close packed (dhcp) structure, which is their room temperature/normal pressure phase, to a face centered cubic (fcc) structure. With additional pressure, all three metals ultimately transform to the orthorhombic α -uranium-type structure. Both americium and californium metals form an additional phase between the cubic and orthorhombic structures; in americium this phase has been reported to be monoclinic,^{8,9} whereas in californium it represents a trigonally distorted fcc structure (see Fig. 6.1). The appearance under pressure of crystal structures of lower symmetries (i.e., orthorhombic, α -uranium-type structure) than those of the frequently observed hexagonal or cubic structures for these metals indicates that participation of f-electrons in the metallic state has occurred (delocalization of the f-electrons).

During this report period, curium metal and berkelium-californium alloys were studied

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Fig. 6.1. Structural forms of the transplutonium metals as a function of pressure.

under pressure. Experiments on curium metal under pressure were of special interest since interpolations for it made from data for americium, berkelium, and californium metals under pressure were not consistent with the limited data (up to 20 GPa of pressure) that had been reported for it.¹⁰

The curium-248 metal used in the present work exhibited a dhcp structure with average atmospheric-pressure lattice parameters of $a_0 = 3.502(5)$ Å and $c_0 = 11.32(2)$ Å, in accord with accepted values for the metal. With the application of pressure the dhcp structure (Cm I) transformed to a fcc structure (Cm II) at ~23 GPa, and this phase converted to the α -uranium-type structure (Cm III) at ~43 GPa. This latter phase was retained up to the maximum applied pressure of 52 GPa. This behavior is summarized in Fig. 6.1; detailed accounts will appear in the literature.^{11,12}

The data for curium metal, collected as the pressure was increased stepwise, are plotted in Fig. 6.2, as relative volumes versus pressure. By making a computer fit of the relative volume and applied pressure data below 23 GPa to the Birch equation of state, a bulk modulus of 29(1) GPa was obtained for the dhcp form of curium metal. This value for curium metal can be compared to values ranging from 23 to 50 GPa for the bulk moduli of americium, berkelium, and californium metals. In contrast, the bulk moduli of the lighter actinides (Th-Pa) are much larger.

From Fig. 6.2 it is apparent that there is a large decrease (21%) in relative volume accompanying the delocalization of curium's 5f electrons. This sudden decrease or collapse in volume for curium is much larger than that found for the same phenomena in americium, berkelium, and californium metals, where the changes ranged from 3-16%. It is also significant that the pressure at which curium metal converts to the α -uranium-type structure (delocalization pressure) is much higher than the corresponding processes for americium, berkelium, and californium metals (see dashed line in Fig. 6.1). These apparent anomalies

Fig. 6.2. Relative volume of the unit cell of curium metal as a function of pressure.

for curium metal reflect its ground-state electronic configuration ($[\text{Rn}]5f^76d^17s^2$). At normal pressure only the $6d^17s^2$ electrons are involved in metallic bonding. It is well known that half-filled electronic sublevels ($5f^7$ for curium) provide a stabilizing effect, so that the involvement of curium 5f electrons in bonding (delocalization of 5f electrons) brought about by applying pressure must counteract the energetic advantage of its ground state electronic configuration.

Studies on $\text{Bk}_{1-x}\text{Cf}_x$ ($x = 0.35$; $x = 0.60$) alloys under high pressure were also undertaken. These alloys were obtained directly from the decay of ^{249}Bk ($t_{1/2} = 325\text{d}$) metal into ^{249}Cf metal. From Fig. 6.1 it can be seen that there are two differences in the behavior of berkelium and californium metals under pressure. One difference is the pressures at which comparable transformations occur; the second is the presence of a distorted cubic phase for californium metal

prior to formation of the α -uranium-type phase. Based on studies made to date, the distorted fcc phase was observed only in the Cf-rich alloys (i.e., where $x = 0.6$). Additional studies are in progress to better characterize the pressure behavior of berkelium-californium alloys.

1. Research sponsored in part by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems (R. G. Haire) and under contract DE-AS05-79ER10348 with The University of Tennessee, Knoxville (J. R. Peterson) and in part by the Commission of the European Communities, Joint Research Center, Karlsruhe, FRG (U. Benedict, C. Dufour, and J. P. Itie).
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6.1.3 Absorption Spectrophotometric Studies of Actinide Compounds Under Pressure¹

(R. G. Haire, J. R. Peterson,² J. P. Young,³ G. M. Begun, and U. Benedict⁴)

Studies of actinide compounds under pressure using solid state absorption spectrophotometry have been initiated. These studies employ a diamond anvil pressure cell designed for use with our microscope spectrophotometer. They were an outgrowth of the experiments carried out on the transplutonium metals under pressure (see section 6.1.2) and also involve a collaborative effort with the European Institute for Transuranium Elements, Karlsruhe, FRG. The aim of these studies is to monitor the effects of pressure on actinide compounds using spectral properties of the materials, which necessitates that the samples transmit light (300-1100 nm wavelength) and have some definitive, preferably known, absorption spectrum. Since the absorbances of transplutonium materials in the above wavelength region are due mainly to f-f transitions and the 5f orbitals have extended radial distributions, it was expected that the f-f absorptions may be perturbed by applying pressure. Structural or coordination changes, significant changes in the electron configurations, and/or the involvement of f electrons in bonding are examples of changes which could result from the application of pressure and be detected by changes in the absorption spectrum.

In these initial pressure studies, samples have included anhydrous Nd_2O_3 , NdCl_3 , AmCl_3 , AmI_3 , CmI_3 , CfBr_3 , and PuI_3 . The most significant changes in absorption spectra of

the samples with pressure have been noted for the samples of AmI_3 and CfBr_3 . The measurements on all of these materials were carried out at room temperature and the pressures on the samples determined using a ruby fluorescence technique (fluorescence from rubies contained in the pressure cell).

The anhydrous triiodides and the oxyiodide (AmOI) of americium had been previously investigated at normal pressure by x-ray diffraction and absorption spectrophotometry as a function of temperature.⁵ In that study it was determined that both an orthorhombic (PuBr_3 -type, 8-coordinate metal ion) structure and a hexagonal (BiI_3 -type, 6-coordinate metal ion) structure existed for AmI_3 . The hexagonal form of this compound is the high temperature form and is obtained by heating the compound above 400°C . This modification can be retained at room temperature by quenching AmI_3 from about 400°C . It has been demonstrated that absorption spectrophotometric analysis at 25°C can be used to differentiate between the two forms of AmI_3 .

The procedure for these pressure studies consisted of spectrophotometrically analyzing the hexagonal crystal form of AmI_3 as a function of pressure, using the special diamond anvil cell. After a pressure of ~ 2 GPa had been reached, the hexagonal form of AmI_3 was found to have transformed into the orthorhombic structure. Applying additional pressure up to a maximum of ~ 9 GPa did not alter the absorption spectrum of the orthorhombic AmI_3 , except to shift the cut-off of transmitted light to longer wavelengths. This shift coincided with a darkening of the sample's color from a golden-yellow to a dark red-brown. The change in the absorption spectrum of AmI_3 with pressure is shown in Figure 6.3, where the spectrum of the hexagonal form (Fig. 6.3A) at normal pressure can be compared to that of the orthorhombic form (Fig. 6.3B) at 7 GPa of applied pressure. After the release of pressure, the orthorhombic form of AmI_3 was retained (Fig. 6.3C).

Fig. 6.3. Absorption spectra of AmI_3 , reflecting the crystal transformations induced by the application of pressure.

Since the cut-off of light transmission shifts to longer wavelengths with the application of pressure, the most useful wavelength region of the absorption spectrum for analysis lies between 500-1100 nm. At 7 GPa of applied pressure the light transmission cut-off occurs just below 500 nm (Fig. 6.3B). This high absorbance below 500 nm and the sample's dark color are not characteristic of the absorption spectrum of the orthorhombic form of AmI_3 . After the pressure was removed from the sample, the light transmission cut-off (see Fig. 6.3C) and a noticeably darker color were retained by the samples. Our present interpretation of the color change and shift of the light transmission cut-off with pressure is that they resulted from either a shift in the charge transfer band of

AmI_3 to longer wavelengths due to a compression of the electron orbitals and/or the generation of very small amounts of iodine in the sample. The latter explanation would account for the retention of this high absorbance after the pressure was released, but at the present time a mechanism for generation of this iodine is not known.

The absorption spectra of the two structural forms differ mainly in the fine structure and the relative intensities of the absorption peaks.⁵ For example, the absorption at $9.2 \times 10^5 \text{ m}^{-1}$ shows that with pressure the single peak characteristic of the hexagonal form of AmI_3 develops into three peaks characteristic of the orthorhombic form.

At least two crystal modifications of anhydrous CfBr_3 are known to exist: a high-temperature, AlCl_3 -type monoclinic form, and a PuBr_3 -type orthorhombic form. Although it is possible to synthesize directly the monoclinic form of CfBr_3 , the orthorhombic form had previously been obtained only by allowing the orthorhombic form of $^{249}\text{BkBr}_3$ to decay to CfBr_3 .⁶ Studies of the monoclinic crystal form of CfBr_3 under pressure have shown that this form converts to the orthorhombic form of CfBr_3 by $\sim 3 \text{ GPa}$. Increasing the pressure from 3 GPa up to 13 GPa produced only two small changes: (1) a loss of light transmission (high absorption) above $20 \times 10^5 \text{ m}^{-1}$; and (2) an increase in the relative intensity of an absorption band at $13 \times 10^5 \text{ m}^{-1}$ (hypersensitive band). Both of these latter changes were found to be reversible with pressure.

Results to date have not indicated that the application of pressure has forced any involvement of the f electrons of these various compounds in bonding. Rather, the application of pressure brought about structural changes, which involved a structure of a larger molecular volume changing to a crystal form with a smaller molecular volume. This reduction in molecular volumes, as measured at room temperature and normal pressure, is $\sim 20\%$ for each compound. These

structural changes with pressure are interpreted as reflecting preferred packing efficiencies in the crystals. Previous X-ray diffraction studies have shown that certain lanthanide halides also undergo structural transformations under pressure.⁷ It is believed that the studies presented here represent the first spectral observation of a pressure induced phase transformation for an actinide halide.

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3. Analytical Chemistry Division.
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6.1.4 Thermochemistry and Enthalpies of Vaporization of Actinide Compounds and Metals (R. G. Haire and J. K. Gibson)

A program exists for determining the thermochemical behavior of actinide metals and compounds. The primary approach has been to determine the enthalpy of vaporization and the vapor pressure of these materials as a function of temperature. In collaboration with Los Alamos National Laboratory, the vapor

pressure as a function of temperature and the enthalpies of vaporization of the first four transplutonium metals have been determined using milligram quantities of the pure metals. For the elements after californium, the limited quantities of these materials necessitates alternate techniques. One approach used successfully for einsteinium employed a dilute alloy (0.22 mol % Es) of einsteinium and ytterbium. Measurements of the vapor pressure of einsteinium over this alloy were made as a function of temperature (470 - 870 K). The enthalpy of sublimation of einsteinium metal, a measure of its cohesive energy, was derived from data obtained from the alloy¹ and determined to be 31.8 kcal·mol⁻¹. The results confirmed that einsteinium metal is the first actinide to be a divalent metal.

A new mass spectrometer-Knudsen cell system has been received and installed in a gloved box so that it can be used with radioactive materials. The atmosphere of the gloved box will be helium to allow handling air and/or moisture sensitive materials. The heating of the Knudsen cell can be accomplished by resistive or electron beam heating. The vapor beam effusing from the cell is analyzed by a dual range (1-511, 2-1023 AMU) mass spectrometer quadrupole. Provisions are available to alternately collect portions of the beams on individual targets for determining the mass transferred as a function of time and temperature. The system is computer interfaced for data acquisition/analysis.

The mass spectrometer system has undergone testing with non-radioactive materials. Several modifications are being made to the system, some of which were necessitated by the fact that the system will be used with radioactive samples. Additional testing of the system is planned before it becomes operational for actinide materials. When completed, the system will be used to extend measurements of vapor pressures of the actinide metals and initiate studies of

actinide oxides and halides. One area of study will be examining actinide samples to identify new and/or unusual species and oxidation states that may exist in the vapor state.

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6.1.5 Magnetic Studies and Characterization of Actinide Metals and Compounds¹

(S. E. Nave,² J. M. Moore,² R. G. Haire, P. G. Huray,² Alan Blaise,³ and M. T. Spaar²
Californium Metal

Measurements on californium-249 metal in magnetic fields to 50 kilogauss have been made in this fiscal year. For temperatures in the range 100K to 340K, a Curie-Weiss behavior has been observed for sufficiently high applied fields (as seen in Figure 6.4 for a typical sample). Here we have plotted the inverse magnetic susceptibility, χ^{-1} , versus temperature for applied fields of 0.80, 1.65, 5, 10, 15, 25, 30, 40, and 50 kilogauss. The curves for the latter four fields are virtually superimposed upon one another and when fit to a Curie-Weiss function yield an effective magnetic moment of $9.7 \pm 0.2 \mu_B$ and a Weiss paramagnetic temperature of $\theta_p = -42 \pm 2K$. This moment is slightly lower than previous measurements⁴ limited to fields below 1600 gauss ($10.7 \mu_B$ and $-16 K < \theta_p < -1K$).

The samples have been examined extensively in the temperature range 45K to 66K and for many applied fields between 5 and 50 kilogauss. The antiferromagnetic transition in this temperature range which was reported in the previous progress report was not observed. We must therefore consider the possibility that this second minor transition may have been due to impurities (possibly resulting from contamination by the atmosphere giving oxide and/or nitride impurities).

Fig. 6.4. Inverse susceptibility versus temperature for californium metal (sample C) at the indicated fields in kilogauss.

Fig. 6.5. Moment per atom in units of Bohr magneton versus temperature for californium metal (sample C) in magnetic fields between 5 and 50 kilogauss.

At temperatures below 50K we have observed a consistent, ordered magnetic transition in all samples, as shown in Figure 6.5. Here we have plotted the average moment per atom, σ , as a function of temperature for a series of applied fields. Two effects are evident: (a) the moment per atom is becoming saturated with the application of the higher fields at temperatures below the transition. This effect is more clearly presented in Figure 6.6 where we have plotted the average moment per atom, as measured at 15K as a function of applied field. Here the moment, σ , is observed to be saturating with the higher fields and when σ is plotted versus inverse field and extrapolated to infinite H , we obtain $\sigma_{\text{sat}}(15\text{K}) = 6.1 \mu_B$.

(b) The onset of ordered magnetism with decreasing temperature occurs at lower

Fig. 6.6. Moment per atom (μ_B) versus applied field for californium metal (sample C) at a temperature of 15K.

temperatures for smaller applied magnetic fields. Thus isomagnetization plots identify the transition temperature, T_C , for the onset of ordered magnetism. In this manner we obtain a $T_C(0 \text{ gauss}) = 51 \pm 2\text{K}$.

We have thus concluded from the studies to date that the magnetism of dhcp californium metal in the 100K to 340 K temperature region is characteristic of paramagnetism with an effective magnetic moment in reasonable agreement with that of californium ions in a $5f^9$ electronic configuration or a $3+$ charge state. The measured low field value is higher than that expected from an intermediate coupling model, which gives $10.2 \mu_B$ by one estimation.⁵ The lower (high field) value of $9.7 \mu_B$ is in agreement with previous measurements on two small (9 μg) samples of the fcc crystal form of californium metal by Fujita, et al.⁵, however these measurements indicated no ordered state down to their lowest measurement temperature of 22K. The effective Weiss temperature is small but negative for all samples in our work and suggest the likelihood of a lower temperature transition to an ordered state. A low temperature transition to an ordered state is indeed observed, but in the limit of high fields, the saturated moment per atom is only $6.1 \mu_B$ rather than a value near the paramagnetic moment values, as expected for a ferromagnetic state. This lower value may be indicative of ferrimagnetism but is more likely due to magnetic anisotropy (crystal or exchange) coupled with samples composed of a few large crystallites.

Californium oxides

Recent measurements on californium-249 oxides have been made on two compounds (a Cf_7O_{12} sample of mass 98 μg and a Cf_2O_3 sample of mass 468 μg) in the temperature range 4.2K to 350K and in applied fields up to 50 kilogauss. The preliminary results for these oxides indicate that plots of χ^{-1} versus temperature are curved over the entire measured temperature range, even at the highest fields. A linear dependence, as

expected in Curie-Weiss behavior, is not observed over any significant temperature region and we are unable to determine a single value for the paramagnetic effective moment for the californium ion in either compound. We are currently examining the influence of systematic experimental errors and are making measurements on other samples before considering the curvature in terms of a crystal-field model. However one clear result of the measurements to date is that no antiferromagnetic transition has been observed in the 45K to 66K temperature range at any applied field. This result precludes the earlier suggestion that the observed antiferromagnetic transition in californium metal may have been explained by oxide contaminant (at least an oxide in the form Cf_2O_3 or Cf_7O_{12}).

Uranium Compounds

In collaboration with the solid state physics and chemistry groups at the Center for Nuclear Studies in Grenoble (CENG) we have attempted to make magnetic measurements on uranium dioxide diluted in a thorium dioxide matrix. This is continuation of work at CENG in the summer of 1983 as reported in the previous progress report. Samples corresponding to two levels of doping were prepared at the time. In the melt the stoichiometry corresponded to 2% and 10% UO_2 . Subsequent γ -counting at CENG to determine the amount of uranium in the prepared crystals indicated only .1% and .2% uranium respectively. It appeared the majority of the uranium was not incorporated into the crystals. These values are critical for determining the ground state of the uranium atom which is split by the crystal field as described in the previous progress report. If the ground state is a Γ_1 state, the saturated low-temperature moment will be $0\mu_B$. The values from γ -counting lead to a value of $2.6 \mu_B$, however the half-life of the nuclear state giving the γ -emission is so long that the error in this value is great due to counting errors. A more accurate determination of the

uranium doping was performed at ORNL using neutron activation analysis. These results indicated a larger amount of uranium and lead to a moment value intermediate to that of either state. In hopes of determining the valence state of uranium by an independent method, optical absorption spectra were obtained for the samples. The spectra were not conclusive due to the small amount of uranium present, but suggested the presence of only the hexavalent state. This atomic state for uranium has no f electrons and thus any such uranium atoms would be nonmagnetic. This could explain why the moment value was too low for the Γ_5 ground state. The U^{6+} was probably a result of preparing the crystals in air. A future attempt will be made to prepare the crystals in an inert atmosphere.

A similar problem was encountered with the compound UOS which was prepared in the form of small single crystals. We had planned to make magnetic measurements on individual crystals as a function of orientation by utilizing the high sensitivity of our susceptometer. Two types of crystals were available: some grew as long thin needles and some grew as flat platelets or stacks of flat platelets. The crystal structure has been shown to be tetragonal of the $PbFCl$ type and by x-ray of the long needle type it was determined that the c axis corresponds to the small dimension of the crystals, i.e., the x axis is perpendicular to the flat platelets. Magnetic measurements were made on both types of crystals and corresponded to measurements of the parallel and perpendicular susceptibilities. The results were not in agreement with previous measurements on the powder, i.e., the average susceptibility $\chi = \chi(\text{parallel}) + (2/3) \chi(\text{perpendicular})$ was not the same as previously measured. The value was considerably smaller which again may indicate that all of the uranium was not in the 4+ charge state. The samples were then x-rayed to obtain a Laue powder pattern to determine their chemical composition. Lines other than those of UOS were present and

corresponded to various oxides of uranium. We thus were lead to conclude that the samples had decomposed (even though stored under alcohol) or contained occlusions of these oxides trapped during crystal growth. It appears the tetravalent state of uranium in such compounds is indeed difficult to prepare and maintain.

1. Research sponsored by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy in part under contract DE-AS05-79ER10348 with The University of Tennessee, Knoxville (S. E. Nave, J. M. Moore, P. G. Huray, A. Blaise, and M. T. Spaar) and in part under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems (R. G. Haire).
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3. Center for Nuclear Studies in Grenoble, Grenoble, France.
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6.1.6 Preparation and Studies of Transplutonium Hydrides and Chalcogenides (J. K. Gibson and R. G. Haire)

The hydrides provide a unique group of compounds for study having properties intermediate between those of the metals and those of ionic compounds. Transplutonium hydrides can therefore provide systems that can be used to probe and better define the nature of 5f electrons in these elements as compared with the 4f electrons in the lanthanide elements. The chalcogenides, especially sulfides, selenides and tellurides, also form compounds which are interesting for

exploring less stable oxidation states of the actinides. Thus, the aim of studies on both groups of these transplutonium compounds is to establish trends and differences between these materials and their 4f counterparts, and to examine the trend toward increased stability of the divalent state when progressing across the actinide series.

The initial goal of the hydride studies was to prepare and determine the physicochemical properties of these transplutonium materials. Subsequently, efforts will be made to determine the composition ranges for specific hydrides of these elements. In this report period, both the berkelium hydride and the curium hydride systems were investigated.

Curium hydrides were prepared by reaction of curium-248 (97% Cm-248, 3% Cm-246) metal with hydrogen under selected temperatures and hydrogen pressures. The products were characterized by x-ray powder diffraction analysis. Several of these syntheses resulted in a product which was indexed on the basis of hexagonal symmetry. Average lattice parameters for these products were $a_0 = 3.769(8)\text{\AA}$ and $c_0 = 6.732(12)\text{\AA}$ and the materials are considered to be $\text{CmH}_{3-\delta}$ by analogy with the behavior of the lanthanide- and lighter actinide-hydrogen systems. Other curium hydride products that had face centered cubic structures were also obtained. These products had average lattice parameter of $a_0 = 5.322(4)\text{\AA}$. These products are considered to represent curium dihydride, CmH_{2+x} . The average cubic parameter obtained in this work is slightly smaller than that ($a_0 = 5.344$) reported previously for curium dihydride.¹ The small difference between these values may be attributable to slight differences in stoichiometry or related to the fact that the curium-244 (higher specific alpha activity) isotope was used in the earlier work. Lattice expansion of compounds due to self-irradiation is a well established phenomenon. Values for δ and x have not determined for these materials. This work² has established that

both a trihydride and a dihydride exists for curium.

The berkelium-hydrogen system was also studied but this work had to contend with the relatively rapid decay ($\sim 2\%$ per week) of berkelium-249 to its californium-249 daughter. As with the curium hydrides, the berkelium hydrides were synthesized directly from reaction of metal with hydrogen. The berkelium hydride products were determined by x-ray diffraction to have either hexagonal or face centered cubic crystal symmetry. The products having an average cubic lattice parameter of $a_0 = 5.248(5)\text{\AA}$ are considered to be berkelium dihydride, BkH_{2+y} , whereas the products with average hexagonal lattice parameters of $a_0 = 3.726(7)\text{\AA}$ and $c_0 = 6.663(20)\text{\AA}$ are taken to be the berkelium trihydride, BkH_{3-z} . Details of the berkelium work have been reported.³

The existence of a hexagonal trihydride for the transplutonium hydrides through berkelium compares with the formation of similar trihydrides by the second half of the lanthanide elements. The stoichiometries of the transplutonium trihydrides are likely to deviate less than that of the dihydrides. Based on the behavior of the lanthanide dihydrides, the value of x and y for CmH_{2+x} and BkH_{2+y} may range from -0.2 to 0.3 .

Efforts have also been initiated with the lanthanide elements to develop synthetic techniques for preparing the monochalcogenides of the transplutonium elements. Control of the chalcogenide stoichiometry by direct combination of precise quantities of the elements is difficult in the microscale required for the transplutonium elements. The present efforts are investigating the preparation of monochalcogenides by either reduction of chalcogenides having higher stoichiometry or by gas-solid reactions utilizing a controlled chalcogenide fugacity.

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6.1.7 Structural Chemistry of Solid Solutions of Lanthanide Titanates

(C. E. Lamberger, G. M. Begun, H. W. Dunn,¹ and S. A. Landry²)

Little is known about the factors controlling the formation and extent of solid solutions when the initial reacting compounds are heterotypic. Because lanthanide titanates, e.g., of the type $\text{Ln}_2\text{Ti}_2\text{O}_7$, crystallize with two structures (monoclinic for $\text{Ln} = \text{La}$ to Nd and cubic pyrochlore for $\text{Ln} = \text{Sm}$ to Lu), and because the lanthanide series provides a wide selection of ionic radii, such compounds were selected for the initial studies of solid solution formation. Titanate-based solid solutions are also of interest in the area of nuclear waste disposal because pyrochlore phases are major constituents in some of the proposed schemes; thus it would be useful to have a model for predicting which and to what extent the actinide elements present in nuclear waste would selectively distribute among titanate phases. Many mixtures with different compositions of pairs of lanthanide oxides (selected from the two structural groups of dititanates) and TiO_2 were reacted and the products examined by x-ray diffraction and Raman spectroscopy. The results indicating either the formation of solid solutions $\text{Ln}_{2-x}\text{Ln}_x\text{Ti}_2\text{O}_7$ (cubic or monoclinic structures) or a polyphase, were used to construct a stability field diagram. This was defined by two parameters, both functions of the ionic radii of lanthanide elements in solid solution. The ordinate δ is the percentual difference of ionic radii ($100 (IR_{\text{Ln}} - IR_{\text{Ln}}^*)/IR_{\text{Ln}}^*$) and the abscissa is either the unit cell volume or the mean ionic radius ($IR_{\text{mean}} = X_{\text{Ln}} IR_{\text{Ln}} + X_{\text{Ln}}^* IR_{\text{Ln}}^*$), where X_i is the atomic fraction of the lanthanide) depending on which data is available. The results are

shown in Fig. 6.7. It is possible to obtain additional information from this stability field diagram by reading from the boundary lines the compositional values at which saturation of the solid solutions, (e.g., the pyrochlore phase) occur and plotting them against the value of their corresponding δ .

Fig. 6.7. Stability diagram of heterotypic, substitutional solid solutions, including some isotypic preparations. δ is the percent difference in ionic radii of lanthanide ions and V the unit cell volumes; Cubic phases: $\circ$ (calculated) and $\bullet$ (measured); Monoclinic phases: Δ , and restricted miscibility (diaphasic): $\diamond$. $\square$: from measured lattice parameter vs X_G (atom fraction of guest ion).

Using values of δ calculated for pairs of trivalent actinides (An^{3+})/pyrochlore-forming lanthanides, the solubility limits of An^{3+} in different pyrochlore titanates is thus predicted by inter- or extrapolation. The results indicated that Pu^{3+} could attain a maximum concentration of 30 at. % and Am^{3+} close to 100%, depending on the lanthanide ion in the pyrochlore phase.

Because Bi^{3+} has an ionic radius in the range of that of the light lanthanides but has a different electronic configuration, the formation of solid solutions of the type $\text{Ln}_{2-y}\text{Bi}_y\text{Ti}_2\text{O}_7$ was also studied. The results showed that cubic solid solutions do occur.

however the formation of monoclinic ones cannot be established with certainty. The region of stability of cubic $\text{Ln}_{2-x}\text{Bi}_x\text{Ti}_2\text{O}_7$ solid solution did not occur at the same abscissa values as those of $\text{Ln}_{2-x}\text{Ln}_x^*\text{Ti}_2\text{O}_7$. This can be seen as an indication that the electronic configuration, thus the bonding, of the guest ion (Bi^{3+}) contributes to controlling the formation of solid solutions. The data from the boundary between the polyphasic and cubic solid solution regions allowed us to predict that about 10 and 30 atom % of Bi could be incorporated into solid solution of, respectively, Pu- and Am-dititanates.

The study of another family of titanates, $\text{Ln}_{2-x}\text{Ln}_x^*\text{Ti}_2\text{O}_{7+2y+3}$ was undertaken because the scarce literature available on pure titanates was not in agreement in regard to the value of y and no information was at all available on their solid solutions. Relying mainly on Raman spectroscopy to detect minor phases present in the many preparations, we were able to conclude that $y = 4.33$ with an upper limit of 4.5 and that the only pure titanates with such stoichiometry that formed under our experimental conditions were those of La to Nd. However, solid solutions containing the heavier lanthanides as solutes did form with what appears to be an orthorhombic structure. These were correlated in a stability field diagram. Manipulation of the data from this diagram led us to predict that Pu^{3+} will form solid solutions with all the lanthanide elements, while Am^{3+} will behave similarly except with Tm, Yb , and Lu. The stability fields diagrams that were generated have thus allowed us to predict the structure of the various actinide titanates and of their solid solutions in lanthanide or bismuth titanates. It is planned to determine how valid these predictions are.

¹Analytical Chemistry Division, ORNL

²Student participant from Centenary College, Shreveport, LA.

6.2 Transeinsteinium Chemistry

6.2.1 Searches for New Radionuclides in Heavy-Ion Nuclear Reactions on ^{254}Es

(R. L. Hahn, E. K. Hulet,² R. W. Loughheed,² R. J. Dougan,² J. F. Wild,² and K. Summerer³)

A collaborative effort has begun to study the nuclear reactions of heavy-ion beams on a target of ^{254}Es . The goals of this research are several: to search for new, neutron-rich isotopes that have been predicted to have relatively long half-lives, such as ^{260}Fm , ^{261}No , ^{261}Lr , and ^{263}Ha ; to define accurately the mass-yield curves of the radioelements ^{100}Fm , ^{101}Md , ^{102}No and ^{103}Lr , for which some data already existed;^{4,5} and to measure the yields of ^{104}Rf and ^{105}Ha , for which no data exist. The results of these studies also have significance with regard to proposed studies of the chemistry of the transfermium elements, by indicating what is experimentally feasible in terms of the production yields and half-lives of the desired elements.

The collaboration began in September, 1984. Several experiments have already been done, and the results obtained to date are quite interesting. ^{254}Es (half-life of 276 d), which had been obtained from the DOE transuranium production program located at HFIR-TRU, was electrodeposited onto a thin metallic foil to form a $48 \mu\text{g}/\text{cm}^2$ (i.e., $3.4 \mu\text{g}$ total ^{254}Es) target for irradiations at the LBL 88-inch cyclotron.

Bombardments were done with an ^{16}O beam to measure the production yields of short-lived (half-life $\leq$ hours) radionuclides. An automated system was used, involving a helium-jet collection apparatus and a wheel that transported the radioactivity past a series of surface-barrier, α -particle detectors. The collection efficiency of the gas-jet system, measured in several different ways, was quite high, 85%. The experimental results indicate that although we clearly observed isotopes of Fm to Lr, we had no indication that we had produced any known

isotopes of Rf or Ha. In particular, we had searched for the new isotope, ^{263}Ha , which we anticipated would be formed via a "preferred" pathway, the ($^{16}\text{O}, \alpha n$) reaction, with a cross section ~ 20 nb. We saw no evidence for this product, and set an upper limit on its cross section of < 2 nb, which is only $\sim 10\%$ of the predicted value.

In other irradiations, we used a beam of the heavier oxygen isotope, ^{18}O , on the ^{254}Es to increase the chances of producing neutron-rich nuclides. We were interested in observing radionuclides with long half-lives, $\geq$ hours. The crucial element of the experiment was the rapid transfer by helicopter of the produced radioactivity from LBL to LLNL, where the different isotopes were segregated by their masses in an isotope separator. In this way, the experimental difficulties involved in identifying different radioisotopes in a mixture were reduced greatly. On the average, the mass-separated samples were placed in the counting systems at Livermore about 60 minutes after the end of the irradiation. To date, we have obtained two significant sets of results from the ^{18}O experiments.

The mass-258 sample showed a spontaneous-fission activity, with 65-minute half-life, that we assign to an isomer in ^{258}Md . This observation offers the first direct confirmation of the existence of this isomer, which had been claimed previously, based on less direct evidence.⁶

The mass-260 sample contained a previously unknown isotope that decays by spontaneous fission with the relatively long half-life of 21 days. From the measured yield, we conclude that the isotope is most likely ^{260}Md , and that it is probably decaying by either β -decay or electron capture to a very short-lived isotope that decays by spontaneous fission, either $^{260}_{102}\text{No}$ or $^{260}_{100}\text{Fm}$.

These results for ^{258}Md and mass-260 are especially interesting because they tell us about the limits of nuclear stability in the heaviest elements in the periodic table, and also give us detailed information about the

fission process (i.e., energy and mass distributions) in isotopes with large numbers of neutrons.

1. Research sponsored in part by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems (R. L. Hahn).
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6.2.2 Aqueous Chemistry: Ion Exchange, Extraction Chromatography, and Solvent Extraction

(G. D. O'Kelley, J. Halperin, R. L. Hahn, O. L. Keller, J. H. Oliver, W. J. McDowell, D. C. Hoffman,² R. J. Silva,³ E. K. Hulet,³ G. T. Seaborg,² A. Ghiorso,² R. W. Loughheed,³ D. Lee,² R. J. Dougan,³ and K. E. Gregorich²)

Renewed interest in studying the chemical properties of elements 102-105 has led to a program with the broad objective of determining the architecture of the periodic table in the transition region at the end of

the actinide series and the beginning of the transactinide elements. As a result of measurements on cross sections for production of heavy nuclides in bombardments of ^{254}Es with heavy ions,⁴ the yields of a number of isotopes of heavy elements with useful half-lives can be predicted with sufficient accuracy to design chemical experiments which require only a few atoms per bombardment.

For our first experiments, we have chosen to investigate some properties of lawrencium, both because the aqueous chemistry of lawrencium remains largely unexplored and because 3-min ^{260}Lr can be made in sufficient yield with the amounts of ^{254}Es now being produced. The primary goals in such first experiments will be to confirm the chemical identification of the most stable oxidation state, believed to be $\text{Lr}(\text{III})$, and to evaluate the ionic radius of Lr^{3+} . The ionic radius is of particular interest, since by use of the modified Born equation of Phillips and Williams⁵ the single-ion hydration energy can be estimated, to complete the Born-Haber cycle for lawrencium.

Our preparations so far have emphasized the development of apparatus and techniques for carrying out experiments on lawrencium with relatively few atoms per bombardment. Experiments will be carried out at the 88-in. cyclotron at the Lawrence Berkeley Laboratory (LBL). The most favorable nuclear reaction for preparing 3-min ^{260}Lr appears to be 276-day ^{254}Es bombarded with 127-MeV ^{22}Ne ions; the cross section for production of ^{260}Lr at this bombarding energy is about one microbarn.⁴ The recent production campaigns for ^{254}Es have so far produced targets of 3 to 4 μg . A typical experiment might employ a 3- μg target of ^{254}Es , 3 mm in diameter, with a ^{22}Ne beam intensity of 0.3 particle μA . The production rate for ^{260}Lr under these conditions is about 11 atoms/minute. In a typical chemical experiment, atoms would be collected for about 9 minutes, (3 half-

lives) so there would be about 40 atoms present at the end of the bombardment. After taking into account losses due to collection of the product atoms, decay during the experiment, and detection efficiency, only about 5 events per bombardment are expected. Thus, such batch-type operations will require many replicate experiments to obtain adequate counting statistics.

A gas-jet system, incorporating a KCl aerosol as a clustering agent, will be used to collect the product atoms in the target chamber and to transport them a distance of about 40 m to the chemistry laboratory. Tests in September, 1984 of an older gas-jet system built several years ago gave a relatively low efficiency ($\sim 50\%$) over a distance of only ~ 7 m and produced excessive salt deposits from the KCl aerosol. Modifications have been made which improved the efficiency over short distances to $\sim 85\%$ and reduced the salt deposited. This system will be tested soon over the full distance of about 40 m and the efficiency over this distance will be determined. A similar test is planned for the gas-jet system used in the experiments discussed above in Section 6.2.1. The results of these two tests will provide the basis for designing the recoil chamber to be used in our chemistry experiments.

Our requirements for data acquisition and data analysis will be met by a system which uses a Digital Equipment Corporation PDP-11/23 PLUS computer. It has the capability to acquire and store spectral data from 8 high-resolution surface-barrier alpha-particle detectors. Provision has been made for limited on-line data analysis with a further capability for transferring data to a larger computer for off-line analysis. This data acquisition system was developed as part of an ORNL-LLNL collaboration.

The identification of Lr^{3+} and the measurement of its ionic radius will be studied by a combination of methods using

ion exchange, extraction chromatography, and solvent extraction. The same general approach was followed a number of years ago⁶ in a study of Mo^{2+} . However, the yields of lawrencium will be much lower, and so these new experiments will require more demanding techniques. Miniature cation-exchange columns using 2-hydroxy-2-methylpropanoic acid (α -hydroxyisobutyric acid, or HIBUT) as eluant have been tested with trivalent lanthanide analogs (Ho, Er, Tm). As an adjunct to the ion-exchange separations, columns for extraction chromatography have been prepared using bis (2-ethylhexyl) phosphoric acid (HDEHP) on various silica-based supports. Currently we use HDEHP on relatively conventional chromatographic supports such as Chromosorb W or Bioglass-500, which have been rendered hydrophobic with dichlorodimethylsilane. We are also evaluating supports which are more uniform and smaller in particle size; however, we have been unable as yet to achieve the rapid flow rates desirable for lawrencium work. In the future we hope to assemble a suitable high-pressure system capable of these higher flow rates.

The position of the elution peak in cation-exchange or extraction chromatography can serve to identify Lr chemically. In addition, elution positions within families of trivalent ions such as the actinides and lanthanides show a regular dependence on ionic radius. By comparison of elution positions of appropriate An^{3+} and Ln^{3+} ions, the ionic radius can be deduced. Our present column procedures (without recourse to high pressure columns) suggest that an elution of Lr^{3+} can be carried out in less than 4 min.

Solvent extraction provides an independent method of characterizing the aquo ion. An inverse third power relationship between extraction coefficient and H^+ concentration would support $3+$ as the formal charge of the Lr ion. Further, as in the column work, correlations between extraction coefficient

and ionic radius for a series of similar ions can be used to evaluate the ionic radius. Rapid batch-type solvent extraction procedures are presently under development using HDEHP as the extractant in dilute nitric acid media.

The use of automated and continuous chemical procedures offers the promise of enhancing experimental statistics. Continuous chemical systems are expected to be more efficient and to have lower chemical losses than batch operations, as well as being more rapid so that less radioactive decay will have taken place before the end of the experiment. We are currently investigating features of the SISAK centrifuge system and the McDowell micro-mixer-settler for solvent extraction studies. A related refinement in alpha-particle measurements making use of liquid-scintillation alpha counting offers the possibility of bypassing the traditional preparation of samples on plates for alpha counting. By using an extracting scintillator,⁷ automatic and continuous procedures for alpha counting can be devised as the final step following other automated procedures. The advantage of such an approach would be both the saving in time for counting sample preparations and the almost 100% counting efficiency (compared to ~35% with solid state detectors) that can be achieved with liquid scintillation spectrometry. However, this advantage is achieved at the expense of ~10-fold lower alpha-particle energy resolution (~300 keV vs ~30 keV), so that the applicability of this latter technique may not be universal.

1. Research sponsored in part by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems (G. D. O'Kelley, J. Halperin, R. L. Hahn, O. L. Keller, J. H. Oliver, and W. J. McDowell).

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7. SEPARATIONS CHEMISTRY

This research focuses on the fundamental role of molecular bonding and structure in determining the chemical selectivity and physical behavior of solvent extraction systems. The findings also apply directly to other phase-transfer separation systems involving ion-exchange resins or membranes. Several experimental approaches are being used: (1) Systematic studies (7.1) are being made of the separate effects of extractant structure and choice of metal ion on the extraction power of synergistic combinations of macrocyclic (crown ether) ligands and organic (sulfonic, carboxylic) acids. (2) More detailed equilibrium and other measurements are being performed on selected systems, including the extraction of alkali and alkaline-earth cations by crown ethers plus a sulfonic acid or a carboxylic acid (7.2.1-3), double-salt formation in the alkylammonium extraction of a molybdophosphate anion (7.2.4), and the aggregation behavior of a dialkylsulfoxide in a wet diluent (7.2.5). (3) Kinetic studies are being made of the extraction of uranium(VI) from phosphoric acid by a dialkylphosphoric acid and a trialkylphosphine oxide (7.2.6). (4) Structural studies are being made by X-ray diffraction of solid compounds (7.3.1-3) and by NMR measurements of solutions (7.3.4) related to selected extraction systems for alkaline-earth and uranium cations.

7.1 Systematic Studies

Systematic studies of candidate separation agents are performed in order to establish whether the reagents have appropriate solubility and phase distribution characteristics and to determine in general which elements or classes of elements are selected, which are rejected, and by what magnitude of separation factor. Emphasis this year has been on macrocycles and other multidentate oxygen coordinators mostly in synergistic combination with organic-phase-soluble cation exchangers.

7.1.1 Solubility and Phase Distribution of SX Reagents

(M. J. McDowell, G. N. Case)

The ability to dissolve in reasonably simple, non-toxic, high flash-point organic diluents and to remain in such diluents when they are contacted with an aqueous phase is important to the practical use of solvent extraction reagents. Table 7.1 shows the toluene solubility and distribution to water of several macrocycles we have tested recently. The effect of substituent groups is obvious. Others have

Table 7.1. Solubility in toluene and distribution to water of macrocycles.

COMPOUND	SOLUBILITY IN TOLUENE (M)	DIST. TO WATER (%)
12-CROWN-4	INFINITE	90
BENZO-14-CROWN-4	> 0.1	< 2
CYCLOHEXO-14-CROWN-4	INFINITE	50
CYCLOHEXO-15-CROWN-5	INFINITE	30
TERT-BUTYLCYCLOHEXO-15-CROWN-5	INFINITE	< 1
DIBENZO-18-CROWN-6	< 0.01	
DI(TERT-BUTYLBENZO)-18-CROWN-16	> 0.2	< 0.1
DICYCLOHEXO-18-CROWN-6	> 0.5	7
DI(TERT-BUTYLCYCLOHEXO)-18-CROWN-6	> 0.2	< 0.1
DICYCLOHEXO-21-CROWN-7	INFINITE	0.2
P-TERT BUTYL-CALIX[6] ARENE	< 0.01	

been reported in an earlier publication.¹ Cyclohexo groups and/or *tert.* butyl groups increase toluene solubility and decrease distribution to water from a toluene solution. Benzo groups sometimes increase toluene solubility and always decrease aqueous solubility or distribution. Hydroxy groups (as in the calixarenes) decrease toluene solubility. Figure 7.1 shows the macrocycles that we are presently using in our tests and their acronyms.

1. W. J. McDowell, G. N. Case, and D. W. Aldrup, "Investigations of Ion-Size-Selective Synergism in Solvent Extraction," *Sep. Sci. Technol.* **18**, 1483-1507 (1983).

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Fig. 7.1. Suitably organophilic macrocycles that are currently being studied.

7.1.2 Synergistic Extraction of Alkali Metals by Macrocycles Plus an Alkyl-Aryl Sulfonic Acid (W. J. McDowell, G. N. Case, F. I. Case)

Screening-type studies of extractions by combinations of multidentate coordinating macrocycles and organophilic cation exchangers have continued. The cation exchanger used most in

recent work has been didodecyl-naphthalene sulfonic acid (HDDNS). Figure 7.2 shows the extraction of tracer levels of sodium, potassium, rubidium and cesium with HDDNS and with HDDNS mixed with each of several macrocycles. If we consider only the cyclohexo-substituted crown ethers, those having the best cavity-size correspondence to the ion size produce the largest synergistic effect. A *tert.*-butylbenzo substituted crown ether, di(*tert.*-butylbenzo)-18-crown-6 is, however, an even stronger synergist in the case of potassium, rubidium, and cesium. This is a surprising result and may have important implications in regard to the way the ion is coordinated by the macrocycle oxygens particularly since this same di-*tert.*-butylbenzo compound is a much poorer coordinator for alkaline earth ions.

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Fig. 7.2. Extraction of Na, K, Rb, and Cs into toluene solutions of 0.1 M HDDNS and 0.1 M HDDNS mixed with 0.05 M macrocycles.

7.1.3 Synergistic Extraction of Alkaline Earth Metals by Macrocycles Plus an Alkyl-Aryl Sulfonic Acid (W. J. McDowell, G. N. Case, F. I. Case)

The systematic studies of alkaline earth ion extraction by combinations of multidentate coordinating macrocycles and organophilic

cation exchangers in toluene have given the results shown in Fig. 7.3. Strontium and barium show the largest synergistic effects and for each element the macrocycles producing the strongest synergistic effect (coordination) is one having a cavity approximating the ion size. Similar results using a neo-carboxylic acid as the cation exchanger have been reported previously. Below 0.2 M nitric acid precipitates were formed in both the strontium and barium extractions in some cases. The nature of the precipitate is not known but from other work (Section 7.2.3) it is believed to be an alkaline earth metal nitrate complex with the macrocycle. Separations of strontium and barium from beryllium and calcium (probably also magnesium) are enhanced greatly by the presence of the appropriate crown ether. The distribution coefficients shown here and in Figs. 7.2 and 7.4 suggest that HDDNS + DC18C6

or D(TBC)18C6 would be a useful system to separate strontium and barium from acidic nitrate systems such as nuclear fuel reprocessing wastes. Preliminary results on radium in this system suggest that it is extracted less strongly than barium and strontium.

Note that for the alkaline earths the cyclohexo substituted macrocycles are stronger synergists than are the benzo substituted compounds (see Fig. 7.2 and Section 7.1.2). Since the benzo substituted macrocycle rings are probably less flexible and may be slightly weaker electron donors (due to the electron withdrawing effect of the benzene rings), these results suggest that the ability of the crown ether oxygens to conform to some 3-dimensional bonding preference of the alkaline earths is important. However, these same cyclohexo-substituted crown ethers, when uncomplexed, may exist with their coordinating oxygens outside

Fig. 7.3. Extraction of Be, Ca, Sr, and Ba into toluene solutions of 0.1 M HDDNS and 0.1 M HDDNS mixed with 0.05 M macrocycles.

Fig. 7.4. Extraction of Ca, Mn(II), Fe(II), Ni(II), Cu(II) and Zn into toluene solutions of 0.1 M HDONS and 0.1 M HDONS mixed with 0.05 M macrocycles.

the macrocycle ring and the alkali metal ions, being less highly charged than the alkaline earth ions, would have greater difficulty in re-orienting the oxygens inside.

7.1.4 Synergistic Extraction of First-Row Transition Metals by Macrocycle Plus an Alkyl-Aryl Sulfonic Acid

(W. J. McDowell, G. N. Case, F. I. Case)

Comparisons of the extraction of some first row transition elements (with calcium included for comparison) are shown in Fig. 7.4. Again, the extractant was didodecyl-naphthalene sulfonic acid (HDONS) alone and mixed with various macrocycles in toluene. The aqueous phase was nitric acid. For the elements iron, cobalt, nickel, and copper the addition of the macrocycle either has no effect or depresses the distribution coefficient, D . The fact that D is depressed indicates an interaction between the HDONS and the macrocycle. Any ion that forms a complex with these compounds must compete with and overcome the macrocycle-HDONS adduct reaction. First-row transition elements

are usually thought of as forming strong complexes or coordination compounds. With the macrocycles, however, they appear to be much weaker than the alkaline earths or even the alkali metals. Possible explanations for this apparent anomaly include: (1) The preference of the first-row transition elements to bond with nitrogen while alkalis and alkaline earths prefer oxygen, (2) tendency of the elements with partially filled d shells to prefer highly structured, 3-dimensional coordination through the formation of covalent bonds and (3) the highly hydrated nature of these ions. It is interesting to note that manganese(II) and zinc(II) that have half filled and filled d shells, respectively, and show less ligand field stabilization than do the intervening elements are synergized (complexed, bonded) by the macrocycle TBC15C5.

The relatively low distribution coefficients shown by this group of elements indicates that they could be rejected in a separation scheme to recover strontium and/or barium using these reagents.

7.1.5 Extraction of Strontium, Barium and Radium by an Acyclic Polyether Dicarboxylic Acid

(W. J. McDowell, G. N. Case)

The compound, bis-1,8-(2'-carboxy-3'-naphthoxy)-3,6-dioxaoctane (BCND), supplied by R. A. Bartsch, Chemistry Dept., Texas Tech University, was found to be soluble in chloroform but not in toluene. The extraction of several alkali and alkaline earths with a chloroform solution of this dicarboxylic acid was examined. The alkali salts of BCND distributed completely to the aqueous phase at low aqueous ionic strength. At an ionic strength of 1 *M* the lithium salt of BCND precipitated from the organic phase. The beryllium, magnesium, and

strontium salts of BCND precipitated in chloroform solution when extracted from aqueous phases <1.0 *M* in alkaline earth chlorides. Extraction of barium and radium from an aqueous phase 0.25 *M* in BaCl₂, SrCl₂, CaCl₂ and MgCl₂ gave barium extraction values vs pH very similar to those found by Kang et al.¹ Radium extraction coefficients were about a factor of 3 higher than those of barium (see Fig. 7.5).

Comparison of barium and radium extraction from 0.5 *M* CsCl gave a Ra/Ba separation factor of 5 in spite of the fact that almost all of the cesium salt of BCND distributed to the aqueous phase. Figure 7.6 shows a comparison of barium and radium extraction from 1.5 *M* SrCl₂ by 0.05 *M* BCND in chloroform. The system was very close to precipitation in all equilibrations. Barium and radium tracers were used to follow the distribution, but the distribution of radium surprisingly failed to respond to pH changes as did barium. The introduction of 0.0075 *M* Ba to the system produced the radium pH dependent curve. The behavior of radium in these experiments is not understood, but in the presence of 0.0075 *M* Ba there appears to be an organic-phase preference for radium of ~20 over the pH range examined.

Fig. 7.5. Extraction of barium and radium from an aqueous phase 0.25 *M* in BaCl₂, SrCl₂, CaCl₂, and MgCl₂ by 0.05 *M* BCND in CHCl₃ by 0.05 *M* BCND as a function of equilibrium aqueous phase pH.

1. S. I. Kang, A. Czech, B. P. Czech, L. E. Stewart and R. A. Bartsch, "Competitive Extraction of Alkaline Earth Cations into Chloroform by Lipophilic Acyclic Polyether Dicarboxylic Acids," Submitted to *Analytical Chemistry*.

7.1.6 Separations and Methods of Alpha Assay for Savannah River Laboratory

(W. J. McDowell, G. N. Case, F. I. Case)

At the request of and in cooperation with the personnel of the Analytical Division of the Savannah River Laboratory¹ we have developed separation schemes and alpha liquid scintillation assay methods using both the PERALS spectrometer^{2,3} and commercial beta liquid scintillation counters for the type of samples commonly encountered there. The main alpha-emitters of interest are uranium and plutonium

Fig. 7.6. Extraction of radium and barium from 1.5 M SrCl_2 by 0.05 M BCND in CHCl_3 as a function of equilibrium aqueous phase pH.

isotopes, and it was a requirement that no perchloric acid be used in the procedures since the use of perchloric acid is discouraged in their laboratories. A flow chart outlining the procedures developed is shown in Fig. 7.7. A programmed book following this flow chart but describing the operations in more detail has been written.

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7.2 Stoichiometry, Equilibria, and Kinetics in Extraction Systems

Investigations of the details of equilibria in the didodecylphenylene sulfonic acid-macrocycle synergistic system appear to be indicating, in general, sulfonic acid-metal-macrocycle adducts with one macrocycle and sufficient sulfonic acid molecules to satisfy the metal valence plus 1 or 2 additional neutral sulfonic acid molecules. There is evidence that the sulfonic acid, when alone, is aggregated in toluene solution and that it forms adducts with the macrocycles, with some more strongly than with others.

7.2.1 Alkali Metal Extraction by Macrocycles Plus an Alkyl-Aryl Sulfonic Acid

(W. J. McDowell, B. A. Moyer, G. N. Case, C. F. Baes, Jr.)

The dependence of the distribution coefficient on the reagent concentrations of both the sulfonic acid (in the presence of a constant concentration of macrocycle) and the macrocycle (in the presence of a constant concentration of sulfonic acid) have been obtained for sodium, potassium, rubidium, and cesium. Also, the distribution coefficient as a function of the mole ratio of sulfonic acid to macrocycle has been examined for the same elements. Figures 7.8 and 7.9 illustrate the type of results obtained. If the sulfonic acid were a monomer in solution, these results would be consistent with a complex containing one sulfonic acid, one potassium and one macrocycle. However, measurements with a vapor-pressure osmometer indicate that the sulfonic acid (HDDNS) is associated to between a dimer and a trimer when alone and that the HDDNS and DC18C6 form a rather strong 1:1 intermolecular compound. If the latter is true the results obtained would still indicate a 1:1:1 (sulfonate:potassium:crown ether) complex. If the adduct is relatively weak the complex with potassium must contain between two and three sulfonates, one as the potassium salt and one or two as the acid, with one DC18C6 for each potassium. A computer program to model the

Fig. 7.7. A flow chart outline for choosing the correct procedure for preparing samples for alpha assay by liquid scintillation methods.

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Fig. 7.8. Dependence of distribution coefficient for potassium, D_K , on reagent concentration; HDDNS varying in the presence of 0.1 M DC18C6 and DC18C6 varying in the presence of 0.1 M HDDNS.

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Fig. 7.9. Potassium distribution coefficient, D_K , as a function of the mole fraction of DC18C6 in a toluene solution of constant total 0.1 molarity.

system has been written and gives curves similar to those observed experimentally.

7.2.2 Alkaline Earth Metal Extraction by Macrocycles Plus an Alkyl-Aryl Sulfonic Acid

(W. J. McDowell, B. A. Moyer, G. N. Case, C. F. Baes, Jr.)

Dependence of the distribution coefficient on the concentration of HDDNS and DC18C6 each in the presence of a constant concentration of the other, have been obtained for strontium and barium. In addition, distribution coefficients for these elements as a function of the crown ether/HDDNS ratio have been observed (continuous variation). Reagent dependence slopes are approximately one in both cases (see Fig. 7.10), but the continuous variation maximum is at 0.25 mole fraction DC18C6 (see Fig. 7.11). Calculations assuming the formation of a strong HDDNS-DC18C6 intermolecular compound show that these data can be consistent with the reaction,

Fig. 7.10. Dependence of the distribution coefficient for strontium, D_{Sr} , on reagent concentration: HDDNS varying in the presence of 0.05 M DC18C6 and DC18C6 varying in the presence of 0.1 M HDDNS.

Fig. 7.11. Strontium distribution coefficient, D_{Sr} , as a function of the mole fraction of DC18C6 in a toluene solution of constant total 0.1 molarity.

where n is either 3 or 4. Least-squares fitting of the data is planned to obtain the exact stoichiometry.

7.2.3 Complexation of Strontium in the Synergistic Extraction System

Dicyclohexano-18-Crown-6, Versatic Acid, Carbon Tetrachloride

(B. A. Moyer, W. J. McDowell, R. J. Ontko,¹ G. N. Case)

The remarkably selective enhancement of the extraction of certain metals that can be achieved by placing appropriate macrocycles in synergistic combination with organophilic cation-exchangers undoubtedly arises from the ability of the macrocycle to provide a coordination environment suitable for a given metal cation. Although distribution measurements usually cannot elucidate the structural nature of the extraction complexes formed, correlations between macrocycle "hole size" and selectivity

patterns suggest that the strongest synergism likely involves an efficient host-guest interaction in which the metal cation "fits" into the ring cavity.²⁻⁴

In an effort to provide more direct physical evidence for macrocycle-metal coordination in macrocycle-synergized metal extraction systems, a series of experiments involving the title system were designed in which infrared spectrophotometric and viscosity measurements of the organic phase could be obtained in addition to distribution measurements. As shown in Fig. 7.12, dicyclohexano-18-crown-6 (abbreviated DC18C6) synergizes Sr extraction by Versatic acid (abbreviated V-acid, a high molecular weight, neo carboxylic acid) in agreement with previous results.² The strontium was extracted from 0.5 M $\text{Sr}(\text{NO}_3)_2$ using added $\text{Sr}(\text{OH})_2$ as the base to neutralize the carboxylic acid, driving the reaction forward. Over the aqueous pH range 6 to 12, 0.1 M V-acid alone in CCl_4 extracts Sr giving the expected slope of 2 (see figure) at low loading. However, the extraction is significantly enhanced at a given pH in the synergistic system 0.1 M V-acid + 0.05 M DC18C6. Negligible amounts of Sr (3.5×10^{-5} M) were extracted by 0.05 M DC18C6 alone.

Fig. 7.12. Synergistic strontium extraction in the system 0.1 M Versatic acid + 0.05 M DC18C6 in carbon tetrachloride at 25°C contacted with 0.5 M $\text{Sr}(\text{NO}_3)_2$.

Characteristics of the distribution data (e.g., initial slope = 1) in the synergistic system together with the fact that a precipitate having the empirical composition $(\text{DC18C6})\text{Sr}(\text{NO}_3)_2$ was isolated from the solvent suggests that nitrate ion may accompany the Sr into the organic phase at intermediate loadings to give mixed-anion complexes like $(\text{DC18C6})\text{Sr}(\text{NO}_3)(\text{OOCR})$ (where OOCR represents the deprotonated Versatic acid). The observation is important in that it provides a possible explanation for distribution behavior in related synergistic systems.^{2,5}

In contact with 0.5 M $\text{Sr}(\text{NO}_3)_2$ saturated with $\text{Sr}(\text{OH})_2$ (pH 11.8), both of the organic phases shown in Fig. 7.12 loaded completely to the expected Sr concentration 0.05 M. (The maximum distribution coefficient is 0.1.) Infrared spectra of these solutions showed that the carboxylic acid was completely deprotonated in each case so that no nitrate anions remain in the organic phase at full loading. In the absence of the crown ether, then, one merely obtains the strontium carboxylate soap in the form of a viscous ($\eta = 16.4$ mPa·S or 16.4 cp) solution indicative of extensive polymerization or aggregation. Remarkably, when the solvent containing the crown ether (0.1 M V-acid + 0.05 M DC18C6) is fully loaded to 0.05 M Sr, polymerization is prevented as noted from the fact that the viscosity, 1.04 mPa·S, remains much closer to the value for pure CCl_4 diluent, 0.92 mPa·S.

The nature of the macrocycle-Sr-carboxylate complex that forms in the fully loaded synergistic system was investigated by observing the changes in viscosity and Fourier transform infrared spectra of the solution as the $\text{Sr}(\text{OOCR})_2$ soap is added to 0.05 M DC18C6 in wet CCl_4 . Figure 7.13 indicates a break in the viscosity vs $\text{Sr}(\text{OOCR})_2/\text{DC18C6}$ mole-ratio plot at a mole ratio of 1.0. In the mole-ratio range 0 to 1, infrared peaks characteristic of the free crown ether disappear and are replaced by peaks characteristic of a complex with the empirical stoichiometry $(\text{DC18C6})\text{Sr}(\text{OOCR})_2 \cdot n\text{H}_2\text{O}$. Water associated with the complex is evident in

Fig. 7.13. Viscosity vs $\text{Sr}(\text{OOCR})_2/\text{DC18C6}$ mole ratio at 25°C. Total $[\text{DC18C6}] = 0.05 \text{ M}$ in wet CCl_4 .

the spectra, and some of the protons are not hydrogen-bonded. The slope of the viscosity plot (Fig. 7.13) suggests that the complex may be monomeric or possibly dimeric.

Interestingly, the viscosity does not increase dramatically as the mole ratio increases above 1.0 as would be expected if the excess $\text{Sr}(\text{OOCR})_2$ soap was present in polymerized form. Instead, both the viscosity and infrared spectral changes suggest that the added $\text{Sr}(\text{OOCR})_2$ attaches to the initial $(\text{DC18C6})\text{Sr}(\text{OOCR})_2 \cdot n\text{H}_2\text{O}$ complex giving oligomers such as $(\text{DC18C6})[\text{Sr}(\text{OOCR})_2]_m \cdot n\text{H}_2\text{O}$.

Overall, the results point to a strong 1:1 interaction between Sr and crown ether in the solvent, and apparently either nitrate or carboxylate may serve as the anion in the complex depending on the pH of the aqueous phase. In terms of the design of practical systems, several conclusions may be drawn. As the macrocycle-Sr interaction serves as the basis for selectivity in the system, ratios of greater than 2 moles of V-acid per mole of crown ether in the solvent would appear to be undesirable by leaving excess cation exchange capacity as well as producing unnecessary increases in viscosity. Modifications to the hydrocarbon exterior of the crown ether may be needed to avoid precipitation problems.

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7.2.4 Trialkylammonium Double Salts Involving Dodecamolybdophosphate Anion

(B. A. Moyer, W. J. McDowell)

Amine extraction systems have long been known for their strong affinity for Mo(VI), but ironically, extraction of this metal has probably led to the most difficult instances of third-phase formation yet encountered in process systems. Recently, we showed that uranium processing problems may be traced to co-extraction of molybdenum followed by formation of the heteropolymolybdate

$\text{PMo}_{12}\text{O}_{40}^{3-}$ (dodecamolybdophosphate, abbreviated DMP) in the solvent as the trialkylammonium salt $(\text{R}_3\text{NH})_3[\text{DMP}]$.¹ Interaction of this salt with the trialkylammonium chloride salt (present in the solvent when appreciable concentrations of chloride are in the aqueous phase) leads to precipitation of unusual solid double salts of the empirical composition

Efforts to understand the nature and formation of these double salts in the past year have not only led to a better understanding of extant process technology (with suggestions for improvement) but have been of more general

value in providing clues both to how different trialkylammonium salts interact and how the properties of the extraction system will be affected by the interaction.

Seven representative tertiary amine extractants examined in this study are shown in Table 7.2. The branching in the alkyl tails of the amines designated "iso" in the chemical name consists of methyl groups randomly distributed along the backbone carbons not adjacent to the nitrogens.² T810A (e.g., Alamine 336), the most widely used commercial tertiary amine extractant, consists of a blend of all possible tertiary amines that can be formed from n-octyl and n-decyl alkyl groups.

Figure 7.14 shows the effect of the alkyl-chain structure and initial aqueous NaCl concentration on the level of DMP that can just be tolerated in the solvent before formation of a third phase. In general, the DMP tolerance of the system increases with the total number of carbons per alkyl group in the tertiary amine, but note that the results for the branched-chain amines form a separate curve from the results for the straight-chain amines. With no chloride present, the branched-chain amines may be approximately compared with the straight-chain amines by replotting (dashed horizontal lines) vs the backbone chain length, suggesting that the DMP tolerance increases primarily with the physical length of the alkyl

Fig. 7.14. Effect of trialkylamine structure and aqueous NaCl concentration on dodecamolybdo phosphate third-phase formation at 25°C. Initial phase compositions: 0.1 : 1 H_2SO_4 plus $Mo(VI)$, H_3PO_4 , and NaCl (aqueous) and 0.05 M amine in n-nonane modified with 0.05 M n-dodecanol (organic, pre-equilibrated with 0.1 M H_2SO_4). $\circ$ - straight-chain amines, Δ - branched-chain amines, and $\square$ - T810A. Horizontal dashed lines indicate replotting the branched-chain data vs backbone chain length.

Table 7.2. High molecular weight trialkylamines

Abbreviation	Chemical name	Formula weight	Average No. carbons per alkyl	Average No. carbons in backbone
TOA	Tri-n-octylamine	354	8	8
TDA	Tri-n-decylamine	438	10	10
TLA	Trilaurylamine	522	12	12
T810A	Tri-n-(octyl,decyl)amine	382	8.7	8.7
TIOA	Triisooctylamine	370	8.0	6.8
TIDA	Triisodecylamine	447	10.1	8.0
TITA	Triisotridecylamine	570	12.7	10.1

chains irrespective of the presence of methyl branching. This result correlates with the notion that intermolecular electrostatic interactions decrease with increasing chain length because of the increasing screening-ability of the chains.³ However, with chloride present, no such correlation could be found since all of the tolerance values for the branched-chain amines were less than 7×10^{-6} M (not shown). Thus, factors other than backbone chain-length (e.g., amine basicity) become important for the branched-chain amines in this case.

It is further apparent from Fig. 7.14 that the presence of aqueous chloride entails a large decrease in the level of DMP that can be tolerated. With chloride present, the comparatively insoluble solid double salts (I) form as demonstrated by analysis of the solid precipitates. Without chloride, one obtains a viscous liquid third phase shown to be a mixed-salt solution phase consisting primarily of $(R_3NH)_3[DMP]$ in combination with variable amounts of trialkylammonium sulfate and bisulfate salts plus diluent and possibly water.

In terms of the design of improved extraction reagents and processes, the above results clearly show that the third-phase problems caused by the otherwise very desirable co-extraction of molybdenum in uranium processing may be effectively ameliorated by employing long-chain tertiary amines with straight vs methyl-branched alkyl chains. In terms of fundamental chemistry, it has been shown that mixed-salt interactions in the solvent play a pivotal role in the third-phase phenomena specifically involving the salt $(R_3NH)_3[DMP]$. More importantly, the results support the general idea⁴ that an entire class of third-phase phenomena and metal distribution behavior in amine extraction may involve mixed-salt interactions as a central influence.

Hydrogen bonding appears to be important in the formation of double salts such as I. The infrared spectra in Fig. 7.15 compare the N-H stretching envelopes for the pure single

Fig. 7.15. Comparison of the infrared transmittance spectra of trialkylammonium salts and double salts (dry samples spread as thin films on NaCl plates). The peaks in the 2800 to 3000 cm^{-1} region are due to C-H stretching; the other absorptions are assigned to N-H stretching modes.

salts $(TOAH)_3[DMP]$ (dotted line) and $(TOAH)Cl$ (dashed line) with the double salt $(TOAH)_3[DMP] \cdot 3(TOAH)Cl$ (solid line). In general, the broad N-H stretching envelope of trialkylammonium single salts shifts markedly according to the strength of the hydrogen-bonding interaction with the anion.⁴ In the Figure, weakly hydrogen-bonding DMP anion gives a stretch at approximately 3100 cm^{-1} , characteristic of little interaction, while strongly hydrogen-bonding chloride anion causes a large shift to approximately 2440 cm^{-1} . With a peak at approximately 2600 cm^{-1} , the spectrum of the double salt does not arise as the simple sum of the spectra of the noninteracting simple salts but implies a new hydrogen-bonding interaction. An almost identical comparison was obtained for the amine TLA.

In view of the stoichiometry of the double salts (I), an attractive interpretation of the spectral data is that the hydrogen-bonding occurs preferentially to the better hydrogen-bonding anion, chloride. One possible

structural formula, then, might be $[R_3NH...Cl...HNR_3]_3[DMF]$. If this idea is proven to be correct (possibly via x-ray crystallography), the inference follows that mixed-salt formation via hydrogen bonding is likely when trialkylammonium salts with widely differing hydrogen-bond strengths occur simultaneously in the solvent. Application of this idea leads to some significant possibilities for understanding and predicting the properties of amine extraction systems.

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7.2.5 Aggregation Behavior of Di-2-ethylhexylsulfoxide in Wet Dodecane Diluent

(B. A. Moyer, W. J. McDowell)

Dialkylsulfoxides (R_2SO) have attracted attention as a promising class of extractants for use in nuclear separations because of the idea that their radiation degradation products will cause less processing difficulties than have been experienced with trialkylphosphates. Limited testing has been encouraging on this point, and we have shown that di(2-ethylhexyl)sulfoxide (DEHSO) extracts U(VI) effectively while overcoming the low alkane solubility inherent in the straight-chain dialkylsulfoxides that have been previously used.¹

In an effort to better understand the extraction of metals from nitric acid solutions by

DEHSO in dodecane diluent, preliminary vapor phase osmometry and water extraction experiments have been carried out to survey the initial state of the extractant in the wet diluent. As compared to three "ideal" standard compounds employed, solutions of DEHSO in wet dodecane exhibit significant departures from ideal behavior at concentrations of approximately 0.1 M or greater. Assuming that the nonideality may be attributable to aggregation phenomena,² the average aggregation number calculated from the data increases from 1.04 ± 0.09 at 0.05 M to 1.65 ± 0.03 at 0.4 M. The data may be mathematically modelled according to a scheme based on the partial formation of tetrameric aggregates.

The extraction of water must be taken into account in any extraction system in order to mathematically treat the variation in the concentrations of hydrated and unhydrated extractant species that occurs as a function of the activity of water in the aqueous phase. For neutral oxygen-donor extractants such as TBP, a relatively simple situation often occurs in which the major hydrated species is the monomeric monohydrate.² To determine whether solutions of DEHSO in dodecane would conform to this pattern or whether more complex behavior indicative of aggregation might be found, Karl Fischer analyses were performed on a series of 0 to 0.4 M DEHSO solutions previously contacted with pure water. After subtracting the water extracted by the dodecane diluent alone, the organic-phase water concentration increased as a percent of the total DEHSO concentration from 10% to 23% over the interval of DEHSO concentrations examined. Together with the osmometric data, the Karl Fischer results suggest that the simple picture involving monomeric DEHSO and $DEHSO \cdot H_2O$ may be complicated by the partial formation of hydrated aggregates. More thorough and precise measurements of water extraction by DEHSO are being undertaken to obtain an accurate quantitative model.

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7.2.6 Interphase Transfer of Uranium Between Phosphoric Acid and DEPA-TOPO Reagent

(F. J. Hurst)

This is a continuation of tests which are being made to refine our DEPA-TOPO process for recovering uranium from wet-process phosphoric acid.¹ Our goal is to make this process more efficient and more economical in order to increase the attractiveness of recovery in smaller plants where an estimated 3000 tons of U_3O_8 per year passes through unrecovered.

Rate constants for the interphase transfer of U(VI) from an acid phase to an organic phase (in this case 0.5 M DEPA-0.125 M TOPO in n-dodecane) has been measured for a variety of conditions, with both pure and commercial acids, using a baffled mixer with a fixed interface (Lewis cell).^{1,2}

In 1959, Burger³ using a Lewis cell found that surface active agents, even at very low concentrations, can reduce the rate of transfer of a solute, in this case uranium, in either direction in a two phase system, and suggested that this was due to a mechanical blocking at the interface.

Several investigators have shown that several uranium phosphate complexes can coexist in phosphoric acid solutions. For example, Baes⁴ suggested the following complex ions, $UO_2H_2PO_4^+$, $UO_2H_3PO_4^{++}$, $UO_2(H_2PO_4)_2$, and $UO_2(H_2PO_4)H_3PO_4^+$, whereas Thamer⁵ suggested that UO_2^{++} , $UO_2H_2PO_4^+$, $UO_2(H_2PO_4)_2$ and $UO_2(H_2PO_4)_2 \cdot H_3PO_4$ are present. Using HPLC techniques with 15 to 25 μ Dowex 50W-X8, a strong acid ion exchange resin, we have also confirmed that at least two and possibly more species can coexist. The distribution of these species is highly dependent on the H_3PO_4 concentration, and in the strong 5-6 M H_3PO_4 solutions that are typical in wet-process

phosphoric acid plants, the dominating species may be neutral as pointed out by Thamer.

In the Lewis cell, equal volumes (70 ml each) of organic and aqueous phases were individually mixed by flat-blade paddles revolving in each phase at 100 rpm. At this speed, the interface is not appreciably disturbed, and the interfacial area is exactly known. A glass baffle arrangement was added to improve mixing and minimize vortex formation, and the cell was jacketed for temperature control. When testing A to O kinetics, two ml samples of organic were taken from just above the interface after two to fifteen min periods using evacuated tubes. Sampling over such a short period of time minimizes the contribution from the reverse reaction. The mathematical equation developed by Horner and Mailen² for aqueous to organic transfer in the Lewis cell, near time equal zero, where $c \sim c_0$ is,

$$k' = \frac{VD}{at} \ln \left[1 - \frac{c}{c_0} \right]$$

where k' = forward rate constant (A to O), c = concentration of uranium in the organic phase after time t , c_0 = initial concentration of uranium in the aqueous phase at $t = 0$, V = volume of organic phase, a = interfacial area, t = interphase contact time, and D = equilibrium distribution coefficient (O/A). The data points were extrapolated back to time zero to obtain the true rate constant.

Effect of H_3PO_4 . Rate constants in both extraction (A to O) and stripping (O to A) modes show a very high dependency on phosphoric acid concentration. For example in the extraction mode, k' showed an approximately 3rd power inverse dependency on H_3PO_4 concentration as k' decreased from 3.8×10^{-2} cm/min in 4 M H_3PO_4 to 6.0×10^{-3} cm/min in 8 M H_3PO_4 , a factor of ~six. In the stripping mode, k increased from 8×10^{-3} cm/min in 4 M H_3PO_4 to 2.6×10^{-2} cm/min in 10 M H_3PO_4 , a factor of over three.

Effect of Temperature. Slopes of Arrhenius plots of $\log k$ and $\log k'$ vs $1/T$ show activa-

tion energies of 12.2 kcal/mole for O to A transfer (stripping), but only 3.7 kcal/mole for the A to O transfer (extraction). The difference of these values give ΔH as 8.5 kcal/mole for the extraction reaction.

Effect of Humic Matter.⁶ As expected from Burger's report,³ organic substances exclusive of the extractant, are the major material that can block the interface and retard the transfer of uranium. For example, the addition of 36 ppm humus to 5 M cp H_3PO_4 reduced the rate constant from 2.4×10^{-2} cm/min to 1.0×10^{-2} cm/min, a factor of 2.4. A significant amount of the added humus⁶ was insoluble in the acid, but readily dissolved when treated with extractant. In normal practice, a significant amount of organic matter present in the acid is going to end up in the solvent. To determine whether or not humus laden solvent would affect the transfer of uranium, we tested a well aged, dark brown sample of barren solvent from an operating plant by contact with 5 M cp H_3PO_4 containing ~0.015 mg U/ml. The rate constant for A to O transfer was 2.0×10^{-2} cm/min at 50°C, or about 80% of the value we obtained with pure solvent and pure H_3PO_4 .

Effect of Defoaming Agents. In addition to humic acids, flotation agents used in beneficiating the rock, and defoaming agents added to control foaming during digestion of the rock may have an adverse effect on the extraction of the uranium, in phase separation, and on the transfer rate between the phases. In four out of five defoamer samples tested, k' decreased from 2.4×10^{-2} cm/min with no defoamer to $\sim 1.4 \times 10^{-2}$ cm/min by the addition of 75 ppm defoamer. One defoamer did not show any decrease in up to 1000 ppm added. Thus each company should test their defoamers and other additives before using them in a uranium recovery plant.

Transfer in Plant Acids. Up to this point, most of our tests have been made with pure cp H_3PO_4 . Table 7.3 gives data for actual wet-process acids. Most of the tests were made at 50°C, since that is the temperature that will probably be used in plant practice. Actually

there is very little difference in rate constants with temperature for the plant acids tested. For example, rate constants measured at 26 and 50°C, respectively were 3.6×10^{-3} and 3.8×10^{-3} cm/min (average of duplicate runs 2 and 3) for an untreated plant acid, and 8.9×10^{-3} and 9.9×10^{-3} cm/min (average of duplicate runs 8 and 9) for a green acid (Table 7.3). For comparison, the rate constant for pure cp phosphoric acid at 50°C was 2.4×10^{-2} cm/min (run 17). Rate constants for two other black acids were 4.2×10^{-3} and 6.6×10^{-3} cm/min (runs 5 & 6). These acids were aged so it is very likely that rate constants obtained with fresh acids may be lower than those shown in Table 7.3.

Rate constants for plant acid that had been cleaned of most of the humic matter by treatment with activated carbon were about 2.5 times higher than uncleaned black acid. After additional carbon treatment in the laboratory, the rate constant increased from 8.7×10^{-3} to 1.53×10^{-2} cm/min, a factor of 4 over untreated acid. Although better, the rate constant is still lower than that obtained with pure acid (2.4×10^{-2} cm/min).

Rate constants for two green acids that were made from calcined rock were about 1.3 to 1.4×10^{-2} cm/min. The rate constant showed an increase of about 25% in three acid samples in which the acid (raffinate), depleted of most of its uranium and organic matter, was spiked with uranium and retested with fresh organic. This indicates that rate constants should increase with each stage as the humus is removed from the acid.

More importantly the data show the large advantage that can be achieved by using activated carbon to clean the acids.

Correlation of Batch and Continuous Data with Rate Constants. Before the rate constant k' (cm/min) can be used for design and scaleup purposes, it must be multiplied by the interfacial area a (cm²cm⁻³) to give an effective rate constant $k'a$ (min⁻¹). For our conditions we have used an extrapolated value of 237.⁷ The $k'a$ values can then be used in equations 1

Table 7.3. Transfer rate constants for the extraction of uranium(VI) from plant samples of wet-process phosphoric acid

Test No.	Plant Acid	[H ₃ PO ₄] M/L	Treatment	Dist. coef.	k' x 10 ⁻² cm/min	k'a ^b min ⁻¹	Retention Time, min	
							Batch ^c	Continuous ^d
1	1 ^a	5.23	none ^e	9.4	0.36	0.853	1.8	7.0
2	1	5.23	none ^e	3.5	0.39	0.924	1.7	6.5
3	1	5.23	none ^e	3.0	0.37	0.877	1.8	6.8
4	1	5.23	j	2.7	0.50	1.190	1.3	5.0
5	2	6.26	none ^e	1.5	0.42	1.00	1.5	6.0
6	3	8.74	none ^e	0.4	0.66	1.55	1.0	3.8
7	4 ^a	5.03	act C ^f	11.5	0.89	2.11	0.7	2.8
8	4	5.03	act C	4.0	0.96	2.28	0.7	2.6
9	4	5.03	act C	3.7	1.02	2.42	0.6	2.5
10	4	5.03	act C ^j	—	1.34	3.18	0.5	1.9
11	4	5.03	act C ^j	—	1.55	3.67	0.4	1.8
12	5	5.17	act C ^g	4.5	0.87	2.06	0.7	2.9
13	5	5.17	act C ^h	5.5	1.53	3.63	0.4	1.7
14	6	5.9	cal ⁱ	2.5	1.37	3.25	0.5	1.8
15	7	6.0	cal ⁱ	2.4	1.30	3.08	0.5	1.9
16	7	6.0	cal ^j	2.2	1.77	4.19	0.4	1.4
17	k	5.0	cp acid	3.6	2.4	5.69	0.3	1.0

^aTest was made at 26°C, others were made at 50°C.

^bk'a = k' x 10⁻² cm min⁻¹ x a cm²cm⁻³ where a (the interfacial area per unit volume of dispersion) is 237 at an aqueous to organic feed ratio of 2/1.¹

^cCalculated from Eq. 1. (Assumes 90% extraction efficiency per stage.)

^dCalculated from Eq. 2. (Assumes 90% extraction efficiency per stage.)

^eBlack acid that was 1 to 2 weeks old.

^fAct C - activated carbon.

^gAct C aged ~1 year.

^hAdditional treatment of test 12 with act C.

ⁱGreen acid produced from calcined rock (cal).

^jSeparated aqueous phase, after removal of most of the uranium, was spiked with uranium (~0.15 mg/ml) and the test repeated.

^kAverage of 9 tests using Cp H₃PO₄ containing ~0.15 g U/L.

and 2 to calculate retention times (Table 7.3).

Ryon et al⁸ reported in a study of the Dapex process, that the rate of uranium extraction with vigorous mixing is first order with respect to the uranium concentration in the aqueous phase, and that the retention time may be calculated by the following equations.

$$\text{Batch: } t = -\ln(1-E) \frac{R}{V} \frac{1}{k'a} \quad (1)$$

$$\text{Continuous: } t = \frac{E}{E-1} \frac{R}{V} \frac{1}{k'a} \quad (2)$$

The rate constant, k'a is related to the stage efficiency, E, the fraction of aqueous in the mixer, R/V, and the contact time, t. R is the volume of aqueous in the mixer and V is the total volume of the mixer. Stage efficiency, E, is defined as:

$$E = \frac{C_0 - C}{C_0 - C_{eq}} \quad (3)$$

where C is the uranium concentration in the aqueous phase at time t , C_0 is the aqueous uranium concentration at $t = 0$, and C_{eq} = concentration of uranium in the aqueous phase at equilibrium. In the Dapex process rate constants were consistently higher in the batch mode than in the continuous mode. Even so, the agreement between the two methods was close enough to warrant the use of a batch technique to compare variables such as impurities, temperature, acid strength, etc.

Retention times for 90% uranium extraction efficiency per stage are included in Table 7.3 for both batch and continuous conditions. As expected, the continuous values are higher than the batch values. Even so, relative values indicates the effect of different acids and their impurities.

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7.2.7 Development of HPLC Analytical Techniques for the Determination of DEPA, TOPO, and Dodecane

(L. O. Gilpatrick)

There is need for a rapid reliable method of analysis suitable for the assay of the organic phase used in the DEPA-TOPO process^{1,2} for uranium by-product recovery from wet process H_3PO_4 manufacture. The several conditions to be met are that there be a single one time procedure to determine all the organic components of the organic phase. The procedure should be rapid and quantitative. High pressure liquid reverse phase chromatography has proven to be a nearly ideal procedure to achieve these aims. Purity of the reagents TOPO and DEPA was easily monitored. Various sources and vendors products were readily compared in the range 95 to 100%.

The system successfully used consisted of a Whatman Partisil PXS 10/25, ODS-2, #1H4056 Column 25 cm long $\times$ 6.3 mm OD packed with 10 μ m particles coated with octadecylsilane. The mobile phase was isocratic 95% B&J methanol, 4.5% H_2O , and 0.5% H_3PO_4 (85% reagent) by volume. Refractive index detection was used and a flow rate of about 1 ml per min. Ten microliters of a mobile phase solution containing 5 μ l per ml of the organic phase was applied to the column. The major components were eluted and well resolved in less than 20 min.

The principal difficulty was the poor retention of di-2-ethylhexyl phosphoric acid (DEPA) which has polar properties and a significant level of ionization in water-containing mixtures. An ion pairing reagent (tetrabutyl ammonium phosphate, 0.05 molar) added to the mobile phase was unsuccessful in increasing DEPA retention on the column. When H_3PO_4 was added to the mobile phase, DEPA ionization was suppressed sufficiently to allow column retention and to give a capacity factor in the range of 0.95 to 1.0. The improved retention is necessary to resolve DEPA from the interfering

unretained species such as H_2O and H_3PO_4 which are always present in the organic phase to be tested.

Simulated extraction mixtures were made from reagent dodecane (~535 g/l); TOPO (50.8 g/l); and DEPA (169.5 g/l). Since dodecane is a "pure" substance it gives only a single response on the HPLC and the spectra looks as in Fig. 7.16-a. The organic extraction phases of industrial origin employ "kerosene" like solvents and these solvents are complex mixtures as seen in Fig. 7.16-b. Interpreting the HPLC spectra in the applied case is hence more uncertain but useful.

Fig. 7.16. HPL-chromatograms for 0.5 M DEPA, 0.125 M TOPO in dodecane (upper) and in a plant extraction solvent (lower). The numbers denote vertical amplification factors. See text for conditions.

Calibration procedures using pure standards proved to be more accurate using an electronic integrator (HP 3390-A) and areas data rather than peak height data. Concentrations can be reproduced to 1% at the present state of development.

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7.3 Structural Studies

Determinations of the molecular structure of extraction complexes have been carried out on the solid state by x-ray diffraction and on solutions by NMR. This information is useful in interpretation of the observed extraction behavior of systems involving these complexes.

7.3.1 Crystal Structure of $Ba(dibutylphosphate)_2 \cdot H_2O \cdot (18-crown-6)$

(J. H. Burns)

The extraction of alkali and alkaline-earth metal ions by organophosphoric acids has been reported to be enhanced by the presence of certain crown ethers in the organic phase.¹⁻³ This synergism is attributed to the formation of an extraction complex in which the metal ion is held in the cavity of the ether ring and for which the anions are provided by the organophilic acid. In order to verify that such a complex could exist and to examine its geometry, $Ba((C_4H_9O)_2PO_2)_2 \cdot H_2O \cdot (18-crown-6)$ was prepared and its structure determined by x-ray diffraction methods. Crystals are triclinic, $P\bar{1}$, with $a=13.79(1)$, $b=17.19(1)$, $c=9.488(6)$ Å, $\alpha=105.78(5)^\circ$, $\beta=83.00(6)^\circ$, $\gamma=107.45(6)^\circ$; there are 2 molecules in the unit cell.

The structure is illustrated in Figure 7.17 which shows two molecules in relation to the unit cell. Each molecule of the complex contains an 18-crown-6 ring which has a Ba^{2+} ion near its center and is capped on one side by a $(C_4H_9O)_2PO_2^-$ ion and on the other by an identical ion plus a water molecule. Five of the O atoms of the crown are nearly coplanar, but the sixth O atom and the Ba atom are 0.68 and 0.6 Å to one side of the plane, respectively. Thus the crown is considerably distorted by the attachment of its O atoms to the Ba atom. The H_2O molecule makes an intramolecular H bond to one phosphate group and an intermolecular H

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Fig. 7.17. Two molecules of $\text{Ba}(\text{dibutylphosphate})_2 \cdot \text{H}_2\text{O} \cdot 18\text{-crown-6}$ in relation to the unit cell.

bond to another, linking molecules in continuous chains.

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7.3.2 Crystal Structure of $(\text{H}_3\text{PO}_4)_2 \cdot 6\text{H}_2\text{O} \cdot (18\text{-crown-6})$

(E. H. Morclander,¹ J. H. Burns)

Crown ethers such as 18-crown-6 and larger are quite flexible, and in complexes usually deploy their O atoms so as to attain an optimum coordination to a metal ion in accord with its size. This has led to the concept of crown ethers having a "hole size", although uncomplexed, crystalline 18-crown-6 is an elongated ring with virtually no cavity.² Another means by which the crown is changed from its uncomplexed geometry is by acceptance of a number of hydrogen bonds from other molecules. In some cases these are provided by a single or pair of guest molecules, e.g. urea,³ in others by linkage through waters of hydration associated with some ionic species, e.g. $\text{Gd}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O} \cdot (18\text{-crown-6})$.⁴

Such a hydrogen bonded lattice compound is formed with H_3PO_4 , 18-crown-6, and H_2O .

Crystals grown by adding 18-crown-6 to concentrated H_3PO_4 were analyzed by x-ray diffraction to determine the stoichiometry and the structure. They are monoclinic, space group $P2_1/c$ with $a=8.494(2)$, $b=10.701(3)$, $c=15.210(5)$ Å and $\beta=104.41(2)^\circ$. There are 2 molecules of $(\text{H}_3\text{PO}_4)_2 \cdot 6\text{H}_2\text{O} \cdot 18\text{-crown-6}$ per unit cell. The H_3PO_4 molecules form hydrogen-bonded dimers (Figure 7.18), which are linked by H_2O molecules to crown-ether rings through a series of hydrogen bonds. All six O atoms of the crown are recipients of hydrogen bonds as shown in Figure 7.19. Because of the constraints imposed by these bonds, the ring adopts the D_{3d} conformation, which it usually has in metal complexes, instead of the C_i symmetry of the uncomplexed ether.

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Fig. 7.18. A dimer of H_3PO_4 molecules and the hydrogen bonds associated with it in the structure of $(\text{H}_3\text{PO}_4)_2 \cdot 6\text{H}_2\text{O} \cdot 18\text{-crown-6}$. Atoms O(5), O(6), and O(7) are part of the crown.

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Fig. 7.19. Unit cell of the crystal structure of $(\text{H}_3\text{PO}_4)_2 \cdot 6\text{H}_2\text{O} \cdot 18\text{-crown-6}$.

7.3.3 Crystal Structure of $\text{UO}_2(\text{NO}_3)_2(\text{tri-}i\text{-butylphosphate})_2$ at 139°K

(J. H. Burns, G. M. Brown, R. R. Ryan¹)

This complex is representative of many that are encountered in the extraction of U(VI) from strong acid solutions. Its structure was studied previously by x-ray and neutron diffraction at room temperature.² A qualitative picture of the molecular geometry was obtained, but the structure could not be refined because of the very large thermal motions of the butyl groups.

New x-ray diffraction data with a crystal at 139°K has been obtained at Los Alamos and the structure was refined, including positions and thermal parameters of the H atoms. There is an 8% shrinkage in volume when the crystal is cooled to this temperature, but no phase transition occurs. At 139°K the triclinic unit cell has $a=8.54(1)$, $b=10.298(2)$, $c=11.501(6)$ Å, $\alpha=98.15(3)$, $\beta=106.38(7)^\circ$, and $\gamma=101.86(4)^\circ$. The space group is $P\bar{1}$ and $Z=1$.

There are discrete, centrosymmetric molecules of $\text{UO}_2(\text{NO}_3)_2((\text{C}_4\text{H}_9\text{O})_3\text{PO})_2$ in the crystal with the configuration shown in Figure 7.20. Each

molecule contains a uranyl ion surrounded at its equator by six coplanar O atoms provided by two bidentate nitrate ions and two monodentate $(\text{C}_4\text{H}_9\text{O})_3\text{PO}$ ligands. This same arrangement has been found in a variety of complexes in which there are other neutral organophosphorus ligands.³ The U=O bond in the uranyl ion is 1.758(3) Å in length; this corresponds to Zachariasen's⁴ bond strength of 2. The bond between the U atom and tributylphosphate is 2.371(4) Å, which is shorter than the bond from U to water. This is in agreement with the fact that tributylphosphate replaces water in the extraction process.

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Fig. 7.20. One molecule of $\text{UO}_2(\text{TiBP})_2(\text{NO}_3)_2$ in the unit cell of the crystal.

7.3.4 Studies of UO_2 -Organophosphorus Systems by NMR

(J. H. Burns, L. L. Brown)

Earlier NMR studies¹ proved useful in relating the structure of molecules in crystals to their structure in solution for several organophosphorus complexes of the uranyl ion. Additional spectra are reported here for related systems. Both ^1H and ^{31}P spectra were obtained in CDCl_3 solutions with TMS and 85% H_3PO_4 as reference materials, respectively. A summary of the chemical shifts are given in Table 7.4.

One question of interest was the possible existence of a dimeric species involving UO_2 , DEHP and TOPO (acronyms defined in Table) that would be analogous to the previously established^{1,2} $\text{UO}_2(\text{DBP})(\text{TOPO})\text{NO}_3$, in which TBPO=tri-n-butylphosphine oxide. The chemical shifts observed in solutions of the proper stoichiometry suggest that the complex does

Table 7.4. NMR Chemical shifts for uranyl-organophosphorus compounds in CCl_3 solutions.

Compound	³¹ P, δ (ppm)			
H ₃ PO ₄ , 85%	0.00			
Bis(2-ethylhexyl phosphoric acid (HDEHP)	1.26			
Tri-n-octylphosphine oxide (TOPO)	42.0			
UO ₂ (DEHP) ₂	4.05			
UO ₂ (TOPO) ₂ (NO ₃) ₂ (Ref. 5)	74.1			
UO ₂ (DEHP)(TOPO)NO ₃	(DEHP)	4.82		
	(TOPO)	71.99		
UO ₂ (DEHP) ₂ (HDEHP) ₂	2.63			
Di-n-butylphosphoric acid (HDBP)	0.94			
UO ₂ (DBP) ₂	5.46			
UO ₂ (DBP) ₂ (HDBP) ₂	1.83			
Tri-i-butylphosphate (TiBP)	-0.98			
UO ₂ (TiBP) ₂ (NO ₃) ₂	0.45			
	¹ H, δ (ppm)			
HDEHP	3.93	1.4	0.89	
UO ₂ (DEHP) ₂	4.13	1.26	0.89	
HDBP	4.029	1.666	1.414	0.932
UO ₂ (DBP) ₂	4.436	1.716	1.428	0.876
UO ₂ (DBP) ₂ (HDBP) ₂	4.220	1.670	1.372	0.878
TiBP	3.80	1.96	0.95	
UO ₂ (TiBP) ₂ (NO ₃) ₂	4.24	2.05	0.98	

exist. Two other species, postulated to exist long ago,³ are $\text{UO}_2(\text{DEHP})_2(\text{HDEHP})_2$ and $\text{UO}_2(\text{DBP})_2(\text{HDBP})_2$, in which excess acid is attached to the neutral complex. No solid-state data on these are available. The presence of a single ^{31}P chemical shift in solutions of this stoichiometry, in each case, is consistent with there being such species; this could also be interpreted as due to rapid exchange between the anion (e.g. DBP^-) attached to the U atom and the protonated anion (e.g. HDBP), each containing the ^{31}P atom.

The spectrum of $\text{UO}_2(\text{TiBP})_2(\text{NO}_3)_2$ in solution is interesting because, although the molecule is very similar in structure⁴ to $\text{UO}_2(\text{TiPO})_2(\text{NO}_3)_2$, the ^{31}P chemical shift is much smaller in the former because of its weaker bonding interaction with the U atom.

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8. ELECTROCHEMISTRY

This program is concerned with the kinetics and mechanistics of coupled interfacial and mass-transport processes that occur during localized corrosion of metals (crevice corrosion, pitting, and stress corrosion cracking). The rates of interfacial reactions involved in corrosion (metal dissolution, oxide film formation, hydrogen evolution, O_2 reduction, etc.) are dependent upon the metal/electrolyte interfacial potential difference and electrolyte composition, and are determined as functions of these basic variables. Factors which effect either of the basic variables are taken into account. These include redox, hydrolytic, complexing, and precipitation reactions, as well as potential and composition gradients arising from iR-drop and limited mass-transport within the restricted geometries (crevices, cracks, etc.) associated with localized corrosion. Materials of interest include pure metals (Ti, V, Mo, Cr, Fe, etc.) and novel "near-surface" alloys prepared by ion implantation and characterized by Rutherford backscattering. Electrochemical and surface characterization techniques, such as in-situ photoacoustic spectroscopy, are employed in this program. Current studies include (1) the use of a precision-made artificial crevice cell for the study and modeling of titanium crevice corrosion under well-defined and controlled conditions, (2) the use of in-situ photoacoustic spectroscopy and differential capacitance measurements for determining the nature (rutile, anatase, etc.) and thickness of passive oxide films formed on titanium, and (3) an evaluation of the specific role of oxidizing anions (such as ClO_3^- and ClO_4^-) in the electrochemical and corrosion behavior of titanium.

8.1 Crevice Corrosion of Titanium

(E. J. Kelly, H. R. Bronstein)

An artificial crevice cell has been employed to study and model crevice corrosion of titanium under well-defined conditions. As previously described, the cell consisted of an accurately machined and polished titanium rod ($r = 0.3$ cm) inserted into a precision-bored hole ($R > r$) in a Plexiglass block to form a single-ended annular crevice having a gap ($G = R - r$) less than 0.02 cm and constant to ± 0.001 cm.¹ The length of the crevice, from $x = 0$ at the innermost recess to $x = L$ at the mouth, was approximately 10.0 cm. A total of nine saturated-calomel reference electrode probes served to monitor the potential (E) of the titanium electrode at various positions within the crevice.

The potential dependence of the net anodic current density (i) corresponding to the corrosion of titanium in 1 N H_2SO_4 ($T=30^\circ C$) is shown in Fig. 8.1. In crevice corrosion experiments, the titanium is initially at open-circuit ($i=0$) and, consequently, exhibits the potential, E_{corr} , at all points within the crevice. Then, at time zero, the

Fig. 8.1. Steady-state anodic polarization curve for titanium in 0.5 M H_2SO_4 ($T=30^\circ C$).

potential of the titanium with respect to a reference electrode located at $x = L$ is set potentiostatically to a value positive to E_{corr} , generally to a value lying within the

passive-state potential region. This establishes a potential gradient and, in accordance with the polarization curve shown in Fig. 8.1, a variation of i within the crevice. A model for crevice corrosion which predicts the potential and current density (i) profiles within the crevice is based on Eqs. 1 and 2,

$$j = \sigma(dE/dx) \quad (1)$$

$$dj/dx = [2ri/(R^2-r^2)] \quad (2)$$

where j represents the current density within the electrolyte phase in the crevice, and σ is the specific conductivity of the electrolyte. Equation 1 is simply Ohm's law, and Eq. 2 is a consequence of the electroneutrality principle. By combining Eqs. 1 and 2, one obtains the operational equation,

$$d^2E/dx^2 = \lambda i \quad (3)$$

where $\lambda = [2r/\sigma(R^2-r^2)] = 1/\sigma G$. On principle, one need only substitute i as a function of E in order to solve Eq. 3. Unfortunately, the equation relating i and E over the entire potential region of interest is far too complex for direct application to the solution of Eq. 3. Consequently, a different approach to Eq. 3 has been adopted. The polarization curve ($i=f(E)$) shown in Fig. 8.1 is divided into N segments such that for each segment, i may be considered to be a linear function of E , i.e.,

$$i_n = A_n E + B_n \quad (E_n < E < E_{n+1}) \quad (4)$$

where A_n and B_n are constants, and $n=(1,2,\dots,N)$. The length of the crevice is divided into K segments, with the k th segment defined by $x_{k-1} < x < x_k (k=1,2,\dots,K)$ and $x_0 = 0$. If $E(x=0)$ resides in the potential region for which $n = \beta$, then for any value of k , $n = (\beta+k-1)$ and $E(x=x_k) = E_{\beta+k}$. When i from Eq. 4 is substituted into Eq. 3, the latter may be solved to give Eq. 5,

$$E = [E_{x=0} + (B_n/A_n)] \cosh \bar{x} \sqrt{\lambda A_n} - (B_n/A_n) + (1/\sqrt{\lambda A_n}) (dE/d\bar{x})_{\bar{x}=0} \sinh \bar{x} \sqrt{\lambda A_n} \quad (5)$$

where $\bar{x} = (x-x_{k-1})$. In using Eq. 5, the boundary condition, $j_{x=0} = 0$ when $k = 1$, requires that $(dE/dx)_{x=0} = 0$. For a specified value of $E_{x=0}$, application of Eq. 5 and its first derivative (dE/dx) over all values of k generates the potential profile within the crevice. The current density (i) profile may then be calculated by means of Eq. 4. In addition, it may be readily shown that the total current (I) emanating from the crevice, and monitored by the potentiostat, is given by Eq. 6,

$$I = 2\pi r \sigma G (dE/dx)_{x=L} \quad (6)$$

Typical results obtained for a 3-segment approximation of the polarization curve (see Fig. 8.1) are shown in Fig. 8.2. It is apparent from the figure that, for a specified length of crevice (for example, $x=L=10$ cm) and gap width, the measured values of I and $E_{x=L}$ uniquely determine the potential and current density profiles. In Fig. 8.3, results obtained for a 3-segment approximation of the polarization curve are compared with those obtained for a much more accurate 22-segment approximation, with $E_{x=0}$ being identical in both cases. Although experimentally measured potential profiles are in closer agreement with the 22-segment model, the 3-segment model is sufficiently accurate for practical purposes. This fact is important in ongoing research where extension of the crevice corrosion model to include the generation and mass transport of redox couples within the crevice has been accomplished for the relatively inaccurate 2-segment model, is feasible for a 3-segment model, and is entirely too cumbersome for a more highly segmented model.²

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Fig. 8.2. Potential (E) and corresponding interfacial current density (i) profiles within a titanium crevice in 0.5 M H₂SO₄ (T=30.0°C). 3-segment model with G = 0.0089 cm for curves (E, E'), and 0.0178 cm for all other curves. I = total current emanating from mouth of crevice 10.0 cm in length (x=0 at innermost recess of crevice).

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Fig. 8.3. Comparison of potential (E) and corresponding interfacial current density (i) profiles obtained for titanium in 0.5 M H₂SO₄ (T=30°C) using 3-segment (B, B') and 22-segment (A, A') models. G = 0.0089 cm.

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8.2 Reduction of Chlorate and Perchlorate Ions at an Active Titanium Electrode

(Gilbert M. Brown)

The polarization curve for titanium in 1.0 M HClO₄ is net cathodic in the potential region

-450 mV to -650 mV vs NaSCE, the potential region of the active-passive transition and $E_{\max}$ in 1.0 M H^+ containing an activating anion. As previously reported,¹ the observed current density is larger than that expected² for the hydrogen evolution reaction (HER) alone, extrapolated to the proton activity of these experiments. An experimental and theoretical analysis of the current density and product yields indicate that this enhanced cathodic current is due to the direct reduction of perchlorate ion at the titanium surface. The reduction of chlorate ion was also briefly studied.

Current density measurements and yields of chloride ion were determined in 1.0 M $HClO_4$ with a relatively large surface area titanium electrode as a function of potential. The difference between the observed current density and that calculated for the HER alone is given in Table 8.1, along with the chloride analyses. The observed current density was constant for the duration of the experiment, and the current density for perchlorate reduction can be determined from Coulomb's law. The current density can be accounted for by the $8e^-$ reduction of perchlorate to chloride (reaction (1)).

The reduction of perchlorate ion to chloride ion at a titanium electrode was reported by Romanushkina, et. al.³ in $HClO_4$ -HCl mixtures. These workers attributed the reaction to a Ti(III)-Ti(IV) catalyzed process given by Eqs. 2-4.

Reactions (2) and (4) are electrochemical processes and reaction (3) is the oxidation of Ti(III) to Ti(IV) by excess perchlorate. The rate expression for reaction (3) in 1.0 M $HClO_4$ is given by Eq. 5,

$$\begin{aligned} \frac{-d[Ti(III)]}{dt} &= 8 \frac{d[Cl^-]}{dt} \\ &= k_3[Ti(III)][ClO_4^-] \end{aligned} \quad (5)$$

The rate constants for reactions (2-4) are either known or an upper limit can be set from reported or measured values. An analysis of

Table 8.1. Current densities and yields of chloride ion in 1.0 M $HClO_4$ (30°C). Electrode area, $A = 12.73 \text{ cm}^2$; Solution volume, $V=100 \text{ ml}$.

E (mV vs NaSCE)	$[Cl^-]$ (mol/l)	t (sec)	i^a ($\mu\text{a}/\text{cm}^2$)	i_{calc}^b ($\mu\text{s}/\text{cm}^2$)
-625	1.27×10^{-3}	3.47×10^5	22	21
-600	1.61×10^{-3}	7.7×10^5	13	17
-525	$<10^{-4}$	8.53×10^5	—	4.5

^aDetermined from the coulometric relationship, $i=(nFV[Cl^-])/(At)$.

^bDifference between the observed current density and that measured for the HER in Ref. 2.

the data (under conditions of product generation in a relatively large volume of solution) should allow a distinction to be made between the catalyzed pathway and direct reduction at the electrode surface. Solution of the coupled differential Eqs. 6 and 7 gives the concentration of Ti(III) as a function of time (Eq. 8):

$$\frac{d[Ti(III)]}{dt} = (I_a/3FV) - k_{obs}[Ti(III)] + (k_4A/V)[Ti(IV)] \quad (6)$$

$$\frac{d[Ti(IV)]}{dt} = k_{obs}[Ti(III)] - (k_4A/V)[Ti(IV)] \quad (7)$$

where I_a is the anodic current for reaction (2), V is the solution volume, A is the electrode area, k_{obs} is the pseudo-first order rate constant for reaction (3), i.e., $k_{obs} = k_3[C10_4^-]$, and k_4 is the rate constant for the reaction of Ti(IV) at the electrode surface.

$$[Ti(III)] = (I_a/3FV) \left\{ \left[\frac{k_{obs}}{(k_{obs}+k_4A/V)^2} \right] \times \left[1 - \exp[-(k_{obs}+k_4A/V)t] \right] + \left[\frac{(k_4A/V)}{(k_{obs}+k_4A/V)} \right] \right\} \quad (8)$$

The time of observation for the experiments reported in Table 8.1 is relatively long, and the exponential term in Eq. 8 can be neglected. Integration of Eq. 9, with Ti(III) given by Eq. 8, gives the time dependence of the concentration of chloride ion (Eq. 10).

$$\frac{d[Cl^-]}{dt} = \frac{1}{8} k_{obs}[Ti(III)] \quad (9)$$

$$[Cl^-] = \frac{I_a k_{obs} t}{24FV} \left[\frac{k_{obs}}{(k_{obs}+k_4A/V)^2} + \frac{(k_4A/V)t}{2(k_{obs}+k_4A/V)} \right] \quad (10)$$

The current density for the anodic dissolution of Ti is less than 10^{-7} amp/cm² at -600 mV vs NaSCE. The rate constant for reduction of Ti(IV) to Ti(III) is dependent on the concentration of a complexing anion,⁴ but it should be $<10^{-4}$ cm/sec. The pseudo-first-order rate constant for the reaction of Ti(III) with perchlorate in 1.0 M HClO₄ is 3×10^{-4} sec⁻¹.⁵ Using the other parameters appropriate for the experiments in Table 8.1, the calculated concentration of chloride ion after 8×10^5 sec is $\sim 3 \times 10^{-5}$ M, a value far lower than the observed concentration. Thus chloride ion in solution is produced by the direct reduction of perchlorate rather than by a catalyzed path involving Ti solution species.

This reaction scheme requires that the stable intermediate product, C10₃⁻, also be reduced at the titanium electrode. Independent experiments suggest that the rate constants for C10₃⁻ reduction are far greater than the C10₄⁻ rate constants. The reactions are assumed to be first order, and the stoichiometries are given by Eq. 1 and Eq. 11.

The rate constants are summarized in Table 8.2. The current for reduction of C10₃⁻ is highly stirring dependent and only weakly dependent on potential. The dependence of the current on mass transport was probably not completely removed in these experiments. The stirring conditions of these experiments produce a diffusion layer thickness, δ , of 10^{-2} to 10^{-3} cm. The diffusion controlled rate constant is D/δ , 10^{-3} to 10^{-2} cm/sec. Thus the rate constants for C10₃⁻ reduction represent a lower limit.

Although perchloric acid is thermodynamically a powerful oxidizing agent, the direct reduction of perchlorate ions at an electrode surface is unusual. There are only a few examples, and most of these are poorly characterized. There are also few examples of the reduction of chlorate ion. There are reasonably well characterized examples of the metal ion catalyzed reduction of C10₄⁻ and C10₃⁻.

Table 8.2. Rate constants for the reaction of perchlorate and chlorate ions at titanium (30°C).

E (mV vs NaSCE)	k, cm/sec ^a		
	ClO ₄ ⁻ (1 M HClO ₄)	ClO ₃ ⁻ (1 M HClO ₄)	ClO ₃ ⁻ (1 M HCl)
-600	2.2 x 10 ⁻⁸	1.7 x 10 ⁻³	1.6 x 10 ⁻³
-550	7.2 x 10 ⁻⁹	1.2 x 10 ⁻³	1.1 x 10 ⁻³
-500	1.3 x 10 ⁻⁹	0.9 x 10 ⁻³	1.4 x 10 ⁻³

^aThe reactions are assumed to be first order in [ClO₄⁻] or [ClO₃⁻], I=nFAkC.

Taube⁵ has recently reviewed the evidence for reduction of ClO₄⁻ in solution. Perchlorate has no low lying unfilled electronic orbitals, and thus it cannot easily accommodate an additional electron to form the ClO₄²⁻ ion. Reduction necessarily occurs via transfer of an oxygen atom. The process in reactions (12) and (13) can be accommodated if some species is available to stabilize O²⁻.

Protons can stabilize O²⁻, and this accounts for the activity of concentrated solutions of HClO₄ as oxidizing agents.

Taube⁶ notes that metal ions are the only species known to reduce ClO₄⁻ at a reasonable rate at ambient temperatures. The most active ions are those forming "yl" ions such as V(IV). Thus the reduction of ClO₄⁻ by V(III) and Ti(III) are understandable if oxygen atom transfer occurs.

The reduction of ClO₄⁻ is a relatively facile process on an active titanium electrode, and this observation can be taken as evidence that

surface bound species are responsible for the catalysis. This catalysis is consistent with the kinetic model proposed by Kelly⁷ for the dissolution of titanium. The surface of Ti in the active and active-passive transition potential region is covered by a monolayer of Ti(II), Ti(III), and Ti(IV) species. At potentials cathodic to E_{max}, Ti(II) is the predominant species. The surface has an oxygen vacancy at least and the potential dependence of perchlorate reduction is consistent with a rate limiting one-electron transfer reaction. The reaction of perchlorate with the adsorbed Ti(II) species by oxygen atom transfer is indicated:

The same mechanistic arguments that have been made for ClO₄⁻ reduction apply to ClO₃⁻ reduction. For the one-electron pathway, ClO₂ is the indicated product, and it is a relatively stable species. This may account for the greatly enhanced reaction rate of ClO₃⁻ over ClO₄⁻.

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8.3 Monitoring of Passive Film Growth by Photoacoustic and Capacitance Measurements

(C. E. Vallet, Gilbert M. Brown, T. P. Jones¹)

Passive film growth at a titanium electrode in 1 N H₂SO₄ solution has been investigated by in-situ photoacoustic spectroscopy and by capacitance measurements. In the few photoacoustic studies coupled with electrochemical measurements which have been reported,²⁻⁶ the photoacoustic results have been used to characterize the film formed at the electrode surface. In addition to the determination of layer structure, we wanted to test the capability of the photoacoustic technique for providing an estimate of film thickness. It is well established⁷ that the film thickness is inversely proportional to the differential capacity for relatively thick films, and recent reports⁸ suggest the capacitance would also be useful for calibrating thinner films. It is of interest to extrapolate the results for films grown at more anodic potentials back to the active-passive transition potential region.

The photoacoustic spectrometer has been described previously.⁹ Large variations in the phase of the photoacoustic signal with wavelength had been observed,¹⁰ which could lead to a distortion of spectra. The data acquisition scheme was modified in order to

calculate the in-phase signal at any wavelength. The electrode was a disc of 1 cm diameter and of 0.025 mm thickness made of a 99.98% titanium foil (Alfa Products). Any oxide layer which may have been on the electrode was eliminated by maintaining the electrode at -0.800 V vs SCE for 1/4 hour. In a series of experiments, the potential was set increasingly positive and measurements were taken after a steady current was observed at the non-illuminated electrode. Figure 8.4 summarizes the photoacoustic results obtained at different electrode potentials on one electrode over a time period of 2-3 weeks. The spectra are all corrected for the source power

Fig. 8.4. In-situ photoacoustic spectra of titanium electrode in 1 N H₂SO₄ solution at various potentials. Spectra are in-phase photoacoustic signals and are corrected for the source power spectrum.

spectrum with a simultaneously recorded photoacoustic spectrum of carbon.¹¹ Exactly identical spectra are obtained over a period of time of several days for the electrode maintained at constant potential. This feature enabled us to combine two successive spectra, each obtained during a 1/2 hour scan, in order to generate the in-phase spectra. No variation in the photoacoustic signal with electrode potential is detectable at wavelengths above

400 nm. The spectra, at lower wavelengths, show a general increase in absorption as the potential is made more positive. The change in absorption starting around 400 nm, is attributable to the optical absorption of the developing oxide layer at the electrode surface. The increase in absorption with more positive potentials reflects the growth of increasingly thick layers. Figure 8.5 shows a typical difference spectrum between the spectra for the electrode at 1 V vs SCE and the electrode maintained cathodic at -0.800 V vs SCE. The position of the absorption band-edge in the passive layer spectrum is compared with photoacoustic spectra obtained with TiO_2 anatase powder (Pfalz & Bauer) and TiO_2 rutile powder (Aldrich) placed on a titanium disc similar to that used as electrode. The band-edge positions of the powdered samples agree with those reported in the literature,¹² 390 nm for rutile and 350 nm for anatase. The absorption band-edge of the passive layer is not as sharp as in the powder spectra; however, its position at about 330–340 nm indicates the possibility of a mixture of oxides with anatase as the predominant constituent. The positions of the absorp-

tion band-edges will be reexamined with a series of measurements at open circuit and compared with substoichiometric oxide (Ti_2O_3) powder spectra. The absorption band height may be correlated qualitatively with the passive layer thickness. A likely significant difference appears between the spectra recorded at a cathodic potential (-0.800 V vs SCE) where the oxide layer is reduced and at an "active" electrode (-0.530 V vs SCE) which denotes the presence of a thin oxide layer at the latter potential. With the assumptions of a film of 15 Å at 0.5 V vs SCE and a linear dependence of absorption with thickness, the layer at the active electrode would have a thickness on the order of a few Angstroms. No significant growth of the layer is apparent in the "active-passive" region, i.e., up to 0 V vs SCE potential. Large increases in absorption occur in the passive region. It should be noted in Fig. 8.4 that the photoacoustic spectra obtained at .5 V vs SCE and at 1 V vs SCE are almost identical. This anomaly is explained by the large increase in photocurrent observed between these potentials.¹³ Therefore, the two photoacoustic spectra cannot be readily compared in terms of layer thickness because the absorbed light energy to heat conversion is different for the two sets of data.¹⁴

The capacitance of the electrode was measured by the potentiostatic step method. The potential of the electrode was maintained at E_{max} until a steady-state current was obtained, and then at -0.3 V vs SCE until near steady-state behavior was observed ($i = 1 \mu\text{A}/\text{cm}^2$). The electrode potential was then changed to a positive value to initiate film growth. The film growth was monitored by periodic capacitance measurements. The total charge passed during film growth was measured by integrating the current. In general, about four hours were required for the capacitance to reach a constant value after setting the potential to a positive value. It was assumed that no significant change in film thickness occurred after this time. The estimate of film

Fig. 8.5. Comparison of absorption band-edge positions in photoacoustic spectra of powdered anatase and rutile TiO_2 with in-situ spectrum of passive layer grown at 1.0 V vs SCE.

thickness by the amount of charge passed and the assumption of 100% current efficiency for formation of a TiO_2 layer gave values which are clearly unrealistic. The formation of relatively thick films on titanium in the 10 to 100 V range, under high field conditions, has been studied, and an anodizing ratio or forming voltage relationship of 25Å/V has been experimentally established.⁷ The parallel plate capacitor model has been successful in correlating the capacitance with film thickness. Laser, et.al.⁸ applied this method to film growth on titanium in the potential range of interest in these experiments. The capacitance was correlated with a film thickness measured by ellipsometry. In our work, the capacitance values measured at +0.5 V, +1.0 V, and +1.5 V are 22 $\mu\text{F}/\text{cm}^2$, 17 $\mu\text{F}/\text{cm}^2$, and 12 $\mu\text{F}/\text{cm}^2$, respectively. Using the plot of Laser, et.al. as a calibration plot leads to values of film thickness of 17Å, 22Å, and 33Å at +0.5 V, +1.0 V, and 1.5 V, respectively. The film thickness can also be estimated by treating the film as a semiconductor with a space charge depletion layer under anodic bias. The thickness of the depletion layer will be equated to the TiO_2 film thickness. Films were grown at +1.0 V, and +1.5 V vs SCE on titanium electrodes for one day. The capacitance was rapidly measured at ± 0.5 V from the forming voltage, and these capacitance/potential data were fitted to the Mott-Schottky equation.¹⁵ The slope of the Mott-Schottky ($1/C^2$ vs E) plot was used to estimate the density of donor states, N_d , which in turn allowed the thickness of the depletion layer, L, to be estimated at the potential of interest. For analysis of these films grown on titanium, a value of 60 was chosen for the dielectric constant of TiO_2 .¹⁶ The calculated values of N_d and L are $1 \times 10^{21} \text{ cm}^{-3}$ and 26Å for the film grown at +1.0 V vs SCE. The values for the film grown at +1.5 V are $7 \times 10^{20} \text{ cm}^{-3}$ and 37Å for N_d and L, respectively. The relatively high density of carriers suggests that the film contains an appreciable amount of Ti(III) or that conversion to TiO_2

from a substoichiometric oxide has not been complete. If the thickness of the depletion layer can be equated to the film thickness, then this result is in remarkably good agreement with the estimate of film thickness by the parallel plate capacitor model or by extrapolation from high voltage anodizing ratios. This good agreement is most likely fortuitous; nonetheless, the film thickness at these potentials is probably within a factor of two of these estimates.

A comparison of literature data and the capacitance measurements in this work suggests the film thickness on a titanium electrode at +0.5 V vs SCE in 1 M H_2SO_4 is within a factor of two of 15Å. The photoacoustic data indicate the formation of an anatase TiO_2 layer and suggest the presence of a layer of few Angstroms in the active-passive transition potential region. These results are consistent with the kinetic model of Kelly¹⁷ which suggests the surface of titanium in this region is covered by a monolayer of low valent species. The correlation of film thickness with photoacoustic signal could not be extended to film growth at higher potentials because a significant fraction of the absorbed light was converted to photocurrent. Measurements made at an electrode maintained more negative than the flat band potential should allow the photoacoustic estimate of thickness of such semiconducting film.

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8.4 Photocurrent Induced by Photoacoustic Measurements in Semi-Conducting TiO_2 Layers

(C. E. Vallet, Gilbert M. Brown, T. P. Jones¹)

Characterization and estimation of the thickness of anodic films grown on titanium, at low overvoltage, is a difficult task. The simultaneous use of different techniques may provide an answer since each individual method needs the knowledge of properties which may be derived by another method. The oxide films anodically grown at a titanium electrode are

photosensitive.²⁻⁴ Figure 8.6 shows the photocurrent produced by the illumination of the electrode, maintained at various potentials, during photoacoustic experiments (dashed curve). The solid lines refer to photocurrents corrected for the light intensity and are related to the photocurrent energy conversion efficiency. No photocurrent is detected at potentials negative or equal to 0 V/SCE. At a potential of +0.5 V/SCE there is a smooth increase of the photocurrent with increasing photon energy; however, at more positive potentials, i.e., 2 V/SCE, a small decrease at wavelengths shorter than 300 nm appears.

ORNL-DWG. 85-7612

Fig. 8.6. Photocurrent induced by in-situ photoacoustic measurements at a titanium electrode in 1 N H_2SO_4 at different potentials. ---- measured; — corrected for light intensity.

Since photoacoustic signals are generated by the energy absorbed by the sample and converted into heat, photocurrent and photoacoustic spectra should be related in terms of the photocurrent energy-conversion efficiency.⁵ Figure 8.7 shows experimental photoacoustic spectra on a titanium electrode (polarized at +3.0 V/SCE) recorded at open circuit and with photocurrent flow (closed). As expected, differences in the two spectra

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Fig. 8.7. Photoacoustic spectra and photocurrent at a titanium electrode in 1 N H₂SO₄ at +3.0 V/SCE: — spectra recorded on open circuit and with current flow; ---- photocurrent.

clearly appear at short wavelengths when the photocurrent (dotted curve) increases sharply. With the assumptions that no luminescence and no photoreaction take place, the photocurrent energy-conversion efficiency, ϕ , can be derived directly from the photoacoustic signals on open circuit, $PAS_{(oc)}$, and on closed circuit, PAS by:⁵

$$\phi = [PAS_{(oc)} - PAS] / PAS_{(oc)} \quad (1)$$

Figure 8.8 compares the photocurrent energy-conversion efficiency obtained by applying Eq. 1 to the data of Fig. 8.7 with the recorded photocurrent (dotted curve) and the photocurrent corrected for the light power spectrum. The corrected photocurrent and ϕ agree for the onset of photocurrent around 380 nm, but discrepancies appear at shorter wavelengths. Artifacts seem to be introduced in the calculation of the corrected photocurrent when a large photocurrent is combined with a small light power. ϕ is calculated from a ratio of quantities obtained with similar accuracy and, therefore, is more reliable. Determination of ϕ by photoacoustic spectrometry at different electrode potentials,

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Fig. 8.8. Comparison of the photocurrent energy conversion, ϕ , with the recorded photocurrent (dotted curve) and the photocurrent corrected for the light power spectrum (solid curve).

together with the photoacoustic determination of optical absorption of the passive layers, should lead to a better understanding of the growth law of these very thin semiconducting oxide layers and to an estimate of their thickness.

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8.5 Effect of Forced Convection on Titanium Corrosion in Acidic Perchlorate Solution (F. A. Posey, Gilbert M. Brown)

Studies on the kinetics of titanium corrosion in acidic sulfate and chloride solutions¹

have demonstrated no effect of motion of the electrolyte relative to the electrode surface on the rates of the anodic (titanium dissolution) or cathodic (hydrogen evolution) partial processes. However, in a recent study on the kinetics of titanium corrosion in acidic perchlorate solutions, we have observed a significant stirring effect that cannot be accounted for by the presence of electroactive impurities. The stirring effect is unusual in that it essentially disappears at sufficiently high stirring rates. The initial results suggested that either the apparent rate of the anodic process increases to a limit with increasing stirring rate or the rate of a cathodic process becomes vanishingly small at high stirring rates. We have carried out some systematic studies on this phenomenon using a rotating disk electrode assembly with which convective diffusion processes may be studied precisely since the Navier-Stokes equations have been solved exactly for this system.² Some results of these studies and a plausible explanation of the observations are discussed below.

A related phenomenon was reported by Romanushkina, Mamylikhina, and Maer,³ who found that the rate of passivation of titanium in $\text{HClO}_4\text{-HCl}$ mixtures decreases as the stirring rate of the solution increases. In this case, passivation of titanium occurs because Ti(IV) ions are formed in the solution due to oxidation of Ti(III) ions (the product of the anodic dissolution reaction of active titanium) by ClO_4^- ions. Eventually enough Ti(IV) ions accumulate in the solution to cause passivation.¹ These authors proposed that, accompanying the passivation phenomenon due to accumulation of Ti(IV) ions, there is a stirring-dependent autocatalytic ECE (electrochemical-chemical-electrochemical sequential reaction steps) process that occurs in the vicinity of the electrode surface. Thus Ti(III) ions produced by the corrosion reaction (electrochemical process) react in the solution phase with ClO_4^- to produce Ti(IV) (chemical process), which is subsequently reduced back

to Ti(III) at the electrode surface (electrochemical process); this cycle repeats itself as influenced by convective diffusion of the soluble species, Ti(III) and Ti(IV) . It was thought that stirring influences the rate of accumulation of Ti(IV) ions near the electrode surface and thus the rate of passivation of titanium. We explored the possibility that this autocatalytic ECE reaction could explain our data on the stirring dependence of the partial processes for titanium corrosion in acidic perchlorate media. An analytical solution to the equations of convective diffusion was derived for this autocatalytic ECE reaction for the case of the rotating disk electrode geometry.⁴ However, the predictions of this theory did not agree with our experimental measurements, and an alternative explanation was sought.

Strong evidence has been presented by Kelly¹ that the surface of titanium in the active state in acidic solutions is populated by aquo, hydroxy, and/or oxy species of Ti(II) and Ti(III) , the kinetics of interconversion redox processes being responsible for the observed maximum in the anodic polarization curve and its dependence upon system variables (pH, etc.). In addition, in a recent review by Taube⁵ on the mechanism of reduction of the perchlorate ion, it was concluded that in all of the cases in which reduction of ClO_4^- by metal ions takes place at room temperature at a reasonable rate, the reduction mechanism proceeds with oxygen atom transfer, and the formation of an "yl" product with the oxidized form of the reducing agent is possible. Whether the reduction is by a $1e^-$ or $2e^-$ change, an important requirement seems to be that the oxidized metal product makes a strong bond to the oxide being released. It is known that unusually strong metal to oxygen bonds are formed in the "yl" ions (titanyl, etc.). On this basis, the observation that actively-corroding titanium is one of the few metals on which reduction of perchlorate proceeds at a measurable rate under ambient conditions becomes understandable; the presence of oxidi-

zable titanium surface intermediates provides a suitable mechanism for ClO_4^- reduction.

The following reaction sequence, based upon these mechanistic considerations, can account for our experimental observations on the stirring dependence of the partial processes for titanium corrosion in acidic perchlorate solution. We may assume that adsorption of perchlorate ions onto the surface of titanium in the active state is a fast process expressed by Eq. 1; here and elsewhere subscript

s denotes a species in the solution phase and subscript a denotes an adsorbed (or chemisorbed) species. The next step in the reaction sequence is reduction of $(\text{ClO}_4)_a$:

In Eq. 2 either a $1e^-$ or $2e^-$ change could take place ($n = 1$ or 2); the identity of the soluble intermediate (ClO_3 or ClO_3^-) has not yet been established (but could be determined in principle using, for example, a rotating ring-disk electrode assembly). Eq. 2 emphasizes the oxygen atom (oxide) transfer in the reduction of ClO_4^- ; alternatively, the reaction may be expressed as:

It should also be noted that, for a $1e^-$ change, the reduction reaction could be expressed by a sequence of steps like the following:

In this sequence the surface intermediate Ti(II) is oxidized to Ti(III) by ClO_4^- and subsequent reduction back to Ti(II) consumes electrons from the external measurement or control circuit. Obviously the sum of Eqs. 2b and 2c is equivalent to Eq. 2a. The next step in the reaction sequence is further reduction of the soluble product of Eqs. 2 or 2a at the electrode surface:

The effect of forced convection on the kinetics of the preceding reaction sequence may be quantified by solution of the equation of convective diffusion for the soluble species $\text{ClO}_3^{(n-1)-}$ for a rotating disk electrode geometry. With use of an expression for the normal component of the fluid velocity near a rotating disk⁶ and with the concentration of $\text{ClO}_3^{(n-1)-}$ in the solution phase denoted by $C(x)$, where x (cm) is distance normal to the electrode surface, the convective diffusion process is described in the steady state by:

$$D \frac{d^2 C(x)}{dx^2} + \frac{0.51}{D} (\omega^3/\nu)^{1/2} x^2 \frac{dC(x)}{dx} = 0 \quad (4)$$

In Eq. 4 ω is rotation rate (radian/s), ν is kinematic viscosity (cm^2/s), and D is the diffusivity (cm^2/s). One boundary condition is given by the net flux of $C(x)$ at $x = 0$,

$$D \left. \frac{dC(x)}{dx} \right|_{x=0} = -k_2 \theta + k_3 C(0), \quad (5)$$

where k_2 (s^{-1}) and k_3 (cm/s) are (potential-dependent) specific rate constants of Eqs. 2 and 3, respectively, and θ is the surface concentration (moles/ cm^2) of $(\text{ClO}_4)_a$. The other boundary condition is simply:

$$\lim_{x \rightarrow \infty} C(x) = 0 \quad (6)$$

Solution of Eq. 4 with the conditions of Eqs. 5 and 6 leads to Eq. 7 for the distribu-

tion of $\text{ClO}_3^{(n-1)-}$ in the electrolyte phase.
In Eq. 7

$$C(x) = (k_2\theta/k_3)$$

$$= \frac{[1 - \gamma(1/3, 0.17\omega^{3/2}k_3^3/Dv^{1/2})/\Gamma(1/3)]}{[1 + 0.62D^{2/3}\omega^{1/2}/k_3v^{1/6}]} \quad (7)$$

$\Gamma(1/3)$ is a gamma function and $\gamma(1/3, z)$ is an incomplete gamma function.⁷ In our experiments we measure the net current, $I(\omega)$ (A), as a function of rotation rate (ω) at constant electrode potential, so that the observed current may be expressed by:

$$I(\omega) = \Sigma(I_a - I_c) - FAK_3C(0), \quad (8)$$

where F is Faraday's constant ($C/2q$.) and A is the electrode area (cm^2). In Eq. 8 the expression $\Sigma(I_a - I_c)$ denotes the sum of the currents of anodic and cathodic partial processes that are independent of stirring rate. Insertion of $C(0)$ from Eq. 7 into Eq. 8 and some arithmetic lead to Eq. 9 for the

$$I(\omega) = I(0) + \frac{FAk_2\theta(0.62D^{2/3}/k_3v^{1/6})\omega^{1/2}}{[1 + (0.62D^{2/3}/k_3v^{1/6})\omega^{1/2}]} \quad (9)$$

observed current as a function of rotation rate. The form of Eq. 9 suggests that it should be possible to estimate $I(0)$ from a plot of $I(\omega)$ vs $\omega^{1/2}$ at low rotation rates. Then it follows that a suitable plotting function may be obtained by rearrangement and inversion of Eq. 9 to give:

$$\frac{1}{I(\omega) - I(0)} = \frac{1}{FAk_2\theta} + \frac{k_3v^{1/6}}{0.62FAk_2\theta D^{2/3}} \cdot \frac{1}{\omega^{1/2}} \quad (10)$$

Consequently both $k_2\theta$ and k_3 may be estimated from the slope and intercept of a plot of $1/[I(\omega) - I(0)]$ vs $\omega^{-1/2}$ with a knowledge of A , D , and v . It should be noted that expressions

of similar form to Eqs. 9 and 10 may be obtained also if the adsorption step in the proposed reaction sequence (cf. Eq. 1) is absent.

A typical plot of net current as a function of $\omega^{1/2}$ is shown in Fig. 8.9. The solid line was calculated from a linear regression fit of the same data plotted according to Eq. 10 and shown in Fig. 8.10. The good fit of the theory to experimental measurements supports the conclusion that the stirring dependence of the partial processes on actively-corroding titanium in acidic perchlorate solution arises because of convective diffusion and reaction of a soluble reduction product of ClO_4^- . We expect in future work to investigate the dependence of the individual rate constants of the reduction sequence, as determined by the preceding technique, on system variables.

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Fig. 8.9. Effect of rotation rate on net current at a titanium rotating disk electrode at constant electrode potential in acidic perchlorate solution. $[\text{HClO}_4] = 1 \text{ M}$, A (electrode area) = 0.24 cm^2 , E (electrode potential) = -0.55 V vs SCE , $T = 30^\circ\text{C}$.

Fig. 8.10. Plot of data shown in Fig. 8.9 according to Eq. 10. Solid line: linear regression fit.

9. CATALYSIS

Substantial advances have been made in defining the role that single electron transfer reactions play in the chemistry of molten salt hydrocracking catalysts. Studies of the catalytic reactions of 1,2-diarylethanes in SbCl_3 -rich melts provided a basis for discriminating between the redox and Lewis acid functionalities of these catalysts. The oxidation of phenothiazine (PTZ) and phenoxazine (POZ) in SbCl_3 -rich melts yielded stable radical cations, $\text{PTZ}^{+\bullet}$ and $\text{POZ}^{+\bullet}$ that could be oxidized to give unusually stable dications, PTZ^{2+} and POZ^{2+} . When oxidation to form radical cations was carried out homogeneously with added oxidants, the oxidation rates were very sensitive to changes in melt acidity because of the effect that this parameter has on the complexation of the neutral heteroaromatics. When the solvent acted as the homogeneous oxidizing agent, there was an additional complication due to the slow reduction kinetics of Sb(III) . Among the oxidants and reductants used in these investigations were the complex ions $\text{M}(\text{bpy})_3^{v+}$ ($\text{M} = \text{Ru}, \text{Fe}, \text{Os}$; $v = 2, 3$; $\text{bpy} = 2,2'$ -bipyridine) whose stabilities and redox characteristics in SbCl_3 -rich melts were investigated. Melt acidity was also found to have a pronounced effect on the reactions of anthracene radical cations. A small change in melt composition was sufficient to shift the reaction pathway from aryl-aryl coupling to chlorination. Some of these reactions were among the most selective oxidative chlorinations ever reported. The reactions of phenyl-substituted anthracene radical cations, which could be followed in some detail, were quite complicated. Research on the molten Lewis acids Ga_2Cl_6 and Ga_2Br_6 showed these materials to be hydrogen transfer catalysts and oxidizing agents with respect to polycyclic arenes. The reduced species in these oxidation reactions is Ga^+ .

Studies of catalytic properties of solid surfaces are described in Section 9.2. This effort involves the development of low-energy ion scattering to probe surface structure and bonding geometry, and the application of various electron spectroscopies to study metal sulfide surfaces. Using ion scattering, the adsorption of S_2 on Mo(001) and the surface topography of amorphous metal surfaces have been examined. The appropriate potentials which describe the ion-solid interaction were also measured. Design work and initial construction have continued on a UHV/reactor system which will couple a high pressure reaction cell to a UHV surface analysis chamber. The system will be used to correlate reactivity and surface properties of metal sulfides.

9.1 Reactions and Catalysis in Molten Salts

9.1.1 Discrimination of Redox and Lewis Acid Catalysis in the Chemistry of

1,2-Diarylethanes in SbCl_3 -Rich Melts

(A. C. Buchanan, III, D. M. Chapman,¹
G. P. Smith)

In a previous report,² we presented preliminary data on the chemistry of a series of 1,2-diarylethanes, $\text{ArCH}_2\text{CH}_2\text{Ar}$ [$\text{Ar} =$ phenyl (DPE), 1-naphthyl (DNE), and 9-anthryl (DAE)] in SbCl_3 -rich melts. This investigation has now been completed, and it demonstrates that the product selectivity for the reaction of these substrates in the molten salt is remarkably dependent on the nature of the aryl group. These results are interpreted in terms of a change in mechanism from Lewis

acid catalysis to redox catalysis by the melt as the aryl group becomes more oxidizable.

DPE is not oxidizable to a radical cation by Sb^{3+} in the melt, and the transalkylation reaction observed is a consequence of Lewis acid catalysis by the melt.³

The selective cleavage of the benzylic (sp^2-sp^3) carbon-carbon bond is a result of the ability of the complexed Lewis acid species in the melt, $SbCl_2^+ \cdot nSbCl_3$, to generate benzylic carbenium ions, probably by hydride abstraction.

Recent experiments lend further support to our earlier results that the transalkylation reaction in the melt is indeed Lewis acid catalyzed and not the result of catalysis by adventitious protons. This is illustrated by the observation that the addition of 0.25 mol % HCl to the $SbCl_3$ melt has only a modest effect on increasing the transalkylation rate (factor of 2-3) at 130°C, while the addition of 1 mol % $AlCl_3$ to the melt (which substantially increases the concentration of $SbCl_2^+ \cdot nSbCl_3$) has a dramatic effect on increasing the reaction rate ($>10^3$).

DAE is much more reactive than DPE, and a quite different reaction is observed for DAE in $SbCl_3$ -rich melts.

The remarkably different product selectivity is attributed to a change in reaction mechanism in which the DAE radical cation,

$C_{14}H_9CH_2CH_2C_{14}H_9^{+\bullet}$, produced by oxidation by Sb^{3+} in the melt is now the key reactive intermediate. This radical cation reacts primarily by a cyclization-hydrogen transfer path to produce the unusual spiro isomer (1) of DAE (yield maximized in the basic $SbCl_3$ -KCl melt), or it reacts by cleavage at the ethylenic sp^3-sp^3

carbon-carbon bond which ultimately produces 9-methylantracene (MA). No intermolecular coupling of this radical cation to produce Scholl condensation products is observed, which is in contrast to the chemistry observed previously for anthracene and other easily oxidized arenes in $SbCl_3$ -rich melts.⁴ The relative rates for the two reaction paths for $DAE^{+\bullet}$ are quite sensitive to reaction temperature with C-C bond cleavage becoming more competitive with intramolecular aryl-aryl coupling at higher temperatures (e.g. the weight ratio of 1: MA is ~10 at 80°C and ~2 at 150°C).

The very high reactivity observed for the DAE radical cation has been confirmed by ESR and cyclic voltammetry (CV) investigations. Even at low concentrations (<1 mM) no steady state concentration of $DAE^{+\bullet}$ in the melts can be observed by ESR, unlike other arenes of similar oxidizability.⁵ Furthermore, CV studies of DAE in a basic $SbCl_3$ - $AlCl_3$ -BPCl (60:19:21 mol %; BP = N-1-butylpyridinium) melt show that the oxidation process is highly irreversible even at 25°C. This behavior is in contrast to the reversible electrochemical oxidation obtained for the related 9,10-dimethylantracene in the same melt.⁶

Preliminary results showed DNE to be intermediate in reactivity between DPE and DAE. We have now found that DNE reacts under the influence of combined Lewis acid and redox catalysis in $SbCl_3$ -rich melts to generate a complex product mixture. Initially the Lewis acid function of the melt induces isomerization of DNE, which is accompanied by some transalkylation as evidenced by the formation of

some naphthalene. As expected the rate of the isomerization process can be substantially increased by enhancing the Lewis acidity of the melt through the addition of small amounts (1-10 mol %) of AlCl_3 .

At longer reaction times the mixture of dinaphthylethane isomers react via redox initiated chemistry in the melt to produce a variety of dibenzophenanthrene and hydrogenated dibenzophenanthrene isomers. Sequences for the formation of two of the major products, picene (2) and benzo[b]chrysene (3), by the intramolecular aryl-aryl coupling path are shown below.

This type of reaction path for the radical cations of the DNE isomers has also been observed for methoxy-substituted 1,2-diphenylethane radical cations produced electrochemically in acetonitrile, which forms substituted dihydrophenanthrenes and then the corresponding phenanthrenes.⁷

Unlike the $\text{DAE}^{+\bullet}$ chemistry in SbCl_3 melts, $\text{DNE}^{+\bullet}$ exhibits no cleavage of the ethylenic C-C bond (to produce methylnaphthalene). $\text{DNE}^{+\bullet}$ is expected to have a larger bond dissociation energy for the central C-C bond than $\text{DAE}^{+\bullet}$ because of the lower resonance stabilization energy for the reactive intermediates produced.⁸ This apparently makes the C-C bond cleavage path for $\text{DNE}^{+\bullet}$ in SbCl_3 at 130°C very unfavorable in competition with intramolecular aryl-aryl coupling.

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9.1.2 Magnetic Resonance Spectra of the Radical Cations and Dications of Phenoxazine and Phenothiazine in SbCl_3 -Rich Melts

(D. M. Chapman,¹ A. C. Buchanan, III, G. P. Smith)

The compounds 10H-phenothiazine (PTZ) and 10H-phenoxazine (POZ) are currently being used as model compounds in a study of the chemistry of nitrogen and sulfur containing heteroaromatics in SbCl_3 -rich molten salt hydrocracking catalysts (see Section 9.1.4). The first part of this study was a characterization of these compounds and their oxidation products in melts.² The present section describes the most recent phase of this characterization, namely, ESR studies which provided unambiguous identifications of the radical cations, $\text{PTZ}^{+\bullet}$ and $\text{POZ}^{+\bullet}$, and demonstrated that they are complexed to solvent via their sulfur and oxygen atoms, respectively; and ^1H -NMR studies which demonstrated that the stable products of one-electron oxidation of the radical cations are the dications, PTZ^{2+} and POZ^{2+} , with their

1. Department of Chemistry, University of Tennessee, Knoxville.
2. A. C. Buchanan, III, D. M. Chapman, and G. P. Smith, *Chem. Div. Annu. Prog. Rep.* Jan. 31, 1984, ORNL-6037, p. 141.
3. Selective transalkylation reactions for other α,ω -diphenylalkanes in SbCl_3 -rich

nitrogenic hydrogens intact. (In most media these hydrogens are quickly lost as protons unless strong protic acids are present.)

The ESR spectra of the radical cations were measured in $\text{SbCl}_3\text{-AlCl}_3\text{-BPCl}$ (60-22-18 mol %) at 20-150°C and in neat molten SbCl_3 at 90-150°C. Examples are shown in Figs. 9.1 and 9.2. The hyperfine splittings in these spectra are much better resolved than those previously published for these ions, and analysis of these spectra indicated that in SbCl_3 -rich melts chalcogen atoms of the radical cations are complexed to Sb(III) from the solvent.

Fig. 9.3 shows the $^1\text{H-NMR}$ spectra of $\sim 0.1 \text{ M}$ solutions of POZ^{2+} and PTZ^{2+} in $\text{SbCl}_3\text{-10 mol \% AlCl}_3$ at 80°C. For PTZ^{2+} two major peaks were observed in the aromatic region (9.02 and 9.23 ppm, 8 protons) and a broad singlet appeared at 15.04 ppm (1 proton). For POZ^{2+} a broad singlet occurred at 9.08 ppm (8 protons) and a very broad resonance at 14.3 ppm was observed. On the basis of the integrals the low-field resonances were assigned to H_{10} , and the reso-

ORNL-DWG 83-18172R

Fig. 9.2. ESR spectrum of PTZ^{+} in SbCl_3 at 130°C. (a) Mod. amp., 8 mG; field, 3249.0 G; freq., 9.102 GHz; scan rate, ca. 1 G min⁻¹. (b) Improved S/N; mod. amp., 125 mG.

ORNL-DWG 83-18171R

Fig. 9.1. ESR spectrum of POZ^{+} in SbCl_3 at 130°C. (a) Mod. amp., 8 mG; field, 3249.0 G; freq., 9.102 GHz; scan rate, ca. 1 G min⁻¹. (b) Improved S/N; mod. amp., 125 mG.

ORNL-DWG 84-14055

Fig. 9.3. $^1\text{H-NMR}$ spectra of (a) PTZ^{2+} and (b) POZ^{2+} in $\text{SbCl}_3\text{-10 mol \% AlCl}_3$ at 80°C.

nances in the 9.00-9.30 region were assigned to the aryl protons. The weighted chemical shifts, δ_{av} , were 9.7 and 9.8 ppm for POZ^{2+} and PTZ^{2+} , respectively. For neutral POZ and PTZ in acetone- d_6 , $\delta_{av} = 6.7$ and 6.9 ppm, respectively. Thus, the charge-induced shifts of the resonances, i.e., $[\delta_{av}(\text{dication}) - \delta_{av}(\text{neutral})] \times 9(\text{protons})/2(\text{electrons})$, were 13.5 and 13.0 ppm per electron for POZ^{2+} and PTZ^{2+} , respectively. These charge-induced shifts are at the upper end of the range for such shifts in arene dications.

1. Department of Chemistry, University of Tennessee, Knoxville.
2. D. M. Chapman, A. C. Buchanan, III, G. P. Smith, and G. Mamantov, *Chem. Div. Annu. Prog. Rep.* Jan. 31, 1984, ORNL-6037, p. 136.

9.1.3 Characterization of Tris(2,2'-bipyridine)

Complexes of Fe, Ru and Os in the II and III Oxidation States in $SbCl_3$ -Rich Melts

(D. M. Chapman,¹ A. C. Buchanan, III, G. P. Smith, G. Mamantov¹)

As an aid to mechanistic studies of redox chemistry in molten salt catalysts, we required oxidizing and reducing agents that are stable in $SbCl_3$ -rich melts, that have distinctive visible absorption spectra and that provide reversible couples over a range of potentials within the electrochemical windows of the melts. The $M(\text{bpy})_3^{v+}$ ($M = \text{Ru, Fe, Os}$; $\text{bpy} = 2,2'$ -bipyridine; $v = 2,3$) complex ions proved to fill this need in the case of $SbCl_3$ - $AlCl_3$ - $BPCl$ ($BPCl = N$ -(1-butyl)pyridinium chloride) mixtures with compositions ranging from 60-19-21 mol % (basic) to 60-22-18 mol % (acidic). Cyclic voltammetry (CV) and double potential step coulometry (DPSC) at glassy carbon electrodes established the reversibility of $M(\text{bpy})_3^{3+/2+}$ couples and yielded values for their formal potentials (E^0) relative to the sat. $SbCl_3$ electrode (Sb metal in $SbCl_3$ saturated with $BPCl$) at 26°C. These E^0 values are displayed in Fig. 9.4 together with the potentials of other relevant couples which we have reported

Fig. 9.4. Formal potentials of various couples in basic and acidic $SbCl_3$ - $BPCl_3$ melts.

previously.² The radii of these ions in both acidic and basic melts were estimated from electrochemically derived diffusion coefficients by means of the Einstein-Stokes relation and found equal to their crystallographic values. Optical absorption spectroscopy and spectro-electrochemistry confirmed the identities of the $M(\text{bpy})_3^{v+}$ complex ions in $SbCl_3$ - $AlCl_3$ - $BPCl$ media and showed that each is stable over extended periods of time.

The homogeneous redox reaction between $Fe(\text{bpy})_3^{2+}$ and $Ru(\text{bpy})_3^{3+}$ in an acidic melt was monitored using a special mixing cell and a rapid (ms) multichannel optical spectrometer developed previously on this program.³ The reaction proceeded as rapidly as the two solutions of the respective complexes could be mixed. The reaction between $Ru(\text{bpy})_3^{2+}$ and $Sb(V)$ in acidic melts was equally rapid.

1. University of Tennessee, Knoxville.
2. (a) D. M. Chapman, G. P. Smith, M. Sýrlie, C. Petrovic, and G. Mamantov, *Chem. Div.*

Annu. Prog. Rep. Jan. 31, 1984, ORNL-6037, p. 134. (b) D. M. Chapman, A. C. Buchanan, III, G. P. Smith, and G. Mamantov, Chem. Div. Annu. Prog. Rep. Jan. 31, 1984, ORNL-6037, p. 136.

3. (a) G. P. Smith, D. M. Chapman, and S. P. Zingg, Chem. Div. Annu. Prog. Rep. Jan. 31, 1984, ORNL-6037, p. 131.
 (b) S. P. Zingg and G. P. Smith, Chem. Div. Annu. Prog. Rep. Jan. 31, 1984, ORNL-6037, p. 137.

9.1.4 Homogeneous Oxidation of Phenothiazine and Phenoxazine in SbCl_3 -Rich Melts

(D. M. Chapman,¹ A. C. Buchanan, III, G. P. Smith, G. Mamantov¹)

One of the important characteristics of molten salt hydrocracking catalysts is an unusual effectiveness for heteroatom removal from feed stocks laden with organic nitrogen and sulfur. With this fact in mind we set out to examine the behavior of heteroaromatics in SbCl_3 -rich melts. Various considerations suggest that single electron transfer (SET) reactions, including oxidation by the melt, should play an important role in the chemistry of many heteroaromatics in these media. For an initial study of such SET processes we wished to avoid extraneous reactions, and in this respect phenothiazine (PTZ) and phenoxazine (POZ) proved to be excellent model compounds. In nonoxidizing melts the neutral compounds are stable and can be externally oxidized to form stable radical cations ($\text{PTZ}^{+\bullet}$ and $\text{POZ}^{+\bullet}$). In oxidizing melts the radical cations are stable and can be externally oxidized to form stable dications (PTZ^{2+} and POZ^{2+}). Furthermore, $\text{SbCl}_3\text{-AlCl}_3\text{-BPCl}$ (BPCl = N-[1-butyl]pyridinium chloride) mixtures with compositions close to that of the 60-20-20 mol % neutral melt have redox properties well-matched to those of PTZ and POZ in that mixtures slightly on the basic side (e.g., 60-19-21 mol %) are nonoxidizing while those slightly on the acid side (e.g., 60-21-19) are oxidizing. In addition, these mixtures are liquid at ambient temperatures and thus provide less thermal activation than the higher melting SbCl_3 -rich systems.

Homogeneous oxidations of PTZ and POZ were carried out at 25-27°C by rapidly mixing solutions of the neutral compounds in nonoxidizing 60-19-21 mol % melts with oxidizing melts. The latter consisted of solutions of Sb(V) or Os(bpy)_3^{3+} (bpy = 2,2'-bipyridine) in nonoxidizing 60-19-21 mol % melts, oxidizing 60-22-18 mol % melts, or solutions of Sb(V) or Ru(bpy)_3^{3+} in 60-22-18 mol % melts. (Note that Sb(V) and Ru(bpy)_3^{3+} are more strongly oxidizing than Sb(III) in 60-22-18 mol % melts.) The progress of the reactions was monitored with a rapid (ms) multichannel spectrometer. In general, the observed reaction times were either short (complete within the mixing time of ~10 s) or very much longer (10^3 to greater than 10^5 s).

The oxidations of PTZ and POZ by added oxidants in basic, nonoxidizing melts were fast. Those in acidic melts depended on the driving force (ΔE^0): With Sb(III) as the sole oxidant the rate was very slow, with Ru(bpy)_3^{3+} present they were moderately slow, while with Sb(V) present they were fast.

This large effect that a small change in the formal composition of the melt has on the rate of oxidation of PTZ and POZ is readily accounted for in terms of Lewis acid-base reactions. (In outlining this model various interactions of secondary importance have been omitted.) The amine- SbCl_3 reaction applied to PTZ and POZ, represented by PXZ, is given in Eq. 1 in two thermodynamically equivalent formulations. The solvent-derived ions are linked by the equilibrium given in Eq. 2, for which the ion-product constant is extremely small.

Thus, uncomplexed PXZ is favored over the complexed form in basic, 60-19-21 mol % melts because of the presence of $(\text{Cl} \cdot 2\text{SbCl}_3)^-$ and the virtual absence of $(\text{SbCl}_2 \cdot x\text{SbCl}_3)^+$ while the reverse relations hold in acidic melts. The

complex $(\text{PXZ} \cdot \text{SbCl}_2)^+$ has a N-Sb bond in which the bonding orbital is derived from the N lone pair orbital on uncomplexed PXZ. The latter is the highest occupied orbital on uncomplexed PXZ and, thus, is the orbital from which an electron is lost in the simple SET reaction given in Eq. 3. As a consequence, oxidation of

the complex by an external oxidant, such as $\text{Ru}(\text{bpy})_3^{3+}$, involves the very unfavorable dissociation process given in two thermodynamically equivalent formulations in Eq. 4.

Because the PXZ are much stronger bases than SbCl_3 , the equilibrium constant for Eq. 1a is large. If we assume that it is very large, then the concentration of uncomplexed PXZ in acidic melts is very small and the rate of Eq. 3 is slow for this reason. In basic melts the concentration of the uncomplexed forms is much greater and the oxidation rate is, accordingly, much faster.

The $(\text{PXZ} \cdot \text{SbCl}_2)^+$ complex is metastable and slowly decomposes via a redox reaction given in Eq. 5 where $[\text{Sb}]$

represents lower oxidation state species of Sb. (This, of course, is the process by which $\text{Sb}(\text{III})$ oxidizes PTZ and POZ in acidic melts.) We find that at least two factors are involved in the slow rate of Eq. 5. First, the initial step involves the heterolytic splitting of the N-Sb bond, an inner-sphere oxidation which, according to Marcus theory,² is inherently much slower than the outer-sphere oxidation that occurs in basic melts between uncomplexed PXZ and added oxidants.

We also found that the reduction of $\text{Sb}(\text{III})$ by $\text{Os}(\text{bpy})_3^{2+}$ in acidic melts is quite slow. In this reaction the oxidation of the Os complex is an outer-sphere process so that the slow kinetics is plausibly attributed to the reduction of $\text{Sb}(\text{III})$ to lower valent $[\text{Sb}]$ species. These $[\text{Sb}]$ species involve Sb-Sb bonds and the radical intermediates involved in their formation with $\text{Os}(\text{bpy})_3^{2+}$ as the reductant should be quite unstable. This reaction is most easily modeled in terms of the simplest form of $[\text{Sb}]$, namely, $\text{Cl}_2\text{Sb} \cdot \text{SbCl}_2$, and the result is displayed in Eqs. 6 and 7. The equilibrium in Eq. 6

is far to the left because of the instability of the radical intermediate so that Eq. 7 becomes a slow reaction. A similar set of reactions may be involved as the first steps in Eq. 5. Although the presence of N-Sb bonds offers alternatives not possible with the Os complex, these routes also involve unstable intermediates and should be slow for that reason. An example is given in Eq. 8.

1. Department of Chemistry, University of Tennessee, Knoxville.
2. L. Eberson, *Adv. Phys. Org. Chem.* **18**, 79 (1982).

9.1.5 Effect of Melt Composition on the Reactions of the Anthracene Radical Cation in SbCl_3 -Rich Media

(D. M. Chapman,¹ A. C. Buchanan, III, G. P. Smith, G. Mamantov¹)

This investigation was a first study of the ways in which the reactions of an arene radical cation in SbCl_3 -rich melts are coupled to the

acid/base properties of the medium. The results were noteworthy in two respects. First, the coupling proved to be very strong; small changes in melt composition around the neutral point completely altered the reaction pathway. Second, we observed, for the first time, reactions in which the solvent-derived base, $(\text{Cl} \cdot 2\text{SbCl}_3)^-$, took part. The radical cations used in this investigation were those of anthracene (AN), generated either by coulometric oxidation at a glassy carbon electrode or homogeneous oxidation with Sb(V) . In the melt mixtures used in this study, AN is relatively stable while AN^+ reacts very rapidly.

A series of experiments was carried out with liquid $\text{SbCl}_3\text{-AlCl}_3\text{-BPCl}$ [BP = $\text{N-(1-butyl)pyridinium chloride}$] mixtures at 25°C with formal compositions of 60-19-21 and 60-21-19 mol % of the respective components. These two compositions lie on either side of the neutral composition 60-20-20 mol % which, because of a chloride exchange reaction between AlCl_3 and BPCl , consists of an approximately 2 M solution of the electrolyte $\text{BP}(\text{AlCl}_4)$ plus very small amounts of the electrolytes formed from the auto-ionization of SbCl_3 , namely, $(\text{SbCl}_2 \cdot x\text{SbCl}_3)\text{AlCl}_4$ and $\text{BP}(\text{Cl} \cdot 2\text{SbCl}_3)$. In the 60-21-19 mol % mixture the concentration of $(\text{SbCl}_2 \cdot x\text{SbCl}_3)\text{AlCl}_4$ is about 0.2 M and that of $\text{BP}(\text{Cl} \cdot 2\text{SbCl}_3)$ is depressed to an exceedingly low value, while in the 60-19-21 mol % mixture the reverse holds.

The oxidation of AN either electrochemically or with SbCl_6^- in 60-19-21 mol % mixtures at temperatures of 25 and 100°C resulted in a very selective chlorination reaction to give exclusively 9-chloroanthracene (9-CA) until nearly all of the AN was consumed at which point 9,10-dichloroanthracene (9,10-DCA) became the product. The reaction stoichiometry for 9-CA formation is shown in Eq. 1.

No other chlorinated products and no condensed products were found. This degree of product

selectivity is quite unusual for the oxidative chlorination of polycyclic arenes.

By contrast the partial (50%) coulometric oxidation of AN in an acidic 60-21-19 mol % melt at 25°C resulted in an aryl-aryl coupling reaction with 2,9'-bianthracene as the principal condensed product. No chlorinated and only a trace of hydrogenated products were found. Aryl-aryl coupling is a common reaction for polycyclic arene radical cations in media of low nucleophilicity and in the present case the protons released by this coupling are presumed to have been accepted by unreacted anthracene to form stable 9H-anthracenium ions, a reaction we previously investigated.

The fact that chlorinated products are favored in a 60-19-21 mol % melt while coupling reactions are favored in a 60-21-19 mol % melt is consistent with the presence of the chloride donor ion $(\text{Cl} \cdot 2\text{SbCl}_3)^-$ in the former and the low nucleophilicity of the latter.

A mixture of SbCl_3 with 10 mol % BPCl ($\sim 1 \text{ M BP}(\text{Cl} \cdot 2\text{SbCl}_3)$) at 100°C was a more active chlorinating agent than the 60-19-21 mol % mixture at the same temperature as evidenced by higher yields of 9,10-DCA, probably as a result of the 5-fold greater $(\text{Cl} \cdot 2\text{SbCl}_3)^-$ concentration. On the other hand, a $\text{SbCl}_3\text{-10 mol \% KCl}$ mixture at 80° was less selective for chlorination and yielded aryl-aryl coupling products in addition to 9-CA and small amounts of chlorinated bianthracenes. In this melt the electrolyte, $\text{K}(\text{Cl} \cdot 2\text{SbCl}_3)$, exists largely as ion pairs and this may account for some deactivation of the chloride donor ion.²

Various lines of evidence indicate that the chlorination reactions observed here are of an ECE type that do not involve elemental chlorine or radical cation disproportionation.

1. Department of Chemistry, University of Tennessee, Knoxville.

2. G. B. Porter and E. C. Baughan, *J. Chem. Soc.* **744** (1958).

9.1.6 Reaction Pathways of Substituted Anthracene Radical Cations in SbCl_3 -Rich Melts (S. P. Zingg, G. P. Smith)

This investigation has been directed toward a mechanistic understanding of the reactions of radical cations in SbCl_3 -rich liquids and toward an evaluation of the impact of the solvent properties, the structure of the substrate, the type of oxidant, and the nature of the nucleophile. The reactions of radical cations in organic aprotic media have been extensively investigated¹ and are invariably complex. Because of the multistep nature of the processes and the large number of intermediates involved, reactions taking place by the same pathway may exhibit widely different kinetic behavior depending upon the reaction conditions. We have previously shown that SbCl_3 -rich liquids stabilize reactive intermediates² such as arenium ions, radical cations of arenes and heteroaromatics and even some dications. Therefore, these unique solvents may have a profound effect on either the kinetics or mechanisms of radical cation reactions.

The anthracenes, particularly 9,10-diphenylanthracene (DPA), have been widely used as substrates in mechanistic investigations to establish the single electron transfer (SET) pathways of aromatic hydrocarbons in aprotic organic solvents. One reason for this choice is the fact that the charge and unpaired electron are concentrated in the center ring so that substitution in the 9,10-positions stabilizes the radical cation and also serves to limit the possible reaction pathways. Because of this extensive background we chose DPA and 9-phenylanthracene (PA) as substrates for our work.

In a previous report³ we discussed the reaction of PA and DPA in SbCl_3 - AlCl_3 - KCl (95-4-1 mol %) at 100°C where the melt served as the oxidant. The reaction of PA^+ proceeded via radical-radical dimerization (presumably at the 10-position) and subsequent oxidative intramolecular condensation to give substituted anthraaceanthrylenes (AAA) and protonated PA.

The reaction of DPA^+ with both the 9- and 10-positions blocked proceeded via two different pathways: (1) cleavage of a phenyl group to give PA and benzene and (2) intramolecular condensation to give rubicene and tetrahydroisorubicene. Both of these reactions were obviously complex multistep processes due to the fact that the intermediates and products formed were themselves easily oxidized by the melt. The same reactions were observed for PA and DPA in 60-21-19 SbCl_3 - AlCl_3 - BPCl at 24°C; however, the oxidations and subsequent reactions were slower in these acidic room temperature melts.

The behavior of the radical cations of PA and DPA generated in basic or nonoxidizing melts illustrated the effects of both substitution in the 9,10-positions of anthracene and the nucleophilicity of the solvent. In basic (excess Cl^-) SbCl_3 -rich liquids it has been shown (see Section 9.1.5) that chloride can act as a nucleophile toward anthracene radical cations. In the 60-19-21 SbCl_3 - AlCl_3 - BPCl melt the excess Cl^- (~0.2 M) was present as the ionized electrolyte (BP^+ , $\text{Cl}^- \cdot 2\text{SbCl}_3$). However, in SbCl_3 - KCl melts the electrolyte K^+ , $\text{Cl}^- \cdot 2\text{SbCl}_3$ was strongly ion paired. The results of product analyses from the reactions of DPA and PA after oxidation in both low and high temperature basic melts are shown in Tables 9.1 and 9.2.

In the absence of nucleophiles (acidic SbCl_3 melts), the fate of the radical cation of PA was dimerization and subsequent follow up reactions. The dimerization could be overcome by reaction of PA^+ with chloride ions if their activity in the melt was sufficiently high. As was observed with anthracene (Section 9.1.5), PA gave almost exclusively the mono-chlorinated product (CIPA) when oxidized coulometrically in a 60-19-21 SbCl_3 - AlCl_3 - BPCl melt with two electrons being required for each molecule of product.

Table 9.1. Amount (w/o) of substances recovered from 9-phenylanthracene decomposition.

Melt Oxidant	SbCl ₃ -AlCl ₃ -BPCI 60-19-21	SbCl ₃ -8% KCl		
	e ⁻ ^a	Sb(V) ^b	Sb(V) ^c	Chloranil ^d
9-Phenylanthracene	49	12	—	15
9-Chloro-10-phenylanthracene	52	—	—	71
2,9-Dichloro-10-phenylanthracene	trace	—	—	—
Anthraaceanthrylenes	—	47	70	10
Bianthracenes	—	2	5	trace
Highly condensed material	—	large	large	trace

^a8.45 mM PA, coulometrically oxidized at +0.68V vs. Sb⁰/SbCl₃ (solid), SbCl₃-BPCI (liquid) for 3 hrs, one equivalent of electrons passed, reaction mixture quenched after 30 min, 24°C.

^b249 mM PA, 30% oxidized, 100°C, 1 hr.

^c250 mM PA, 100% oxidized, 100°C, 1 hr.

^d250 mM PA, 1:1 mole ratio chloranil:PA, 100°C, 1 hr.

Table 9.2. Amount (w/o) of substances recovered from 9,10-diphenylanthracene decomposition.

Melt Oxidant	SbCl ₃ -AlCl ₃ -BPCI 60-19-21	SbCl ₃ -8% KCl
	e ⁻ ^a	Sb(V) ^b
9,10-Diphenylanthracene	43	47
2-Chloro-9,10-diphenylanthracene	36	16
Dichloro-9,10-diphenylanthracene	1	14
9,10-Dichloro-9,10-dihydro- 9,10-diphenylanthracene	~10	—
Condensed	—	trace

^a7.87 mM DPA, coulometrically oxidized at +0.68 V for 3 hrs, one equivalent of electrons passed, reaction mixture quenched after 48 hrs, 24°C.

^b252 mM DPA, 100% oxidized, 100°C, 1 hr.

However, when PA was oxidized by Sb(V) in SbCl₃-8% KCl only condensed materials were formed. Anthracene under the same conditions gave a mixture of chlorinated and condensed products (mostly bianthryls). Substitution of a phenyl group in the 9-position served to stabilize the initial dication intermediate formed by radical-radical dimerization. Thus in melts with low Cl⁻ activity dimerization was the predominant reaction pathway for PA. The primary products were not bianthryls, however, but

other condensed species (probably AAAs). The oxidation of PA (4e⁻ are required for each molecule of AAA) was much greater than can be accounted for by the Sb(V) added. The probable reason for this is that the bianthryls initially formed were more easily oxidized because of the phenyl substituents and were further oxidized by the melt.

When chloranil (C₆Cl₄O₂) was used to oxidize PA in SbCl₃-8% KCl at 100°C, a mixture of products was observed with the primary product

being ClPA. The increased Cl^- activity may be due to complexation of the chloranil by SbCl_3 ($\text{C}_6\text{Cl}_4\text{O}_2 \cdot \text{SbCl}_2^+$, $[\text{Cl} \cdot 2\text{SbCl}_3]^-$) which also serves to increase the oxidizing strength of chloranil. In this reaction chloranil was the sole oxidant.

The reaction of DPA in both the low and high temperature melts resulted in predominantly chlorinated products. DPA^+ cannot dimerize and intramolecular condensation, although it occurred in the acidic non-nucleophilic melts, was probably not favored since it must proceed through a strained 5 membered ring intermediate. UV-visible spectroscopy showed that 9,10-dichloro-9,10-dihydro-9,10-diphenylanthracene ($\text{Cl}_2\text{H}_2\text{DPA}$) was formed in situ in the low temperature melt, however $\text{Cl}_2\text{H}_2\text{DPA}$ was transformed to 2-chloro-9,10-diphenylanthracene (ClDPA) by chromatography or heating. The mono- and dichlorinated products (ClDPA and Cl_2DPA) were formed in situ in the high temperature melt which also showed a much lower selectivity for the mono-chlorinated product. In both melts the chlorinated products accounted well for the amount of oxidant used. In $\text{SbCl}_3\text{-AlCl}_3\text{-BPCl}$ melts, ClDPA and $\text{Cl}_2\text{H}_2\text{DPA}$ required 0.72 and 0.20 equivalents of oxidant respectively. In $\text{SbCl}_3\text{-8\% KCl}$, ClDPA and Cl_2DPA required 0.32 and 0.56 equivalents of oxidant respectively.

The reactions of PA and DPA in the 60-19-21 $\text{SbCl}_3\text{-AlCl}_3\text{-BPCl}$ melt were also studied by electrochemistry, spectroelectrochemistry and UV-vis spectroscopy to obtain kinetic and mechanistic information on the reactions. Cyclic voltammetry showed DPA ($E_{1/2} = +0.55$ V vs $\text{Sb}^0/\text{SbCl}_3(\text{solid})$, $\text{SbCl}_3\text{-BPCl}(\text{liquid})$) to be more easily oxidized than PA ($E_{1/2} = +0.61$ V). The voltammograms for DPA showed reversible behavior even at fairly slow scan rates while PA was only quasireversible.

At very slow scan rates (≤ 10 mV/sec) the CV studies of PA showed a post anodic peak at +0.73 V and no cathodic peaks. Spectroelectrochemical studies using a rapid multichannel spectrometer and an optically transparent electrode showed a rapid conversion of PA ($\lambda = 357, 377, 396$ nm) to ClPA ($\lambda =$

367, 387, 407 nm) during the electrolysis at +0.68 V. The radical cation of PA was observed but was not stable. The spectra were very complex, indicative of the presence of other intermediates during the electrolysis and open circuit decay. These results were all consistent with an ECEC mechanism.

In the final step chloride acted as a base rather than a nucleophile. HCl was observed during quenching of these reactions.

Spectroelectrochemical studies at lower potentials and fast mixing studies will help to further identify some of the intermediates.

The radical cation of DPA was extraordinarily stable. The products observed and the second order kinetics were, however, consistent with the half-regenerative mechanism which has previously been suggested for this reaction.⁴

As the radical cation of DPA decayed the bands due to regenerated DPA grew in. (The chlorinated product $\text{Cl}_2\text{H}_2\text{DPA}$ could not be observed directly due to the melt UV cutoff.) A weak band was observed at ~ 425 nm which formed and decayed with the radical cation of DPA. We attribute this band to the radical intermediate which should be in equilibrium with DPA^+ .

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4. J. F. Evans and H. N. Blount, *J. Org. Chem.* **41**, 516 (1976).
5. J. F. Evans and H. N. Blount, *J. Phys. Chem.* **83**, 1970 (1979).

9.1.7 Electron and Hydrogen Transfer Reactions of Arenes in Molten Gallium(III) Halide-Rich Systems

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

The gallium(III) halides (Ga_2Cl_6 and Ga_2Br_6) dissolved in organic solvents are excellent Friedel-Crafts alkylation and acylation catalysts, frequently used in preference to the aluminum halides for basic investigations of catalytic mechanisms. The neat melts of these substances are also very active hydrocracking catalysts at elevated temperatures. In these applications it has generally been assumed that the activity of the gallium trihalides is due exclusively to their high Lewis acidity. However, the meager thermodynamic data on the gallium(III) halides shows that they are much more easily reduced than the corresponding aluminum halides and this suggests the possibility that they may have a redox functionality in addition to their acid functionality. In a previous report¹ we presented preliminary evidence to the effect that a melt of neat Ga_2Cl_6 is a strong enough oxidant to stoichiometrically oxidize pyrene (1), anthracene (2) and naphthalene (3) but not naphthalene (4). We have now firmly established this behavior and shown that the reduced form of gallium is Ga^+ , which acts as a cationic species in the melt. We have also found that substantial additions of GaCl_3 have interesting effects on the redox and acid-base properties of Ga_2Cl_6 and we took a preliminary look at Ga_2Br_6 , which proved to be a weaker oxidant than Ga_2Cl_6 .

When small amounts of 1, 2 and 3 were dissolved in neat, molten Ga_2Cl_6 at 100°C , they were oxidized to their radical cations, which were highly persistent and yielded strong ESR spectra with well-resolved hyperfine structure. More concentrated solutions of these arenes (~2 mol %) were oxidized stoichiometrically according to the following reaction in which ArH is the arene, ArH_2^+ is the corresponding

arenium ion and Ar-Ar stands for a mixture of oligomerized arenes. The arenium ions were identified and quantified by *in situ* $^1\text{H-NMR}$ while Ga^+ was identified and quantified by *in situ* $^{71}\text{Ga-NMR}$. The $\text{ArH}_2^+:\text{Ga}^+$ mole ratio was found to be 2:1 to within an uncertainty of 10%. The oligomerized arenes were recovered following hydrolysis of the melt, then separated chromatographically and the major constituents were identified and quantified by standard procedures. The quantity of ArH recovered following hydrolysis was in agreement with that expected from the hydrolysis of ArH_2^+ (as determined by *in situ* $^1\text{H-NMR}$) and the quantity of the latter was, in turn, in agreement with that expected from the loss of hydrogen accompanying oligomerization. The arenium ion yields were 60-70%.

The oxidative coupling of arenes accompanied by the release of protons, as shown in Eq. 1, is a well-known aspect of arene radical cation chemistry. A less common feature of this reaction is the capture of the released protons by the neutral arene to form stable arenium ions in an aprotic medium. However, we have shown that the same reaction also occurs in molten SbCl_3 -10 mol % AlCl_3 mixtures for the same arenes. In this SbCl_3 -rich medium, the oxidant is Sb(III) .

We also investigated the reactions of these same arenes in molten Ga_2Br_6 at 130°C using identical techniques. The Ga_2Br_6 melt appears to be less oxidizing than is Ga_2Cl_6 . In general we found that in Ga_2Br_6 only a part of the arene was oxidized to yield arenium ions

while the rest underwent a catalytic hydrogen transfer reaction to form a complex mixture of condensed and hydrogenated arenes. For example, with 3, the most oxidizable arene studied, only 20% arenium ion was formed but a considerable quantity of hydrogenated material was recovered. With 1, little or no arenium ion was formed, the products were mostly condensed and hydrocondensed compounds. A comparison of the ^1H -NMR spectra for 2 in Ga_2Cl_6 and in Ga_2Br_6 is shown in Fig. 9.5. A salient feature of the anthracenium ion spectrum, peaks at 5 and 9.6 ppm, is absent from the spectrum in Ga_2Br_6 while the aliphatic peaks from 1 to 4 ppm do not appear in the Ga_2Cl_6 spectrum. The results in Ga_2Br_6 were similar to those found

when SbCl_3 is made only slightly oxidizing by the addition of ~1% AlCl_3 . The ^1H -NMR spectra and product mix found after 2 was held at 130° for less than 1/2 hr in Ga_2Br_6 or 1% AlCl_3 - SbCl_3 was similar to those found for the catalytic hydrogenation-condensation reaction for 2 in neat SbCl_3 after ~24 hrs at 130° .

The addition of macro quantities of GaCl to Ga_2Cl_6 has some pronounced effects on the behavior of dissolved arenes that are qualitatively accounted for by the following model: The principal acid-base equilibria are given by Eq. 2 and 3 while the thermodynamics of arene oxidation is described by Eq. 4 and 5.

In all cases the counter ions are uncomplexed Ga^+ . It follows from these model equations that as the formal GaCl_3 : GaCl ratio decreases, the Lewis acidity, as measured by pCl^- , and E° for the $\text{Ga}^{3+}/\text{Ga}^+$ couple both decrease in the neighborhood of compositions corresponding to the molten compounds Ga^+ , Ga_2Cl_7^- (the 2:1 compound) and Ga^+ , GaCl_4^- (the 1:1 compound). That is, the GaCl_3 - GaCl system behaves like a dibasic acid with titration points at 2:1 and 1:1. On the GaCl -rich side of 1:1 the melt is a Lewis base while at other compositions it is an acid.

The behavior of 1, 2 and 3 on the GaCl_3 -rich side of 2:1 is described above. In the molten 2:1 composition 2 and 3 are not stoichiometrically oxidized but, rather, undergo a rapid, catalytic hydrogenation-condensation reaction, while 1, which is less oxidizable than 2 and 3, does not react at all. In the neat molten (1:1) composition 2 shows very little if any reaction under forcing conditions, viz., 180°C for 30 min.

Fig. 9.5. ^1H -NMR spectra for anthracene in molten GaBr_3 and in molten GaCl_3 .

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9.2 Surface Science and Heterogeneous Catalysis

9.2.1 Low Energy Ion Scattering Measurements on Clean and Sulfided Molybdenum Surfaces

(S. H. Overbury, B. M. DeKoven,¹
D. R. Huntley)

In connection with our interest in studying hydrodesulfurization reactions on sulfided transition metals, we have undertaken the initial step of examining the interaction of S with a clean Mo surface. We have applied low energy ion scattering to study the bonding geometry and structure of the sulfided surface of Mo(001). The surface was dosed with S₂ from a solid state electrochemical cell in UHV in a controlled manner. The resulting coverage of S was measured by AES and the surface periodicity and quality of adsorbate ordering was characterized by LEED. These surfaces were then examined by K⁺ and Li⁺ ion scattering.

Analysis of the measured energy distributions and their dependence upon incidence angle resulted in the following conclusions. The S adatoms are located above the Mo surface rather than incorporated into it. This result is demonstrated in K⁺ scattering by the attenuation of the features characteristic of scattering from surface Mo. The double scattering peak (at E/E_i = 0.78) for clean Mo is totally eclipsed at the highest coverage and the single scattering peak (at E/E_i = 0.66) is reduced to a shoulder (Fig. 9.6). More evidence comes from the polar incident angle dependence in Li⁺ scattering. At large incident angles, sharp peaks due to Li⁺ single scattering from both S and Mo are observed at coverages near 0.4 monolayers (ML). At very grazing incidence only an S peak is observed. At higher coverages a Mo peak is not visible at any incident angle while the S gives a sharp peak even at very grazing angles.

The data are consistent with the S adatoms located in four-fold hollow adsorption sites for coverages $\lesssim$ 0.5 ML. The principal evidence is the faster attenuation of the Mo-Mo double scattering peak with increasing S coverage compared to the Mo single scattering peak. Adatoms in these sites would block double scattering along the [110] azimuth. This behavior has been observed previously for C and O overlayers on Mo(001).² This hypothesis has been confirmed by computer simulation for 0.5 ML coverage. Energy distributions have been computed for an ordered configuration of S atoms on the four-fold sites of unrelaxed Mo(001). Agreement with experiment is obtained for an adatom height of 1.0 Å. Reducing the height to 0.80 Å or below reduces the agreement. Computer simulations were performed for a surface with 0.75 ML of S atoms arranged according to three different models for the observed c(4×2) ordering. The models tested included one in which all S adatoms occupy four-fold sites (at height 1.0 Å) and two models in which some of the S atoms are located in two-fold sites. All three models qualitatively reproduce the observed attenuation of the Mo single and double scattering peaks and lead to intensity build-up at E/E_i ≈ 0.50 (Fig. 9.6). Agreement is not yet sufficient to select one model over another, so structural details at the higher coverages are not yet clarified.

The ion scattering was also found to be sensitive to the ordering of the S layer. Annealing to 1000 K at constant coverage (0.4 ML) sharpens all the features in the scattered energy distribution, with most of the change occurring between 700 and 800 K. A corresponding sharpening of the LEED pattern is also observed.

The computer simulations of the K⁺ scattering from the sulfided Mo(001) were initially hindered by generally poor agreement with experimental energy distributions. This was the case also for the clean Mo(001) surface where the disagreement could not be attributed to the unknown surface structure. One

Fig. 9.6. Backscattered K^+ energy distributions are shown as a function of S coverage. The surfaces were annealed to 1000 K and produced the indicated LEED patterns.

difficulty was the uncertainty of the proper scattering potential. This situation was corrected by systematic measurements of the "cut-off" angles observed in the incident angle dependence for Li^+ , Na^+ and K^+ at various energies (≤ 2500 eV). Comparison with the cut-off angles calculated for various scattering potentials determined that an empirical form proposed by Ziegler et al.,³ gave good agreement. Comparable agreement was obtained with a Thomas-Fermi Moliere potential, when the screening length was adjusted. Using the Ziegler potential in the computer simulations improved the overall agreement between computed and experimental energy distributions for both the clean and sulfided surface.

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9.2.2 The Structure of Amorphous Surfaces by Low Energy Ion Scattering Spectroscopy

(S. H. Overbury, D. R. Huntley)

Recent studies of the catalytic properties of amorphous metallic glasses have prompted an interest in their surface structure. Although extensive work has been done to determine the bulk structure of these metallic glasses, virtually nothing is known about the surface structure. A simple bulk termination model would result in a surface which is rough on an atomic scale. Alternatively, the surface may relax to minimize the surface free energy, resulting in a smooth surface. Catalytic results on Pd-Si and Fe-B based alloys seem to suggest that the surface of these metallic glasses is rough on an atomic scale, and that this roughness is maintained even after bulk crystallization.¹ We have applied angle and energy resolved lithium ion scattering to study the surface topography of an amorphous $Fe_{80}B_{20}$ ribbon (Allied Chemical METGLAS 2605). Structural information was obtained from measurements of the iron single scattering peak intensity as a function of incident polar angle. On a smooth surface, scattering is blocked at grazing incident or exit angles due to shadowing by neighboring atoms. On a rough surface, scattering may occur at grazing angles from atoms which protrude above the surface and are not shadowed by neighboring atoms. It is therefore expected that the incident angle dependence from a rough surface will be broader and have higher intensity at low and high (for fixed scattering angle) incident angles than that from a smooth surface.

Measurements were made on both sides of the amorphous ribbon. This was done because there may be differences between the side which contacted the cooling substrate, the rapidly quenched (RQ) side, and the opposite

free surface (FS) side. The angular dependence obtained from the RQ side was extremely broad, and had relatively large intensity at low and high angles of incidence compared to either a polished Mo(001) single crystal or a polished Fe polycrystalline foil. The angular dependence from the FS side of the ribbon was somewhat sharper, having smaller intensity at grazing incident angles, but was still broad compared to that from a single crystal.

The rapidly quenched surface was extensively sputtered and then the sample was gradually crystallized by a sequence of annealing steps. The angular distribution from the RQ side was measured repeatedly during the annealing process. Although the conditions were sufficient to fully crystallize the bulk, and an increase in the iron content on the RQ surface was observed by Auger electron spectroscopy (AES), no significant changes in the angular distribution occurred. This is in qualitative agreement with the catalytic results which show no major differences in selectivity between the amorphous and crystallized material.

The ion scattering results point to several conclusions. The amorphous surface is atomically rough as indicated by the broad angle dependence. Also there is a clear difference between the FS and the RQ sides of the ribbon which is consistent with a higher degree of crystallinity on the free surface side. The annealing experiments on the RQ side demonstrate that bulk crystallization does not alter the surface roughness.

The Auger measurements show that there are composition differences between the two sides and that changes in surface composition occur during bulk crystallization. The FS side has more iron initially than the RQ side. Annealing the sputtered surface causes the iron intensity to increase on the RQ side consistent with the formation of α iron at the surface, in agreement with other studies.²

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9.2.3 Studies of Reactions on Transition Metal Sulfide Surfaces. Design of a UHV/Reaction System for Surface Analysis (D. R. Huntley, S. H. Overbury)

Transition metal sulfides are active catalysts for hydrodesulfurization, hydrogenation and hydrocracking of fossil fuels. Despite an immense literature, little is known about these catalytic reactions at the molecular level. One very powerful method of obtaining such information is through a combined study of the surface properties of the catalyst, the interactions between the surface and the reactant molecules and the catalytic reaction itself.

Our approach will be to combine studies of catalytic activity at pressures of ~ 100 torr with surface analysis at pressures of $\sim 10^{-10}$ torr. This approach has been successfully applied by other researchers to study CO hydrogenation on Fe, hydrogenation on noble metals and ethylene epoxidation on silver. We have designed and are currently building a custom ultra-high vacuum chamber and a contiguous reaction chamber. The system will include a transfer mechanism which should allow the sample to be moved between the reaction cell and the UHV chamber without being exposed to the atmosphere. The analytical tools which will be incorporated include an Auger electron spectrometer for monitoring surface composition, a high resolution electron energy loss spectrometer for characterizing the molecular species adsorbed on the surface, a quadrupole mass spectrometer for use in thermal desorption studies, and a gas chromatograph for separating and identifying reaction products from the reaction chamber. This combination

of techniques will allow us to carefully characterize a variety of catalyst surfaces before and after catalytic reactions.

We have identified several possible models for hydrodesulfurization catalysts. Initially, we are interested in studying model molybdenum catalysts, since molybdenum disulfide is thought to be the active phase in the industrial cobalt molybdate hydro-treating catalysts. Although the natural cleavage plane of perfect molybdenum disulfide single crystals is practically inert, it may be possible to introduce defects which model the catalytically active sites through oxygen etching or inert gas sputtering. Another possible model for the reactive surface can be prepared by adsorbing sulfur (either as H_2S or S_2) on a single crystal molybdenum surface. Some preliminary research has demonstrated that these sulfided molybdenum surfaces can be catalytically

active, and our ion scattering studies of clean and adsorbate covered $Mo(001)$ surfaces have yielded important structural information. These initial data indicate that these surfaces will be both characterizable and reactive. A third approach involves the deposition of small molybdenum compounds (e.g., $Mo(CO)_6$) on a flat alumina or silica surface followed by oxidation or sulfidation to form supported molybdenum oxides or sulfides. This approach has the advantage of being the closest model to the real industrial catalysts, but will probably result in the most difficult surface to characterize. We will also extend these model studies by including other transition metals such as ruthenium. The goal of this research is to draw correlations between catalytic reactions and surface properties of a variety of transition metal sulfide model catalysts.

10. CHEMICAL PHYSICS

This section describes recent research in structural chemistry and photoelectron spectroscopy.

Knowledge of chemical structure at the atomic and molecular level is necessary for understanding and predicting chemical and physical properties. The structural-chemistry program provides such knowledge through the techniques of x-ray and neutron diffraction and through development of computational methods for interpreting the experimental data. A computational modeling study (Section 10.1.1) shows that crystal packing causes out-of-plane distortions of the naphthalene nucleus in naphthalene molecules bearing phenyl substituents, distortions that earlier were thought to be inherent in the isolated molecules. The isotopic substitution method, using three isotopes of dysprosium, has been applied in the neutron-diffraction study (Section 10.1.2) of the hydration of the Dy^{3+} ion in $DyCl_3$ solution in D_2O . Significant new information of the theoretical interest has been obtained. A new four-circle automatic diffractometer (Section 10.1.3) has been installed at the HFIR for neutron diffraction studies on single crystals and fibers.

Using synchrotron radiation coupled with angle-resolved photoelectron spectroscopy, the basis of the photoelectron dynamics of atoms and molecules is being investigated. Studies on atomic metal vapors (Section 10.2.1) have been concentrated on resonant phenomena and autoionization, including new studies on argon and ytterbium. The most recent results on silver near the Cooper minimum clarify important differences between atomic and metallic behavior. Recent studies with free molecules (Section 10.2.2) include an extensive expansion of our work on autoionization in N_2O , a detailed examination of the Cooper minimum as revealed through a homologous series of fluorochloromethanes, and the measurement of shape resonances from the ejection of core shell electrons from $SiCl_4$.

10.1 Structural Chemistry

10.1.1 Crystal Packing Forces and the Molecular Geometries of the Phenyl-naphthalenes

(W. R. Busing)

The crystal structures of 1,8-diphenyl-naphthalene (DPNAP)¹ and 1,4,5,8-tetraphenyl-naphthalene (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. 10.1, 1.6° and 10.8° for DPNAP and TPNAP, respectively. These angles would be zero for a planar naphthalene moiety.

Clough, Kung, Marsh, and Roberts³ have proposed that this difference is inherent in the molecules themselves. They suggest that in DPNAP the stress on the 1,8 side of the naphthalene can be relieved by in-plane changes of distances and angles on the 4,5 side of the ring system. In TPNAP, on the other hand, both sides are stressed similarly, and out-of-plane distortions provide the only relief.

Fig. 10.1 Molecules of 1,8-diphenyl-naphthalene (DPNAP) and 1,4,5,8-tetraphenyl-naphthalene (TPNAP) showing the average conformation angles observed in the crystal structures.

An alternative explanation is that in the two crystal structures the molecules are subject to rather different crystal packing forces and that it is these forces which determine the observed molecular geometries. Indeed the structures are quite different, the DPNAP molecules adopting an anti-parallel arrangement and the TPNAP molecules packing in herringbone fashion.

One way of testing these hypotheses is to construct computational models of the two crystal structures. The ability of the model to reproduce the experimental lattice parameters and the observed geometries of the molecules in the crystal is taken as evidence of its validity. The same model is then used to predict the structures of the isolated molecules. These gas-phase structures are not known experimentally, but the predicted geometries can be compared. If the difference in the naphthalene planarity is inherent in the molecules, then it should appear in the calculated molecular structures.

We have previously reported results of this kind of calculation⁴ which seemed to show that crystal packing forces play the predominant role in determining the geometries of these molecules. In those calculations, however, we used a simplified model in which all bond distances and many bond angles were constrained to have the values observed in the crystal. It can be argued that such a model is not really a fair test of the Clough, Kunz, Marsh, Roberts hypothesis, because these distances and angles cannot readjust when the packing forces are removed. Now we have repeated these calculations and obtained similar results with a model that allows complete flexibility of the naphthalene moiety.

For DPNAP the 10 carbon atoms and 6 hydrogen atoms of the nucleus were allowed to move independently, each with 3 degrees of freedom. The two naphthalene-phenyl links were constrained to constant length and allowed to pivot on carbons 1 and 8, each with 2 degrees of freedom. The remaining

atoms of the two phenyls were treated as rigid groups pivoting on the links with 3 degrees of freedom each. These 58 internal coordinates and the 4 parameters of the monoclinic unit cell make a total of 62 structural variables to be adjusted.

For TPNAP the problem is somewhat smaller because the molecule is situated on a center of inversion. Only 5 carbon atoms, 2 hydrogen atoms, 2 phenyl-naphthalene links, and 2 rigid phenyl groups are taken as independent. The other half of the molecule is generated by this center. There are then 31 internal degrees of freedom and 4 lattice parameters for a total of 35 variables.

The energy of each model is computed using a potential which includes the exp-6-1 function of Williams and Starr⁵ for each intermolecular or intramolecular nonbonded interaction. Two torsion potentials of the form $V_{\phi} = E_{\phi} (1 - \cos^2 \phi)/4$ represent the conjugation energies of the ring-ring links and the pi bonds of naphthalene, respectively. A quadratic potential $V_{op} = (k_{op}/2)d_{op}^2$, where d_{op} is an out-of-plane distance and k_{op} is a force constant, also tends to keep the naphthalene and phenyl-naphthalene links planar. A potential $V_{\alpha} = (k_{\alpha}/2)(\alpha - 120^\circ)^2$, included for every variable bond angle α , tends to keep these angles at 120° . Three potentials of the form $V_d = (k_d/2)(d - d_0)^2$ are included for the two kinds of C-C bonds and for the C-H bonds of naphthalene. Again, k_{α} and k_d are force constants, and the d_0 's are also constants of the potential.

Initial values of the 10 parameters of the intramolecular potential were taken from the literature^{6,7,8} and adjusted by trial and error to make the calculated minimum energy crystal structures agree as well as possible with those observed. Good agreement was obtained, with bond distances reproduced to within 0.01 Å, bond angles to 0.5°, lattice parameters to less than 2%, and torsion angles to about 1°. Some of these results are listed in Table 10.1.

Table 10.1 Observed and calculated structural parameters for 1,8-diphenylnaphthalene (DPNAP) and 1,4,5,8-tetraphenylnaphthalene (TPNAP)

	Crystal				Isolated
	Obs	Calc	Calc-Obs	%	Molecule
DPNAP					
a(A)	8.58	8.41	-0.17	-2.0	
b	20.03	19.84	-0.19	-0.9	
c	9.72	9.66	-0.06	-0.6	
$\beta(^{\circ})$	116.7	115.7	-1.0		
ϕ	-66.4	-66.5	-0.1		-52.8
χ	1.6	2.0	0.4		6.4
TPNAP					
a(A)	6.46	6.46	0.00	0.0	
b	24.33	24.19	-0.12	-0.6	
c	8.02	7.90	-0.12	-1.5	
$\beta(^{\circ})$	114.3	114.1	-0.2		
ϕ	-53.4	-52.3	1.1		-62.5
χ	10.8	10.8	0.0		6.7

Similar calculations were then made minimizing the energies of the isolated molecules, and the torsion angles obtained in this way are also listed in the table. It can be seen that, although the ring-ring angles ϕ differ by 10° , the in-ring angles χ , which measure the distortion of the naphthalene nucleus, are almost identical. We conclude that, because the crystals have different packing arrangements, the crystal packing forces have different effects on the ring-ring torsion angle ϕ , increasing its magnitude in DPNAP and reducing it in TPNAP. These same forces cause the naphthalene distortion angle χ to be reduced in DPNAP and increased in TPNAP. The intramolecular forces invoked by Clough, Kung, Marsh, and Roberts affect bond distances, bond angles, and phenyl rotations, but they have little effect on the naphthalene planarity.

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10.1.2 Neutron Diffraction by Aqueous Solutions: Cation Hydration in Rare Earth Chlorides

(B. K. Annis, R. L. Hahn, A. H. Marten)

Study of the hydration of trivalent lanthanide ions is of interest because of the claims made by Spedding et al.¹ that, as a result of the lanthanide contraction, i.e., the reduction in cationic radius that occurs in going from the light to the heavy rare earths, the hydration number of the heavy lanthanide ions is one unit less than that of the light lanthanide aqua ions. In the present work we have used neutron scattering to study the hydration of the Dy^{3+} ion in 2.38 M solutions of $DyCl_3$.

Differences in the angular distributions measured for solutions containing various isotopes of dysprosium may be combined to give the radial distribution of atoms about the dysprosium ion. Examples of such differences used in this study are shown in Fig. 10.2 and the details of the computational procedure leading to the radial distribution function may be found elsewhere.^{2,3}

The radial distribution function is given by

$$G_{Dy}(r) = 0.283 g_{DyO} + 0.650 g_{DyH} \quad (1)$$

where the $g_{\alpha\beta}$ are the various atom-atom

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Fig. 10.2. Difference curves derived from differential cross sections. The curves for ^{164}Dy - ^{162}Dy have been divided by two to fit the figure.

radial distribution functions, and small terms in g_{DyDy} and g_{DyCl} have been dropped. The radial distribution function corresponding to Eq. (1) is plotted as the dotted line in Fig. 10.3. Of the features in the function $G_{\text{Dy}}(r)$, the peaks at 2.4 and 3.0 Å can be interpreted by the following procedure. The integral

$$N(r) = 4\pi\rho \int r^2 G_{\text{Dy}}(r) dr \quad (2)$$

evaluated from 2.0 Å to the first minimum at 2.70 Å has a value $N_1 = 7.10$. The integral of Eq. (2) over the second peak from 2.70 to 3.50 Å has a value $N_2 = 14.52$. From the definition of the atom pair distribution functions, the number of γ atoms with atom fraction c_γ around an α atom is

$$n = 4\pi c_\gamma \rho \int r^2 g_{\alpha\gamma}(r) dr. \quad (3)$$

If we combine Eqs. (2) and (3) and tentatively assign the peaks at 2.4 and 3.0 Å respectively to the $\text{Dy}\cdots\text{O}$ and $\text{Dy}\cdots\text{Dy}$ interactions, we find that $n_1 = 7.87$, $n_2 = 13.9$, and $n_2/n_1 = 1.8$. This ratio is in reasonable agreement with the expected value

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Fig. 10.3. Radial distributions, $G_{\text{Dy}}(r)$, obtained from data of Fig. 10.2 (dotted curve); the solid curve was computed using an extrapolation technique and demonstrates that the finite range of the experimental data has no significant effect on the radial distribution functions.

of $n_2/n_1 = 2$ for D_2O , and the principal source of this discrepancy is the poor area definition due to the substantial overlap of the peaks in the vicinity of 2.7 Å. In the case of NdCl_3 in $\text{D}_2\text{O}^{1,2}$ the first peak was considerably narrower than in the case for the dysprosium solution, and a value of $n_2/n_1 = 1.9$ was obtained. An estimate of the hydration number of water molecules around a dysprosium ion can be obtained from the average quantity $(n_1 + n_2)/2$. In this manner we found a hydration number of 7.4 ± 0.5 .

An alternative method of data analysis involves fitting the difference data of Fig. 10.2 by a function of the form

$$0.283 w \hat{w}_{\text{DyO}}(k) + 0.650 w \hat{w}_{\text{DyDy}}(k)$$

$$\text{with } \hat{w}_{\alpha\gamma}(k) = j_0(kR_{\alpha\gamma}) \exp(-\frac{1}{2}k^2 R_{\alpha\gamma}^2)$$

This leads to a function $G_{\text{Dy}}(r)$ for which (apart from correction terms of order

$(\Delta_{\alpha\gamma}/R_{\alpha\gamma})^2$, $R_{\alpha\gamma}$ is the peak position, and $2.35 \Delta_{\alpha\gamma}$ is the full width at half maximum of the distribution for the separation of atoms α and γ in the first coordination sphere of a dysprosium ion. The quantity, w , is the total number of water molecules in this sphere. The desired values of w , L , and R for the $\text{Dy}\cdots\text{O}$ and $\text{Dy}\cdots\text{O}$ interactions were then obtained by least squares fitting of the experimental data for values of $k > 2.7 \text{ \AA}^{-1}$. The resulting distances R_{DyO} and R_{DyO} are 2.37 and 3.04 $\text{\AA}$, respectively, and the least-squares value of the hydration number, w , is 7.4 ± 0.1 which is identical to that obtained in the analysis of the function $G_{\text{Dy}}(r)$. The overall uncertainty of the hydration number is estimated to be ± 0.5 . The parameters obtained from this analysis are listed in Table 10.2.

The interatomic distances permit an estimation of the orientation or "tilt" of the water molecules about the ionic core. By assuming the O atoms to be equidistant from Dy^{3+} and using the known geometry of the water molecules, we obtained a "tilt" angle of $17 \pm 3^\circ$. A "tilt" angle of 0° corresponds to the dipole moment of the water molecule pointing away from the ionic core while an angle of 55° implies that one of the "lone pair" orbitals points toward the core. The $\text{Dy}^{3+}\text{-D}_2\text{O}$ result is quite similar to that

obtained earlier³ for $\text{Nd}^{3+}\text{-D}_2\text{O}$ and is somewhat smaller than angles observed for mono and divalent ions. The decrease in coordination number found by the neutron diffraction results for $\text{Nd}^{3+}(8.5)^2$ and $\text{Dy}^{3+}(7.4)$ is in good agreement with results derived from x-ray diffraction⁴ and support the hypothesis that the nature of the hydration sphere changes with the ionic core radius.

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10.1.3 A New Neutron Diffractometer for Studying Single Crystals and Fibers

(George M. Brown, W. R. Busing, W. E. Thiessen)

A modern four-circle computer-controlled neutron diffractometer suitable for the study of single crystals or of oriented polymer fibers has been installed at the HFIR. The new instrument is controlled through a PDP 11/44 computer with three disk drives. The

Table 10.2. Hydration of rare-earth ions, M^{3+}

M^{3+}	$r_{\text{M}^{3+}}(\text{\AA})^a$	$r_{\text{MO}}(\text{\AA})$	$r_{\text{MD}}(\text{\AA})$	N	$N(\text{X-RAY})^4$
Nd^{3+}	1.16	2.48	3.13	8.5	8.9
Dy^{3+}	1.03	2.37	3.04	7.4	7.9

Tilt Angle

Nd^{3+}	$24 \pm 4^\circ$
Dy^{3+}	$17 \pm 3^\circ$

^aIonic radii from R. D. Shannon, Acta Crystallographica **A32**, 751 (1976).

crystal orienter of the instrument, unlike the old one it replaces, is sufficiently massive to support the rather heavy cold head of a closed-cycle helium refrigerator capable of cooling a crystal sample to ~ 15 K. The chi circle is offset from the 2 θ - ω axis to allow attachment of the cold head. Alternatively, a furnace for studying high temperature phase transitions could be mounted on the instrument.

The new diffractometer has been aligned to the neutron beam and its operation has been tested. The computer programs for controlling the diffractometer and collecting data are being improved. The design is being developed for the necessary vacuum shroud and the crystal mount for the cold tip of the helium refrigerator, which is to be added later.

The new instrument with its more powerful computer and its improved mechanical design will allow collection of better data more efficiently and, when the high and low temperature devices are added, at temperatures not previously available to us.

10.2 Photoelectron Spectrometry with the use of Synchrotron Radiation

10.2.1 Resonance and Photoionization Processes in Metal Vapor Atoms

(M. O. Krause, A. Svensson¹, T. A. Carlson, F. Cerrina²)

During this period we studied resonance processes that involve two or more electrons or channels and simple photoionization processes that involve a single electron. Autoionization resonances are common in openshell atoms and we had previously characterized resonances in Mn, Ga, and Pb in which electrons of weakly bound inner subshells are excited into partially filled outer subshells in competition with the ionization of outer electrons. This work has now been extended to include the strong 5p resonance in Yb. In this case excitation proceeds to the empty 5d level which couples strongly with the

energetically close 4f level. Although the thrust of our work is aimed at openshell metal atoms, another closed shell atom, Ar, was included in our program to delineate a typical window resonance series.

Photoionization processes in which a single electron from the s, p and d subshells of the rare gas atoms are ejected had been studied previously by us and others. Several metal atoms have also been examined in the preceding years. We have now finalized a study of the 4d electrons of free Ag atoms over a wide energy range and, most importantly, we have expanded this work to include f electrons. The Yb atom proved especially suitable to measure the properties of the 4f electrons.

In all our experiments we measured the partial photoionization cross sections σ and the photoelectron angular distribution parameter β using our electron spectrometer at the synchrotron radiation facility in Stoughton, Wisconsin. Two electron energy analyzers were employed as in our previous work; however, most recently, we added a third analyzer to increase the data acquisition rate and, especially, to be able to provide a reference standard for the cross section determinations simultaneously with the data recording. Extensive use of the constant-ionic-state technique which we introduced earlier into our metal-vapor work was a key for being able to scrutinize resonance structures in great detail and with good reliability due to the rapid scanning ability that allowed the recording of up to 400 data points in less than one hour.

The measured dynamic parameters σ and β could in some cases be compared with theoretical predictions, in other cases they may serve as a testing ground for further theoretical developments.

The 4d electrons in silver. Silver like the other 1b elements has one s electron in the outermost level and a completely filled d subshell. Hence the d level splits into four terms which can, in principle at least, be

investigated individually. So far we have looked at the individual term components of this simple exponent of an open-shell atom at very low photon energies. However, the limited resolution of present monochromators did not allow us to resolve the components at higher photon energies, greater than about 25 eV. Hence we measured the dynamic parameters α and β as an average over the entire 4d manifold and compared the results with theoretical calculations that are available for the neighboring, closed shell atom Pd. In particular, we utilized a grasshopper monochromator which had just come on line at the Tantalus Storage Ring to penetrate into the region of the 4d Cooper minimum in the vicinity of 135 eV photon energy (energies above 110 eV can be effectively used with only this type of monochromator at Tantalus). The region of the minimum is especially important because it responds sensitively to the quality of the wavefunctions used in the theoretical models. The experiment at the higher energies concludes one phase of our Ag work, which involved measurements with 4 different monochromators at two different radiation sources, SRC at Stoughton and SURF II at NBS. Fig. 10.4 shows the results for the average β parameter from 14.5 to 140 eV photon energy. As seen from the graph, the Hermann-Skillman (HS) results³ for Ag agree satisfactorily but not exactly with the data, while the relativistic random phase approximation (RRPA) which includes many electron effects, compares well with the experiment. The fact that the RRPA results⁴ are for Pd is of minor significance: an approximate transformation of the results to Ag by contracting the curve along the energy scale by $Z^2(\text{Ag})/Z^2(\text{Pd})$ would lead to an improved agreement in the Cooper minimum. A comparison of the atomic data with data⁵ for Ag in the solid metallic state⁵ shows good agreement at the lower photon energies and a much shallower dip at the Cooper minimum for the metal than for the atom. The 4d electrons which are incorporated in the

Fig. 10.4. The photoelectron angular distribution parameter β of the 4d subshell of silver. Atomic data of our work are compared with the data for metallic Ag (Ref. 5) and theory, namely the RRPA results for the neighboring Pd (Ref. 4) and the HS results for Ag (Ref. 3). Note (a) the good agreement between the atomic values and the many-body (RRPA) model, and (b) the marked difference between the atomic and condensed matter data about the Cooper minimum.

conduction band of the metal obviously remain effectively localized, and hence atomic-like, but the small differences in the potential, and wavefunctions, that occur between the metal and the atom do manifest themselves in the region of the minimum. In addition, the region assigned to the 4d electrons in the conduction band could contain electrons of other symmetries, especially s symmetry, so that a pure d contribution cannot be extracted from the measurements on the metal.

A more detailed account of the Ag work, including a discussion of the cross section data is being prepared.

The 4f electrons in Ytterbium. The dynamic parameters of the p and d electrons in closed shell atoms, which present no severe calculational problems, have been shown to be well described by the RRPA model.⁶ However, the success of the model had not been demonstrated for the f electrons. Aside from Hg, another closed shell atom, Yb, offers itself for a test of theory. We measured both α and β for the 4f electrons of Yb and

the results are shown in Fig. 10.5 together with the theoretical predictions.⁷ Outside the 5p autoionization region the experimental and theoretical β parameters are seen to be in good accord. Similarly, the cross section *dape* *once* is found to be virtually the same for the theoretical and experimental data. Although a definitive test would require the determination of the *absolute* cross section, the present work shows that the RRPA model can be regarded as being realistic for predicting the properties of the f electrons.

The 3s autoionization resonance in argon.

This resonance and the analogous resonances in the other rare gases were observed originally in absorption. We now measured the variation of σ and β in a photoelectron

emission study through the first three resonances of the $3s^2 3p^6(^1S_0) + 3s3p^5 np(^1P_1)$ series, $n = 4, 5$ and 6. In a high resolution experiment, we distinguished the two available exit channels that leave the residual ion in either the $3s^2 3p^5(^2P_{3/2})$ or $3s^2 3p^5(^2P_{1/2})$ state. We characterized the resonance windows for the first time in great detail by using the constant-ionic-state technique. At the present, no theoretical calculations exist for this resonance, but a numerical evaluation of existing models for resonance with two closely lying exit channels can be anticipated so that experiment and theory can be intercompared.

The 5p resonance in Yb. As for Ar, this resonance occurs in a closed shell atom. However, the 5d subshell which is reached by the $5p + 5d$ resonance transition lies just below the 4f subshell, and hence a strong interaction takes place between the $5p + 5d$ transition and the direct ionization process $4f + eg, ed$. This autoionization resonance resembles those in transition series elements in which the resonance transition goes to a partially filled subshell, as for example, the 3d subshell in Mn. Similar to the $3p + 3d$ resonance transition in Mn reported recently⁸ the cross sections for the $4f_{7/2}$ and $4f_{5/2}$ subshells experience a strong enhancement, and the corresponding β parameters are subject to wide excursions. The RRPA calculations reveal the effects of the resonances, but a good agreement with the experimental data remains to be established by including all the important channel interactions in the calculation.

While the case of Mn could be regarded as a model for resonances in the low Z region involving $p + d$ transitions decaying into $d + ef$ channels, the case of Yb may serve as an ideal case to delineate $p + d$ transitions decaying into $f + eg$ channels in the higher Z region.

Fig. 10.5. Comparison of the measured dynamic parameters for atomic ytterbium with the theoretical predictions by the RRPA model (Ref. 7). Consider the values above 40 eV outside the 5p resonance region. The experimental σ values are normalized to theory at 40 eV.

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10.2.2 Photoelectron Dynamics of Free Molecules

(T. A. Carlson, M. O. Krause, A. Svensson,¹ F. Cerrina,² J. W. Taylor,³ T. A. Whitley,⁴ F. A. Grimm,⁴ B. P. Pullen,⁵ G. Von Wald³)

The purpose of this program is to help lay the foundation of photoelectron dynamics of molecules, through the use of synchrotron radiation coupled with angle-resolved photoelectron spectroscopy. Three crucial phenomena associated with photoelectron dynamics have been studied over the past year. They involve (1) autoionization, (2) the Cooper minimum and (3) threshold effects, especially shape resonances, for core shell electrons. Two studies mentioned in a previous annual report⁶ have been substantially expanded. They are concerned with autoionization in N_2O and the investigation of the Cooper minimum for a series of closely related halogenated methanes. In a third experiment the core shell 2p electrons of $SiCl_4$ have been measured for the cross sections and angular distribution as a function of photon energy, yielding excellent agreement with theory. Some of the more striking discoveries for these three investigations will be illustrated below.

Comprehensive study of autoionization. By use of the constant ionic state (CIS) method and employment of dual electron

spectrometers, an in-depth study of the autoionization in N_2O has been carried out with synchrotron radiation. In the CIS method the setting of a monochromator is advanced by computer in synchronization with changes in the electrostatic spectrometers so data are always collected at the kinetic energy of the photoelectron that corresponds to a given final ionic state. This method increases the data taking-capacity more than a hundred fold and allows for fine steps in the photon energy and a well resolved band pass for the photons, both essential for the study of autoionization. By mounting two electron spectrometers on a platform perpendicular to the photon beam it has been possible to measure simultaneously the intensity of photoelectron ejection, parallel and perpendicular to the polarization vector, from which measurements the angular distribution parameter, β , can be determined.

In the previous Chemistry Annual,⁶ preliminary results on N_2O were discussed. During the past year substantial new material has been gathered. CIS data from the integrated vibrational spectra have been obtained for the 1st band ($X^2\Pi$) of N_2O from a photon energy of 13.5 to 20.5 eV and from 17.0 to 20.5 eV for the 2nd band ($A^2\Sigma^+$) and from 10 to 23 eV for the third band ($B^2\Pi$). In addition CIS runs were made for the individual vibrational bands: (0,0,0); (1,0,0); and (2,0,0) for the $X^2\Pi$ state and (0,0,0); (1,0,0); and 0,0,1) for the $A^2\Sigma^+$ state. Photoelectron spectra showing the full vibrational spectra were taken at the peaks for most of the prominent resonances. These data comprise one of the most comprehensive angle-resolved photoelectron spectral studies of the autoionization to be made for a molecule.

Fig. 10.6 shows schematically the basic features of the autoionization processes in N_2O . There is one Rydberg series converging to the $A^2\Sigma^+$ state. This series feeds the $X^2\Pi$ state. A second Rydberg series converges to the $C^2\Sigma^+$ state and it can feed any of the three $X^2\Pi$, $A^2\Sigma^+$ and $B^2\Pi$ states. In addition

Figure 10.6. Schematic diagram of the processes leading to photoionization in N_2O . Direct photoionization goes to the final states corresponding to its first four bands in the photoelectron spectrum of the valence shells. In addition there are two step processes involving first resonant absorption into intermediate states indicated by dashes and then in two electron reorganization (autoionization) to the final state, the autoionized electron carrying away the same kinetic energy as a photoelectron. Note various vibrational states can be evolved in the final state. Not all possible processes are shown, but only examples of different types.

to branching to the various electronic states, there is also branching to the various vibrational states. In Fig. 10.7 are shown the CIS spectra for the (0,0,0) and (2,0,0) vibrational bands. It is clear from comparing the spectra that the angular

Figure 10.7. Some typical CIS spectra from N_2O . Note the dependence of the spectra on the vibrational state and angle as defined between the polarization vector and direction of the photoelectron.

distributions depend strongly on both which resonance is involved and to which final vibrational state the resonance state decays. Many detailed observations have been made. For example, the third and fourth resonant lines at a photon energy of 14.07 and 14.21 eV, which are reportedly⁷ due to Rydberg series leading to excited vibrational states, decay preferentially to the higher vibrational states. These lines also indicated the β values to be unusually high. It was also noted that the first window

resonance at 17.56 eV, which is associated with an $np\sigma$ state, decays preferentially to the $X^2\Pi$ state and that the β value goes through a minimum at the minimum in the resonance, while in contrast, the second window resonance associated with an $np\pi$ state decays nearly exclusively to the $A^2\Sigma^+$ state, while its β value shows a maximum at the minimum in the resonance.

The richness of observations from photoelectron spectroscopy that are now available for the different autoionization processes encourages the hope that a systematic characterization is possible and that a better understanding of the interaction of the different photoionization channels will be forthcoming.

Freons and the Cooper Minimum. It has been observed in the study of the cross sections of certain atomic orbitals as a function of photon energy that a minimum occurs. This minimum, known as a Cooper minimum,⁸ arises because the matrix element describing a transition to a major channel undergoes a change in sign as a function of photon energy. For this to occur, the initial orbital should possess a radial node. It has also been determined that certain molecular orbitals, particularly lone pair orbitals that most closely mimic atomic behavior, also show the presence of a Cooper minimum. For example, compounds containing chlorine such as CCl_4 show the presence of a Cooper minimum.⁹ In contrast,¹⁰ the lone-pair orbitals of CF_4 do not give rise to a Cooper minimum, which is reasonable because the $2p$ orbital of a fluorine atom does not have a radial node.

In the present investigation a series of Freons (CCl_xF_{4-x}) have been measured for a photon energy just above the first ionization potential to 80 eV. From these experiments the cross sections and angular distribution parameter, β , have been determined for most of the individual valence orbitals. (The β values are also affected by the Cooper minimum, which for an ideal atomic case,

photoionization of a $3p$ orbital, will lead to a zero value at the minimum.) As anticipated, Cooper minima are most clearly reflected in the study of those orbitals designated by molecular orbital theory to be chlorine lone-pair orbitals. There is a distinct drop in the β value plotted as a function of photon energy at approximately 43 eV. Some variation in the energy of the minimum is found, dependent on the photoelectron energy and the nature of the initial orbital, but the variation is usually within a few volts. For some of the lone pair orbitals (i.e., the t_1 of CCl_4 and the a_2, e of CCl_3F) the β dips close to zero. In other cases (the b_1 of CCl_2F_2 and the e of $CClF_3$) the β values do not reach zero at the Cooper minimum. In still others (the a_2, a_1 of CCl_2F_2) the dip is even smaller. It is postulated that the extent to which β drops to zero at the Cooper minimum constitutes a criterion for how close a molecular orbital approaches atomic like behavior. This idea is currently being correlated to such molecular orbital character as population density.

Orbitals other than the lone-pair orbitals have also been examined, and in some cases of bonding orbitals a partial Cooper minimum can be observed. In such cases the orbital usually contains a high contribution of chlorine $3p$ character. In addition to Cooper minima, possible shape resonances are noted as evidenced by excursions in the β value at photon energies from 15 to 25 eV. It is hoped that a systematic study of the Cooper minimum and shape resonance in the homologous series of fluoro-chloro methanes will provide a deeper understanding of the photoelectron dynamics of tetrahedrally constructed molecules.

Threshold Effects on the $2p$ subshell of $SiCl_4$. A number of experimental studies and theoretical calculations have illustrated that cross sections and angular distribution parameters measured just above the ionization potential of core shells are strongly influenced by the molecular potential,

particularly with regard to shape resonances.¹¹ In our present work we have looked at the cross section and β values from photoionization in the 2p shell of silicon for SiCl_4 . An earlier study¹² on the valence shells revealed the presence of strong shape resonances. Likewise, shape resonances are present in the photoionization of the Si 2p subshell as shown by calculation based on the multiple scattering X_α method. In Fig. 10.8 comparison between calculated and experimental values gives excellent agreement.

The good agreement in Fig. 10.8 gives confidence to our ability to describe the effect of shape resonances in SiCl_4 . It is thus important to note that the calculation on the cross section for 2s shell gives similar results as those for the 2p shell

except for the magnitude and the absence of a central peak due to resonance in the e channel. Because the cross sections for the 2p shell allows for transitions to both t_2 and e channels, while symmetry restrictions allow for only contributions to the t_2 channel in the case of the 2s subshell, the difference in the spectra can be taken as due to the e channel alone. By comparing behavior of the 2p and 2s subshells of silicon, we can in principle unravel the contributions of the different channels. A study of the 2s shell would thus allow for a unique test of the different contributions of more than one channel in photoionization. Such an experimental test is being planned.

Figure 10.8. Plot of the angular distribution's parameter, β , as a function of photon energy for the Si2p subshell of SiCl_4 . The ionization potential is taken as 190.3 eV. The upper portion of the plot is from experimental data taken with synchrotron radiation. The calculated values shown below have been obtained by use of the X_α multiple scattering method.

1. Graduate student, Royal Institute of Technology, Stockholm, Sweden.
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3. University of Wisconsin, Madison, Wisconsin.
4. University of Tennessee, Knoxville, Tennessee.
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11. THEORETICAL CHEMISTRY

Six topics are covered in this Part. Sections 11.1 and 11.2 are concerned with statistical mechanics of lattice fluids and fluid mixtures, respectively. Both microscopic structure and thermodynamic properties are treated. Section 11.3.1 is concerned with how energy in one vibrational mode of a molecule is transferred to other degrees of freedom of the molecule. Sections 11.3.2, 11.4, and 11.5 are concerned with scattering. Section 11.3.2 treats the transfer of energy between a system of molecules and neutrons. Section 11.4 discusses the effects of a beam of electrons on the conductivity of a system, and it also discusses the ionization in the system produced by the electron beam. In Section 11.5, a number of mechanisms are discussed by means of which a beam of electrostatically neutral atoms may produce electromagnetic radiation when it collides with a solid.

11.1 An Application of the Statistical Mechanical Monte Carlo Method

(E. Johnson)

The Monte Carlo method has become a very prominent and useful part of statistical mechanics. Some of the results which are obtained from the Monte Carlo method in a rather straightforward manner can be obtained experimentally only after performing difficult experiments. Because of this, Monte Carlo results often facilitate the analysis of experimental data. For most systems, the results of applying techniques of statistical mechanics based on integral equations are not exact. The reason for this is that most of the integral equations used are approximate. Monte Carlo results are usually accurate, so the accuracy of integral equation results may be determined by comparison with Monte Carlo results.

The main reason for doing Monte Carlo studies in the Structural Chemistry Group at this time is to evaluate the accuracy of a pair of statistical mechanical integral equations which was derived recently.¹ These equations differ from most statistical mechanical integral equations used for calculations, because they are exact and they may be solved without introducing approximations into the form of the equations. The first equation of this pair relates the pair distribution function to the pair potential and the three particle distribution function. The second equation relates the three particle distribution function to the pair

distribution function. These equations are applicable to classical systems which have a pairwise additive potential energy function. The second equation has only been solved on a lattice.² As the unit cell of a lattice fluid approaches zero,³ the properties of the lattice fluid approaches the properties of a "regular fluid". Solutions to the second equation are obtained by using expansions in terms of a complete set of basis functions. Since no basis set used is perfect, the solutions obtained are not exact, but solutions accurate to nine significant figures have been obtained for certain lattice gases.²

Since Monte Carlo results were desired for lattice fluids, it was necessary to adapt the Monte Carlo method to this case, because apparently no Monte Carlo particle distribution functions for lattice fluids have been published.⁴ The accuracy of the Monte Carlo pair distribution functions for lattice gases was checked by comparing Monte Carlo pair distribution functions for the two-dimensional nearest neighbor interaction lattice gas with exact pair distribution functions for this system. The statistical mechanics of the two-dimensional nearest neighbor interaction lattice gas is known exactly when half of the lattice sites are occupied.^{2,5} Monte Carlo results which are accurate to within one percent of the exact results are not difficult to obtain.⁶ The accuracy of the distribution functions of the pair of exact equations mentioned above was examined

by comparing pair distribution functions obtained from them for the two-dimensional next nearest neighbor interaction lattice gas with Monte Carlo pair distribution functions for the system.^{2,6} The integral equation results were within the limits of uncertainty of the Monte Carlo results.

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11.2 Statistical Mechanical Studies of Fluid Mixtures

(E. Johnson, J. D. Kovac¹)

There appears to be only two published reports on the treatment of molecular fluid mixtures using integral equations of statistical mechanics.^{2,3} In both reports, atoms were assumed to be hard spheres and molecules were assumed to consist of fused hard spheres. Also, both reports used the Reference Interaction Site Model (RISM) integral equation. Some of the problems associated with using hard sphere interactions for atoms and molecules are discussed in reference 3. It is best to use intermolecular pair potentials which have regions of attractive interaction. The microscopic structure and thermodynamic properties presented in references 2 and 3 were obtained indirectly. A direct procedure for obtaining structural information for systems with a pair potential that is not of the fused hard sphere type was presented several years ago.^{4,5} A computer

program based on this procedure was written recently for mixtures.⁶ This procedure largely overcomes the problems found using the fused hard sphere procedure or indirect method. The results obtained using the direct method are in better agreement with results of computer simulations.⁶

Statements in reference 7 indicate that the thermodynamic pressure cannot always be obtained solely from the RISM compressibility equation. These statements are based on the fact that for certain thermodynamic states, the RISM equation does not have a solution. This region of no solution corresponds to the existence of thermodynamic equilibrium between two or more phases. We have shown that these regions of phase equilibrium may be avoided when the pressure is obtained from the RISM compressibility equation.⁶ Our procedure is based on the fact that the RISM compressibility equation pressure is apparently a state function. This state function behavior of the RISM equation was demonstrated numerically. This procedure allows pressure to be determined solely from the RISM equation.

Our work on mixtures has two main goals. The first is the treatment of a system which contains surfactant, water, and inorganic salt molecules. The second is the treatment of ionic solutions.

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11.3 Chemical Dynamics of Molecular Processes

11.3.1 Theoretical Investigation of Vibrational Energy Transfer in Polyatomic Molecules

(S. K. Gray¹, M. S. Child¹, D. W. Noid)

Knowledge of the relation between classical and quantum mechanics deepens our understanding of the nature of molecular dynamics which lies by virtue of its mass and length scales on the boundary between classical and quantum behavior. Classical S matrix theory provides one of our most precise sources of insight, which was applied to develop a new theory² for the Franck-Condon factor amplitudes,

$$S_{N_L N_U} = \langle N_L | N_U \rangle = \int dx \langle N_L | x \rangle \langle x | N_U \rangle, \quad (1)$$

that determine the vibrational structure in electronic transitions.

The theory outlined below is restricted to situations in which the classical motions on both initial and final potential surfaces are quasi-periodic³. Thus, both initial and final quantum states are represented by quantized invariant tori, the phase points of which are denoted by (p_L, x_L) and (p_U, x_U) , respectively. However, we will also find it convenient to describe the tori of angle-action variables (n_L, q_L) for the lower and (n_U, q_U) for the upper surface.

Following the general arguments of Miller [4], the two tori are connected by a set of N phase points in a common cartesian space, satisfying the Franck-Condon conditions

$$(p_L^{(k)}, x_L^{(k)}) = (p_U^{(k)}, x_U^{(k)}), \quad k = 1, \dots, N. \quad (2)$$

The classical S matrix theory is developed solely in terms of the associated semiclassical phases ϕ_k and Jacobian factors J_k given in the present context by

$$\phi = F_{2L}(n_L, x_L^{(k)}) - F_{2U}(n_U, x_U^{(k)}) \quad (3)$$

and

$$J_k = (2\pi)^4 \frac{\partial(n_{1U}, n_{2U}, \dots)}{\partial(q_{1L}, q_{2L}, \dots)} \quad (4)$$

where F_{2L} and F_{2U} are the F_2 type classical generators of the canonical transformations from cartesian to angle-action variables on the lower and upper surfaces, respectively. J_k represents the variation of upper state action variables with respect to lower state angles (at fixed n_L). The numerical problems lie in determination of the tori and the calculation of ϕ_k and J_k at each root phase point.

Primitive semiclassical approximation.

The simplest and only unique semiclassical approximation is the primitive form,³ which for two degrees of freedom reads

$$S_{n_L n_U}^{\text{PSC}} = \sum_{k=1}^N (2\pi i) |J_k|^{-1/2} \exp(i\phi_k + i\sigma_k \pi/4) \quad (5)$$

where σ_k takes the values -2, 0, or 2, according to whether ϕ_k is a minimum, a saddle point, or a phase maximum with respect to variation in the initial angle space, q_L .

While simple to apply, equation (5) suffers from the notorious defect that it diverges for phase points close to the caustics of the classical motion. It is therefore typically only as accurate as a JWKB description of the parent wavefunction.

Uniform approximation. The purpose of a uniform approximation is to combine the classically determined quantities $\{\phi_k, J_k\}$ in a form designed to remove the singularities present in the primitive approximation. The functionality of the approximation depends on the number of contributing trajectories (i.e., the number of $\{\phi_k, J_k\}$ combinations) and the dimensionality of the observation space. In the present two-dimensional

Franck-Condon problem, which typically gives rise to four trajectories, the appropriate general form is the hyperbolic umbilic approximation outlined by Connor.⁵

The uniform semiclassical theory was shown to give excellent agreement with exact quantum mechanics for our chosen model, with a substantially superior performance to the frozen gaussian method,⁶ although the latter is of useful accuracy for many purposes. This suggests that the residual weakness of the FG method is not attributable to deficiencies in the semiclassical approach, but rather to its global treatment of motion on the upper state surface. Both methods employ Franck-Condon transitions from the same lower state phase space orbit, but only the classical S matrix method recognizes the specific quantized tori on the upper state potential.

It is also pertinent to examine other strengths and limitations of the two semiclassical methods. The FG approach has major advantages with respect to flexibility and ease of operation. In particular, no distinction is made between classically allowed and classically forbidden transitions, our FG results obtained for some of the latter

being comparable in accuracy with those shown in Table 11.1. There is also no difficulty in extension to systems with more than two degrees of freedom. The treatment of forbidden transitions in the present method could be handled by analytic continuation.

Finally, we note that both methods have been tested here only for transitions from the zero-point level of a separable harmonic potential. Of these constraints, only relaxation of the separability would pose other than trivial complications for the present method, and non-separability could readily also be handled. The frozen gaussian method can easily be adapted to excited harmonic initial states, but does become more involved when anharmonicity or non-separability in the lower surface is introduced owing to the necessity of obtaining and/or approximating with gaussians the initial state wavefunction.

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2. S. K. Gray, M. S. Child, and D. W. Noid, Mol. Phys. (in press).

TABLE 11.1

Comparative quantum (Q) semiclassical (SC) and frozen gaussian (FG) upper state eigenvalues, $E_{N_{\mu}}$, and Franck-Condon factors $|S_{N_{\mu}, N_{\mu}}|^2$ for $N_{\mu} = (0, 0)$. The entries PSC and USC refer to the primitive and uniform approximations, respectively.

$N_{\mu 1}$	$N_{\mu 2}$	$E_{N_{\mu}}$		$ S_{N_{\mu}, N_{\mu}} ^2$				
				Q	FG	Q	PSC	USC
0	1	2.2781	2.2784	2.31	0.081	0.151	0.082	0.05
1	1	2.9583	2.9584	2.98	0.083	0.130	0.085	0.08
0	2	3.5479	3.5482	3.56	0.127	0.175	0.132	0.12
2	1	3.6347	3.6352	3.63	0.044	0.133	0.044	0.04
1	2	4.2162	4.2164	4.23	0.104	0.139	0.104	0.10
0	3	4.8043	4.8047	4.81	0.123	0.180	0.123	0.14
1	3	5.4597	5.4599	5.49	0.073	0.147	0.077	0.08
0	4	6.0463	6.0466	6.08	0.079	0.228	0.082	0.08

3. See, for example, D. W. Noid, M. L. Koszykowski, and R. A. Marcus, *Ann. Phys. Chem.* **32**, 267 (1981).
4. W. H. Miller, *Adv. Chem. Phys.* **30**, 77 (1976).
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11.3.2 Semiclassical Calculation of Neutron Molecular Spectra for Polyatomic Molecules

(B. Chang,⁹ D. W. Noid)

There is a growing recognition that neutron spectroscopy is rapidly becoming an important, and sometimes even a unique, experimental technique for probing the structures and the internal motions of hydrogen containing molecules.¹ The molecular systems which can be probed by neutron spectroscopy range from the very small, e.g., H_2O , to the very large, e.g., an amorphous solid of hydrocarbon polymers. It is well known that for even very simple molecules such as CH_4 or C_6H_6 , a large percentage of the modes are neither infrared nor Raman active and have been termed silent modes.² Exact quantum mechanical techniques for the calculation of neutron spectra, however, have been applied successfully only to the very small molecular systems.³ The bottleneck in the quantum mechanical calculations of scattering processes involving molecules having many atoms is the problem of needing a large number of internal basis functions to expand the wavefunction. Recently, we developed a semiclassical method for obtaining the partial differential cross section of the neutron collision from the cross correlation functions of the vibrational-rotational motions of the target molecule.⁴ In particular, we applied our technique, developed first in infrared spectroscopy,⁵ of using classical trajectories, corresponding to quantum states, to calculate the cross correlations of the internal motions of the molecule. This technique has met considerable success in

calculating the infrared spectra of model systems and was found to be in excellent agreement with exact quantum calculations.

The classic work of van Hove⁶ established the formal correspondence between the total partial differential cross section of a neutron-polyatomic molecule collision and the correlation functions of the vibrational-rotational motions of the target molecules.

The formal theory, which was also derived later, by Gordon,⁷ Marshall and Lovesay,¹ and McQuarrie⁸ gives the total partial cross section as

$$\frac{d^2\sigma}{d\Omega dE'} = \frac{k^1}{k} \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt e^{-i\omega t} \phi(t), \quad (1)$$

where

$$\phi(t) = \sum_{ll'} \sum_{vv'} \overline{\langle \hat{b}_{lv} \exp\{-i\mathbf{Q} \cdot \hat{\mathbf{R}}(0)\} \hat{b}_{l'v'} \exp\{i\mathbf{Q} \cdot \hat{\mathbf{R}}(t)\} \rangle}_{lv}$$

Equation (1) is the first order Born approximation of the time dependent Schrodinger equation for a neutron scattered by a collection of interacting molecules.

The time correlation function $\phi(t)$ is the correlation function of the scattering amplitude, $\hat{b}_{lv} \exp(i\mathbf{Q} \cdot \hat{\mathbf{R}}_{lv}(t))$. In infrared spectroscopy, the analogous and the more familiar correlation function is the correlation function of the dipole moment function of $R_{lv}(t)$, in particular $\mu(R_{lv}(t))$. Comparing the roles of $\phi(t)$ and $\langle \mu(0)\mu(r(t)) \rangle$, note that $\phi(t)$ gives the total partial differential cross section in neutron spectroscopy and that $\langle \mu(0)\mu(r(t)) \rangle$ gives the power spectrum in infrared spectroscopy. The theory relating physical observables to their appropriate quantum mechanical time correlation functions is presented in a unified way by Gordon.⁷

In the last few years, much work has been devoted to the semiclassical calculation of infrared spectra. A concise review of this

work can be found in Ref. 5. For the calculation of infrared spectra with both linear and nonlinear dipole moment functions, it has been found to be more accurate if the mean quantum number is used for the calculation. This choice of a correspondence principle for spectral intensity and frequencies is found to be extremely accurate in the cases previously studied. It also turns out that for the Morse oscillator, the transition frequencies are exactly the same as the quantum mechanical ones.

In order to test the validity of this method for neutron spectra, the semiclassical results were compared to the quantum mechanical results for two models of HCl.⁴ We found that the semiclassical results were in excellent agreement with the quantum mechanical results for small angle scattering ($k \ll \lambda^{-1}$ where λ is the oscillator wavelength). We also found that the semiclassical results of the Morse oscillator were significantly better than the results given by the quantum mechanical harmonic oscillator approximation. Thus, this semiclassical method may potentially become a valuable tool for accurate calculations of systems described by realistic intramolecular potential surfaces.

In future work, we plan to extend the semiclassical method to treat the large angle scattering cross sections more accurately through use of a better correspondence principle, and to extend this work to realistic models of polyatomic molecules and polymers.

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9. Lawrence Livermore National Laboratory, Livermore, CA 94550.

11.4 Nonlinear Energy Deposition by Intense Electron Beams

(O. H. Crawford, R. H. Ritchie¹)

Ionization and transient conductivity of a material under irradiation by an intense electron beam can effect beam propagation in the medium and alter the energy deposition rate. This year, our efforts in this area have focused on the problem of analyzing the experiments of Vaisburd and Tavanov.² These workers measured the electrical conductivity of thin samples of alkali halide crystals during irradiation by intense MeV electron beams.

In order to determine accurately the spectrum of secondary electrons generated in the samples, we have revised extensively our computer program for calculating the electron slowing-down-cascade spectrum in extended solids. We have employed differential cross sections for production of secondary electrons from each shell that are correlated for exchange effects in a consistent manner. The semi-empirical form of the shell cross sections used in the earlier form of the code are corrected in the neighborhood of the threshold energy for each shell using experimental photoabsorption data. The contribution of Auger electrons from the decay of each shell to the electron slowing-down spectra is included by computing the number of holes generated in each shell by all secondary electrons for which this is energetically possible. Intra-atomic electron-hole cascades are then assumed to occur,

giving rise to spectra of Auger electrons characteristic of each atomic constituent.

We have improved our computer programs for transport of subexcitation electrons (i.e., conduction electrons whose energy is too low to produce further ionization) in the following ways. Scattering by acoustical photons was found to be important, and is now taken into account. The increase in lattice temperature during irradiation and its effect on electron-hole recombination and mobility are now incorporated into the code. The time dependence of the conductivity is treated correctly so that the transient response at the beginning and the end of a beam pulse can be computed.

Comparison was made with the conductivity measurements of Vaisburd and Tavanov² on NaCl subjected to pulses of a 0.3 MeV electron beam at current densities of 1-400 A/cm². Only range-thin samples (thickness < 0.3 mm) were considered. The theory for the steady-state conductivity (during irradiation) was found to agree qualitatively with the experiment, although the quantitative agreement is not yet complete. Also, the scaling of conductivity with beam current I_B is in approximate agreement, the theory and experiment giving $(I_B)^{0.5}$ and $(I_B)^{0.4}$, respectively.

The evaluation of the conductivity with time is also of interest. The present theory predicts a response time on the order of 10 ps (assuming a 1 kA/cm² 4.5 MeV beam) which is consistent with the observations.² We must point out, however, that the decay of the conductivity is not exponential, and has a long tail, so the concept of response time should be treated with caution. Another important point is that the response time decreases with increasing beam current density. This is because the density of holes goes up, thereby decreasing the lifetime of thermal electrons. This is why the conductivity response time discussed here is so much shorter than the ones observed in classical (low-current) photoconductivity measurements.

Calculations were also performed for higher beam energies and intensities, for comparison

with future experiments. One interesting feature of the model, which needs to be tested experimentally, is that the $(I_B)^{0.5}$ scaling discussed above for the conductivity is predicted to change to a linear scaling for higher beam current densities. In the case of a 4 MeV electron beam on range-thin NaCl, this change occurs at 10⁴ A/cm². However, several important problems remain to be solved before the theory can be applied with confidence at these higher beam intensities.

This research was sponsored by the Naval Surface Weapons Laboratory.

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11.5 Optical Emission from Atom-Bombarded Surfaces

(O. H. Crawford, R. H. Ritchie¹)

It has long been appreciated that light is emitted in the bombardment of solids with energetic charged particles. However, prior to this work, the possibility of similar emissions from neutral atom-solid bombardment received little attention.

In this initial period of the project, basic theories were developed for several mechanisms by which light is predicted to be emitted when energetic atomic beams strike and penetrate solid targets. Results are presented below under the general headings of transition radiation, surface plasmon generation, optical bremsstrahlung, and luminescence of insulating layers.

Transition Radiation. The Hamiltonian operator H for the system of interest may be written as follows:

$$H = H_{\text{Atom}} + H_{\text{Solid}} + H_{\text{Field}} + H_{\text{AS}} + H_{\text{AF}} + H_{\text{SF}} \quad (1)$$

where the first three terms are for the atom (or other projectile), the solid, and the electromagnetic field, while the remaining terms describe the pairwise interactions.

The interaction between the solid and the electromagnetic field is large in the optical region of the spectrum. Therefore, in the following, we assume it is taken account of exactly (at least in principle) in calculating the field.

We solve the time-dependent Schrodinger equation to first order in H_{AF} (considered as a perturbation) while ignoring H_{AS} , for an atom approaching and penetrating a solid. The probability that the atom is excited to state j and that a photon is emitted in frequency interval $d\omega$ into solid angle $d\Omega$ is then determined. We find that the emission probability in the $0 \rightarrow 0$ case, where the atom remains in the ground state, is identical to the probability of transition radiation from a bare proton or electron, except for a factor $|F_{00}(k)|^2$, where F is a dynamic form factor,

$$F_{j0}(k) = \langle j | 1 - e^{-ik \cdot r} | 0 \rangle. \quad (2)$$

This result is the same as would be given by treating the atom as the equivalent (spherically symmetric) static negative charge cloud and positive nucleus. However, the bulk of the transition radiation comes from the $j \neq 0$ terms. We conclude that the ratio of transition radiation from H atoms, to that from protons or electrons at the same velocity, is given roughly by

$$\frac{Y(H)}{Y(H^+)} = \sum_j |F_{j0}|^2 = 2|F_{00}|^2 = (ka_0^2)^2 = \left(\frac{\hbar\omega}{V}\alpha_0\right)^2 \quad (3)$$

where $\hbar\omega$ is the sum of the mean excitation energy of the atom and the observed photon energy.

As an example, for transition radiation at 2000 Å from a 100 MeV beam, Eq. (3) gives

$$\frac{Y(H)}{Y(H^+)} \approx 2 \times 10^{-4}. \quad (4)$$

Surface Plasmon Generation. Besides generating transition radiation, charged

particles striking metal surfaces can excite surface plasmons. These can decay either radiatively (given some surface roughness) or nonradiatively. We have, during this reporting period, made a preliminary investigation of the probability of surface plasmon generation in atom-solid collisions, considering two different mechanisms.

The first mechanism considered, direct excitation by the atom, is caused by the interaction of the projectile with the electromagnetic field. This mechanism is described in the same way as the generation of transition radiation, discussed above, except that here it is the surface plasmon component of the field that enters the calculation. The expression found for the probability that a surface plasmon of wavevector k is generated and that the atom undergoes a $0 \rightarrow j$ transition is similar to that for the excitation of a surface plasmon by a bare proton or electron, except for multiplication by the square of the modulus of a form factor.

A second mechanism for surface plasmon generation is as follows. The atom is ionized by interaction with the medium and subsequently the proton and electron may generate a surface plasmon. The probability of P_k of generation of a surface plasmon of wavevector k was found in a derivation that ignores collisions subsequent to ionization and neglects retardation. The result is strongly dependent on the angle α between the velocities of the electron and proton after ionization. For small α , P_k goes to zero as $\sin^2 \alpha$ because of cancellation of the fields of the electron and proton, whereas as α approaches $\pi/2$, P_k increases without limit because the electron travels nearly parallel to the surface, which is optimal for surface plasmon generation.

For the total yield, P_k is summed over all k and α (weighted by the differential ionization cross section). We find the yield to be less than that from the direct mechanism discussed above, when only angles $\alpha < \pi/4$ are

considered. However, inclusion of larger angles leads to an infinite yield, due to the singularity mentioned above at $\pi/2$. Of course, this model is unrealistic because collisions past the first are ignored, but the result suggests that significant yields of surface plasmons might be generated by the mechanism under consideration. A more complete model would include cascade electrons, as well as electrons detached from the beam.

Optical Bremsstrahlung. Bremsstrahlung from a neutral H beam penetrating a solid will arise predominantly from collisions between the projectile electron and (screened) atomic nuclei of the medium. The bremsstrahlung yield from a single collision may be shown to a good approximation to be proportional to

$$\sum_j \int \frac{dK}{K} \left| F_{j0}^H(K) \right|^2 \left| F_{00}^T(K) \right|^2$$

where the sum is over the atom's final states (the important ones being in the continuum), the two form factors F^H and F^T are for beam and target atoms, respectively, and the proportionality factor is insensitive to whether the electron is initially bound or free. Employing the Thomas-Fermi model for the target leads to the result that the integrand in the above expression is negli-

gible unless $K \gtrsim Z^{1/3} a_0^{-1}$ where Z is the target's atomic number. For these (large) values of K , $F_{j0}^H(K)$ may be replaced by a free-electron form factor without much error. Therefore, the single-collision bremsstrahlung yield from a ground state H atom is approximately the same as for an electron of the same speed. In subsequent collisions, after the projectile is excited or ionized, the comparison is even closer, so we may conclude that the total bremsstrahlung yields of swift hydrogen and free electrons are similar.

Luminescence of Insulating Layer. Insulating media have an additional mechanism for optical emission when subject to ionizing radiation. Because of the band gap, nonradiative decay of excited electronic states is inhibited, giving time for fluorescence to occur.

In measuring optical emissions from metals under electron bombardment, it is typically found that fluorescence from an oxide layer overwhelms that from other sources until the surface is thoroughly cleaned in vacuo. Such emission should undoubtedly be significant during bombardment by atoms as well.

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1. Health & Safety Research Division, ORNL.

12. NUCLEAR WASTE CHEMISTRY

Several research topics in the Chemistry Division are directly related to chemical problems of high-level radioactive waste disposal. Safety analyses of radioactive waste disposal depends upon reliable prediction of radionuclide migration in the event of penetration of the nuclear waste repository by groundwater and flow of the groundwater to the accessible environment. Prediction of the interaction of migrating nuclides with host geological formations is dependent upon knowledge of the speciation of the nuclides. In Section 12.1, research is described concerning the effects of valence states of the nuclides on the sorption of these nuclides by minerals in the formations. In particular the sorption behavior of Tc(VII) and Np(V) is discussed. This type of information is used by the U.S. Nuclear Regulatory Commission (NRC) for the assessment of the performance of proposed repository sites. In the other sections, other types of chemical support for assessment activities are described. For example, in Section 12.4, evaluation of parameters for the migration of technetium and uranium in host-rock formations is given.

12.1 Valence Effects on Sorption of Nuclides on Geological Materials

(R. E. Meyer, W. D. Arnold, F. I. Case)

Estimation of the rates of migration of nuclides from nuclear waste repositories requires knowledge of the interaction of these nuclides with the components of the geological formations in the path of the migration. These interactions will be dependent upon the valence state and speciation of the nuclide. If the chemical state of the nuclide is not known in sorption experiments, then use of the data for safety analysis is open to question. Experiments designed to measure interaction of multi-valent nuclides and minerals must therefore include some form of valence state and speciation control. In addition, the speciation of the the sorbed products should be determined, if possible. The reaction path and kinetics of sorption reactions should be studied in enough detail in the laboratory to assess the nature and extent of sorption and precipitation reactions in actual repository situations.

In order to help determine the nature of the speciation of Tc(VII) and Np(V) reactants and products in sorption reactions, the sensitivity of sorption to groundwater composition was studied. For both Tc and Np, sorption on basalt was much greater from 0.1 M NaCl than from synthetic groundwaters.

Because this effect was observed for both Tc and Np, it was hypothesized that the chloride ion promotes attack of one or more of the phases of basalt in such a way as to make ferrous ion accessible to the nuclides. The ferrous ion is thought to be the component of basalt that can reduce Tc(VII) and Np(V) to lower valence states which are more easily sorbed. Also, reduced valence states of these nuclides can form insoluble oxides if the nuclides are present in sufficient concentration. The presence of carbonate ion reduces sorption of Np(V) on basalt and other minerals in a pH range where carbonate complexes are formed.

Sorption of Tc on basalt is unusually sensitive to oxygen and to the surface state of the basalt. Only when the strictest oxygen-removal techniques were used were we able to demonstrate any sorption of Tc.

Safety analysis of technetium migration requires knowledge of the solubility and speciation of Tc(IV) in groundwaters. A detailed examination of the literature revealed that the data on hydrolysis and solubility of technetium (IV) oxides and hydroxides were contradictory. Studies were therefore initiated to determine the concentration and nature of the species in equilibrium with technetium (IV) oxide. Initial efforts were made with technetium (IV) oxide formed by reduction with hydrazine. A tenta-

tive solubility of about 2×10^{-8} mol/L Tc was determined in equilibration experiments with a synthetic groundwater formulation.

The results of these and previous experiments from this project are used to assess the probability of occurrence of reduction and sorption reactions in repository environments thought to be reducing. One of the important conclusions is that at the relatively low temperatures of far field interactions, it will be quite difficult to demonstrate reduction of technetium unless the nature of the minerals in the water flowpath are known and their surfaces are characterized.

The results of this project are presented in topical reports which are prepared annually.^{1,2,3}

1. R. E. Meyer, W. D. Arnold, F. Case, S.-Y. Shian, and D. A. Palmer, Valence Effects on Adsorption - A Preliminary Assessment of the Effects of Valence State Control on Sorption Measurement, NUREG/CR-2863 ORNL-5905 (1983).
2. R. E. Meyer, W. D. Arnold, and F. I. Case, Valence Effects on the Sorption of Nuclides on Rocks and Minerals, NUREG/CR-3389 ORNL-5978 (1984).
3. R. E. Meyer, W. D. Arnold, and F. I. Case, Valence Effects on the Sorption of Nuclides on Rocks and Minerals. II., NUREG/CR-4114 ORNL-6137 (1985).

12.2 Uncertainties in Assessment of Long-Term Collective Dose and Health Effects from Geologic Disposal of High-Level Waste

(R. E. Meyer, G. D. O'Kelley, D. C. Kocher¹)

Work on this topic in the Chemistry Division has emphasized geochemical considerations of significance to licensing action by the U.S. Nuclear Regulatory Commission (NRC) concerning high-level nuclear waste repositories. Activities have involved various technical issues related to the NRC final

rule on disposal of radioactive waste in geologic repositories. The results of these considerations are presented to the NRC as informal or formal (NUREG) reports.

During the past year a NUREG report² was completed which presented a detailed study of the chemical factors involved in the interaction of water-mobilized nuclides with the geologic formations of the host formation, including sorption phenomena, redox processes, hydrolysis, complexation, solubility, and formation of polymeric and colloidal forms of the nuclides. A discussion and review was given in the report of these factors along with their pertinence to the migration of the nuclides and development of the computer codes for the prediction of this migration.

In addition a preliminary section of another report was completed which dealt with the changes in groundwater composition that may occur as the groundwater migrates to the waste package in the event of the breach of a repository. Possible changes in composition of the groundwater due to reaction at high and low temperatures were discussed. Particular emphasis was given to possible changes of redox properties of the system as the groundwater migrated.

1. Health and Safety Research Division.
2. G. D. O'Kelley and R. E. Meyer, The Role of Geochemical Factors in the Assessment and Regulation of Geological Disposal of High-Level Radioactive Waste, NUREG/CR-3490 ORNL-5089 (1984).

12.3 Survey of Metabolic Data Appropriate to High-Level Waste Disposition: Chemical Species in the Environment

(R. E. Meyer, G. D. O'Kelley, K. F. Eckerman,¹ R. W. Ledgett¹)

The purpose of this project is to provide the High-Level Waste Licensing Branch of the U. S. Nuclear Regulatory Commission (NRC) with a limited evaluation of the influence of

Division was preparation of a review of the available literature on the chemical forms of these four elements at concentrations in the environment accessible to man. To this end, a large number of references were identified and examined for information on this subject, and a final NUREG report has been published. A number of research needs were identified in this report. Some of these are: (1) More experimental determinations of formation constants for actinide complexes, especially carbonates, in the pH region of natural waters. (2) Increased attention to experimental determination of the presence of colloidal particles, and if present, to the composition of colloidal particles in groundwaters. (3) A critical review and examination of experimental methods of determining speciation at trace levels in the laboratory and in the field.

1. Health and Safety Research Division.
K. F. Eckerman, R. W. Leggett, R. F. Meyer, and G. D. O'Kelley, Determination of Metabolic Data Appropriate for HLW Dosimetry (ICRP-30), I., NUREG/CR-3577 ORNL/TM-8939 (1984).

environment. It is not possible to demonstrate that the quantities of radionuclides that can be transported from the repository and translocated within acceptable limits. Particular emphasis has been given to sorption of technetium and uranium on various samples of crushed basalt of the type found at the Hanford, Washington, proposed site for high-level waste.

During the past year experiments included determination of sorption isotherms of technetium and uranium on crushed basalt under oxic (air present) and anoxic (argon atmosphere) conditions. No significant sorption of technetium was observed under oxic conditions, and moderate sorption was observed under anoxic conditions if great care was taken to remove the last traces of oxygen from the synthetic groundwaters used in the experiments. There was little effect of changing the temperature from 25°C to 60°C. Moderate sorption was observed after 14-day contact periods and after 50-day contact the sorption was observed to increase slightly. Sorption isotherms indicated a saturation capacity of the basalt of from about 6×10^{-6} mol/kg to 2×10^{-5} mol/kg for the basalt samples used. For uranium, moderate to low sorption was observed on the basalt samples. There was

essentially no difference between sorption under oxic and anoxic conditions.

These results are compared to those of the Basalt Waste Isolation Project at Hanford. Details of these experiments and comparisons are presented in NUREG annual and quarterly reports.^{1,2,3,4}

1. A. D. Kelmers, R. J. Clark, N. H. Cutshall, G. K. Jacobs, J. S. Johnson, J. H. Kessler, R. E. Meyer, Evaluation of Radionuclide Geochemical Information Developed by DOE High-Level Nuclear Waste Repository Site Projects, NUREG/CR 3730 ORNL/TM-9109, 1984.
2. A. D. Kelmers, J. H. Kessler, W. D. Arnold, R. E. Meyer, N. H. Cutshall, G. K. Jacobs, S. Y. Lee, Progress in Evaluation of Radionuclide Geochemical Information Developed by DOE High-Level Nuclear Waste Repository Site Projects: Report for October-December 1983, NUREG/CR-3851, Vol. 1, ORNL/TM-9191/V1.
3. A. D. Kelmers, J. H. Kessler, W. D. Arnold, R. E. Meyer, N. H. Cutshall, G. K. Jacobs, S. Y. Lee, R. J. Clark, Progress on Evaluation of Radionuclide Geochemical Information Developed by DOE High-Level Waste Repository Site Projects: Report for January-March 1984, NUREG/CR-3851, Vol. 2, ORNL/TM-9191/V2.
4. A. D. Kelmers, W. D. Arnold, R. E. Meyer, F. J. Smith, G. K. Jacobs, and S. Y. Lee, Progress in Evaluation of Radionuclide Geochemical Information Developed by DOE High-Level Nuclear Waste Repository Site Projects: Report for April-June 1984, NUREG/CR-3851, Vol. 3, ORNL/TM-9191/V3.

12.5 Review and Evaluation of Literature on Geochemical Issues Pertinent to the Disposal of High-Level Radioactive Wastes: Technical Assistance to Geochemistry-Section Personnel of the Nuclear Regulatory Commission

(J. G. Blencoe)

The Department of Energy (DOE), the Nuclear Regulatory Commission (NRC), and the

Environmental Protection Agency (EPA) are currently spearheading a national program to develop a safe method for disposal of high-level radioactive wastes (HLW). The DOE has determined that research and development activities related to this effort should be concentrated on testing the feasibility of using mined repositories as hosts for the wastes. The idea behind this approach is that a combination of man-made and natural barriers will isolate the wastes so that they will never pose a threat to the public.

The Nuclear Waste Policy Act of 1982 (Public Law 97-425) formally defines the individual responsibilities of the DOE, NRC, and EPA in effecting the disposal of civilian (commercial) HLW. The EPA is responsible for developing "... generally applicable standards for protection of the general environment from offsite releases from radioactive materials in repositories." The NRC is responsible for implementing the EPA standards, and also must develop and issue "... technical requirements and criteria that it will apply in approving or disapproving (i) applications for authorization to construct repositories; (ii) applications for licenses to receive and possess spent nuclear fuel and high-level radioactive waste in such repositories; and (iii) applications for authorization for closure and decommissioning such repositories." The DOE is responsible for collecting the data needed for site characterization, and for constructing and operating a repository in accordance with NRC regulations.

Most of the natural barriers to radionuclide migration from an HLW repository are geochemical in nature. For example, although groundwater is the likely vehicle by which radionuclides can be transported from a repository, it is also true that only small amounts of radionuclides will dissolve in groundwater. Consequently, the low solubilities of radionuclides in groundwater can be viewed collectively as an important barrier to radionuclide migration. Other geochemical barriers to radionuclide migration include sorption of dissolved radionuclides by minerals

in the rocks through which radionuclide-bearing groundwaters travel, and diffusion of radionuclides into the more-or-less static groundwater which occupies the pore spaces of rocks adjacent to radionuclide-release pathways (aquifers). These various examples of geochemical barriers to radionuclide migration illustrate why the performance of a proposed repository cannot be predicted satisfactorily without an extensive body of information concerning geochemical conditions that are anticipated to exist in and around the repository after it has been constructed and radioactive wastes have been emplaced.

The overall purpose of the technical assistance project is to aid NRC geochemistry personnel in determining what additional geochemical information about a candidate-repository site is required prior to the time that the NRC must decide whether or not to issue a license to construct the repository. More specifically, it is the responsibility of project staff members to provide technical assistance to the NRC by performing the following tasks: (1) acquire and assess all of the available geochemical data for candidate-repository sites, (2) evaluate extant DOE programs for determining the geochemical characteristics of potential repository sites, (3) review and appraise reports, papers, and the parts of DOE site-characterization plans that deal with

geochemical issues pertinent to candidate repository sites, and (4) review draft technical material written by NRC geochemistry personnel for inclusion in NRC documents. The results of these various activities are usually transmitted to the NRC in the form of reports that identify and attempt to resolve particular geochemical issues and concerns. Examples of documents written for the project over the past year include "topical review" papers on the solubility and sorption of radionuclides in basalt-groundwater and tuff-groundwater systems, and reviews of numerous reports and papers that deal with issues pertinent to the candidate-repository sites at Hanford, Washington, and the Nevada Test Site. Project staff also have the responsibility to attend meetings, symposia, workshops, etc. that deal with geochemical aspects of the disposal of high-level radioactive wastes. After attending such a meeting, a staff member must prepare a trip report in which he outlines the agenda of the meeting, the most important new information that was presented at the meeting, and his general impressions of the usefulness of the meeting. This trip report is then sent to the NRC staff for their examination and evaluation. This year various staff members attended approximately 10 different meetings which dealt partly or entirely with geochemical issues related to the disposal of high-level radioactive wastes.

13. CHEMICAL APPLICATIONS OF ARTIFICIAL INTELLIGENCE

The computational chemistry projects in this section utilize a combination of nonnumerical and numerical techniques. Chemical problems which are not suited for strictly algorithmic solutions can sometimes be solved with expert systems methods and other techniques from the field of artificial intelligence. These projects are funded through a variety of sources including the Department of Defense and the Department of the Treasury.

13.1 INKY: An Expert System for Printing Ink Chemistry¹

(C. K. Johnson, M. M. Burnett²)

The Bureau of Engraving and Printing (BEP), a branch of the Treasury Department, is the world's largest printer of securities. It prints all U.S. currency and most of the U.S. postage stamps. There are about 40 printing presses at their Washington, DC location utilizing a variety of printing methods, particularly intaglio, gravure and offset lithography. BEP also has its own ink mill which produces many of the inks used there. Roughly 3000 different production inks have been formulated and produced at BEP during the past 25 years. For each of these inks, from one to 60 trial inks were first formulated and tested to insure proper coloration and printing properties for a particular printed product on a specific printing press. Intaglio printing uses engraved plates and produces detailed images which deter counterfeiting efforts, partially through the inherent difficulty of carrying out the intaglio process.

Ink chemistry involves many of the same physical properties basic to other industrial surface coating fields such as the paint industry. Dispersions of colored pigments in special varnishes and solvents are formulated to match the rheology, printing, drying and coloration requirements. However, quantifying the key properties in terms of physical measurements has proven to be a difficult research task, and ink making remains more of an art than a science. Experience is the chief factor used by the ink maker and press operator in producing high quality printing. This situation provides an ideal application area for artificial intelligence expert systems.

An expert system, INKY, using both artificial intelligence and conventional programming methods, is under development to provide computer assistance in formulating new inks and troubleshooting ink-related printing problems. As usual, the first step in the knowledge engineering operation is a systems analysis of the operational procedures and involves extensive interviews and data collection. Our current database for development purposes includes 73 recent postage stamps using 49 inks formulated for the solvent-wipe, paper-wipe, and water-wipe intaglio presses and 24 offset press inks. Gravure inks are not included in this initial study. About 50 of the 130 components in the ink mill inventory are used in these inks. Statistical characterization of the composition data using principal component and linear dependency analyses produced eight formulation prototypes for the vehicle portion of the formulas. The prototypes represent known regions of valid vehicle composition within the multidimensional simplex space of ink mixtures. Each formulation example within a prototype family may be considered as a perturbation from the mean for that prototype governed by some set of heuristic rules for the perturbation. We also have composition data on each separate trial ink made while formulating each production ink, but unfortunately the ink makers' reasons for making each trial step are documented sparsely, and it is often unclear which properties (e.g., printing, drying or coloration) were inadequate at a given stage. However, with experience we should be able to deduce the ink chemists' motives at selected formulation steps and derive heuristic rules relating formulation changes to ink deficiencies. Similar rules also are being derived through interrogation of the expert ink

makers and the two approaches should provide crosschecks on philosophical consistency.

Relationships between ink color and component pigment color also are not as straightforward as the uninitiated might assume. The psychology of tricolor vision is intimately involved in color measurement since the final arbiter in color disputes is the human eye. At present, visual color matching is used at BEP, but it is increasingly apparent that computer color-matching will become increasingly important in ink making; consequentially, computational color-matching methods are being integrated into INKY. Commercial computer-automated color-matching instruments are starting to be used on an experimental basis at BEP.

Our basic INKY model includes mathematical methods for mixture optimization and color matching using algorithms of numerical analysis. The heuristic rule methods of artificial intelligence will generate the input parameters and interpret the output results. Although many problems can be handled in a strictly heuristic form, the present problem seems to require an integration of mixture and color manipulation that only numerical analysis methods can provide. The problem also has a strong database requirement involving the printed products, ink formulas, ink components and press factors, in addition to the heuristic knowledge base requirements on vehicle and color prototypes and perturbation rules. This integration of artificial intelligence, numerical analysis, and database management methods utilizes the c-language-based OPS83 production-rule system written at Carnegie-Mellon University which can interact with other c-language database and numerical routines conveniently within the UNIX operating system of our VAX-750 computer.

13.2 Structure-Activity Relationships in Trichothecene Mycotoxins¹

(C. K. Johnson, M. N. Burnett²)

The trichothecene mycotoxins are naturally occurring sesquiterpenoid fungal toxins which produce a number of toxic effects, including the inhibition of protein synthesis. The literature search described in the 1984 annual report³ found more than 200 of these mycotoxins with protein synthesis inhibition data on about 50 of them. Computer databases and an atlas illustrating the structures also were described. The epoxide group common to all 12,13-epoxy-trichothecenes is essential to their toxic behavior. The research described here was designed to evaluate the contributions of other trichothecene chemical subgroups to the inhibition of protein synthesis.

The Free-Wilson method for quantitative structure-activity relationship (QSAR) analysis was selected for this problem. Singular-value decomposition (SVD) was used in order to circumvent singularities that might occur during the least-squares solution of observational equations with dependent linear combinations of variables. Our SVD computational approach also incorporated a mechanism for specifying additional experimental data requirements needed to prevent singularities, thus providing a very convenient procedure for design of new experiments. Lists of additional molecules which might be examined experimentally to obtain an unambiguous Free-Wilson analysis are produced by the program.

The trichothecene skeleton, shown in Fig. 13.1, has substituents R1, R2, R3, R4, and R5 at C3, C4, C15, C7, and C8, respectively. R2 and R3 may be combined into a 14-atom chain bridging C4 and C15 producing a macrocyclic ring. Macrocyclic trichothecenes such as roridin and verrucarins show the greatest inhibition of protein synthesis in the entire series. The Free-Wilson analysis allows determination of the relative importance of different groups at a given site. The activity sequence for R1 is trimethylammoniumacetoxymethoxy > hydroxymethoxy > oxo > acetoxymethoxy > H indicating a charged or polar interaction, such as hydrogen bonding, at that site.

1. Research sponsored by the Bureau of Engraving and Printing under interagency agreement with the Department of Energy.
2. Postdoctoral research associate from the University of Tennessee.

ORNL-DWG 85-9071

Fig. 13.1. 12,13-Epoxytrichothec-9-ene: the parent skeletal structure for the mycotoxin trichothecene series.

The R2 activity sequence is crotonoxy > acetoxy > hydroxy > H, which indicates that a bulky group is important. At R3 acetoxy > hydroxy while the reverse is true at R4, but neither substituent increases the activity over simple hydrogen. Lastly, R5 has the sequence isovaleroxy > oxo > H > hydroxy = acetoxy.

The above results combine the available whole-cell data for rabbits, mice, guinea pigs, rats, birds, and humans and are subject to criticism for this pooling of data. However, species differences are included as variables in the analysis to factor out the species effects assuming that species differences are simply scaled sensitivities. Interpretation of the species parameters indicates that rabbits and mice have the greatest susceptibilities to the trichothecenes while rats are most resistant. Organ level toxicities of the mycotoxins measured by LD-50 experiments have quite a different pattern than that for protein synthesis inhibition. The Free-Wilson analysis shows that compounds with small hydrogen-bonding groups at R2 and large bulky groups at R1 seem to have increased toxicity, but the species effects are much less consistent than those for protein synthesis inhibition. All trichothecene mycotoxins seem to exert their protein synthesis inhibition at a single ribosomal site while a multitude of action sites are associated with the diverse organ level toxicity effects.

1. Research sponsored by the U.S. Army Chemical Research and Development Center.
2. Postdoctoral research associate from the University of Tennessee.
3. Chem. Div. Annu. Prog. Rep. January 31, 1984, ORNL-6037, p. 191.

13.3 Computational Reasoning by Analogy

(C. K. Johnson)

A common problem-solving technique used by people confronted by an unfamiliar situation is to search for analogies between the current problem and others for which a solution and solution method are known. Analogical reasoning also is used in predicting what might happen in a new situation based on what happened in related situations. It seems reasonable that computational aids for this reasoning process would be useful if the computer can be programmed to recognize and evaluate non-trivial analogies.

ORSIG-AI, the ad-hoc Oak Ridge Special Interest Group for Artificial Intelligence, has a project underway called the Devil's Advocate Reasoning Program (DARP). This group of researchers, engineers, and mathematicians from the Oak Ridge facilities and computer science graduate students from the University of Tennessee are trying to simulate the reasoning that a safety engineer uses to spot potential accidents in chemical processing facilities. One of the approaches being followed is a comparison of the engineering flow diagrams for facilities under study with case history representations of known accidents in order to find relevant similarities if they exist. The first step is to represent case history scenarios in a form suitable for computer reasoning. We are currently evaluating causal semantic nets, such as the one shown in Fig. 13.2, for this purpose based on the pioneering work of Professor Patrick Winston of MIT in reasoning by analogy. The main problem is to develop a suitable analogy matcher that focuses attention on items of importance for the questions at hand while ignoring details unessential to the questions.

thesis of a user-specified molecule, is considered solved when all of its subtasks (and their subtasks, etc.) are solved. Solution of a subtask implies either that the associated chemical structure is recognized by the system as being "in stores" or that a synthesis is already known to the system for it. Given the incomplete (and inevitably ambiguous) nature of the system's chemical knowledge, it is entirely possible that a synthesis attempt might not succeed, and might not terminate. Thus, the system must be provided with some mechanism for recognizing when it is making little or no progress in an attempted synthesis, and for recovering at some chemically reasonable point so that it can try a different approach. The current version of the program embodies code which supports these two related features.

In addition to methods for recovering from fruitless synthesis attempts, a system such as ours must embody schemes which can provide a sense of direction to what would otherwise be a combinatorially explosive task. We have found that a few relatively simple heuristics can do much to provide this sense. Two of these involve considerations of the forms of "target sites," those system-identifiable chemical substructures for which potential synthetic methods are stored. We find that it is generally best to select for application the target site which is likely to result in the smallest precursor (or precursors). If no target site dominates under this heuristic, the one which contains the largest part of the fragment under consideration should be selected. Another useful heuristic suggests the selection of the target site which is more likely to lead to multiple precursors (since it is likely to be easier to synthesize several smaller precursors than one large one).

We are just beginning to incorporate knowledge about another very useful chemical notion, that of chemical constraints. It is, in many cases, possible to rule out for application one or another target site on the basis of some characteristic which the fragment in which it occurs

exhibits. Thus, we are beginning to associate with target sites lists which describe the set of constraints (both positive and negative) which must be satisfied if the target site can be successfully applied. When all the target sites have been found in a fragment and the evaluations (listed in the previous paragraph) performed, the system will examine the constraint list for the selected target site to determine if, in the context of the current fragment, the constraints are satisfied. Some will not be and will be of such a form that they can clearly not be satisfied by any chemical manipulations. Others may require only the protection of certain groups, etc., and may thus suggest subtasks which the system can readily perform to that the selected target site can ultimately be applied. Failing in such attempts, the system will select the next most appropriate target site and try again.

Of considerable importance to the human chemist is the notion of the "known sequence", a set of reactions which, given the discovery of some initial target site, could reasonably be expected to lead to that site. We have captured this concept in a set of rules which can, in effect, detect the possibility of applying a known sequence and direct the synthetic process accordingly. Should one of the chemical transformations implied by the known sequence be found inapplicable at some step, rules within this new body of code respond to this failure and force the synthesis to continue under the direction of the heuristics described in the previous paragraphs.

Current efforts are directed toward the implementation of two more very important concepts, learning and reasoning by (chemical) analogy. We are writing code to support the first of these now and should soon have provided the system with the capability for recognizing structures for which it has developed successful syntheses. (Such a capability is present even now, but is not automated.) Automation of this capability will make the program self-extending and will, as more and more structures become

"system-known," lead to a considerable reduction in the time required to synthesize a new compound.

Our work on reasoning by chemical analogy is only just beginning. In a limited sense, the system already possesses this capability, since rules for finding and applying target sites are of a fairly general form and embody something of the notion of chemical analogues. At present, the sense of analogy is primarily a local one, extending only over the part of a structure,

spanned by a target site, and does not incorporate a larger scale awareness of the entire molecular structure under consideration. We hope to provide this larger scale of sensitivity by giving the system a sense of symmetry, of group relations and group similarities, and the like, coupled with procedural rules capable of directing a synthesis as these larger scale considerations suggest.

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1. Consultant. I & C. Division.

14. SPECIAL TOPICS

14.1 Microemulsion Fuels

(W. L. Griffith, A. C. Compere)

This activity was initiated in April 1984 to develop a technology base on the physical, chemical, and combustion properties of microemulsion fuels. These fuels, which have very small droplets, usually 2 to 100 nanometers diameter, of an aqueous phase in base fuel, provide a method for altering fuel combustion properties. Among the fuel properties that can be changed are: NOX and particulate emissions, octane and cetane ratings, viscosity, combustion temperature, dispersion during combustion, and explosion resistance. Compared to the substantial research background for work in engine design, the microemulsion fuels technology base is small. ORNL facilities for small angle neutron and x-ray scattering, dynamic light scattering, electron microscopy, and analytical chemistry will be used as appropriate to provide correlations between combustion and physical-chemical properties. Model systems will be used to provide insight into the properties of microemulsion fuels. The knowledge gained will be used to support advanced fuels development for innovative and conventional engines.

To plan areas where small angle neutron scattering would be most useful, preliminary experiments were performed using the HFIR and ORR facilities. The data obtained were analyzed using subroutines developed by Caponetti for similar water in oil microemulsions stabilized by potassium oleate. These programs are being improved by mathematical analysis and specific experimental design. Fig. 14.1 shows a fit for a reference system containing, per mole of oleic acid, 17 moles of D_2O , 6 moles of 1-pentanol, 6 moles of hexadecane, and 1 mole of ethanolamine. The model illustrated here is based on mono-disperse oleate ellipsoids, a configuration which at this point seems to give best agreement with experiments.

Figure 14.1 SANS from w/o microemulsion comprised of 1 mole oleic acid, 1.0 mole ethanolamine, 5.8 moles 1-pentanol, 5.4 moles hexadecane, and 17.5 moles D_2O . Main parameters: core, 2.5 nm; eccentricity, 4.3; penetrability factor (fraction of stoichiometric volume dispersed phase) 0.9; and hard shell radius, 2.8 nm.

14.2 Mechanism of Photooxidative Degradation of 2,4-Dinitrotoluene in Aqueous Solution

(P. C. Ho)

This research was supported by the U.S. Army Toxic and Hazardous Materials Agency to study the mechanism of photooxidative degradation of 2,4-dinitrotoluene (DNT) in aqueous solution. Last year we reported the beginning of this study. We present here the results of the photooxidation of DNT and some of the reaction intermediates, which are produced during the photooxidation of DNT, when exposed in aqueous solution to hydrogen peroxide and radiation from a medium-pressure mercury vapor lamp. Table 14.1 gives the effect of hydrogen peroxide concentration on the extent of photooxidative degradation of DNT. It can be seen that the most effective condition for degradation of aqueous DNT solutions was found to consist of a molar ratio of H_2O_2 /DNT in the range 26 to 52.

Table 14.1

Effect of Hydrogen Peroxide Concentration and Time of Exposure on the Extent of Photooxidative Degradation of DNT

H_2O_2 /DNT (molar ratio)	Time of Exposure (min)	Percentage DNT Elimination	Concentration of DNT and other Intermediates in solutions (ppm)				
			2,4-Dinitro- benzyl- alcohol		2,4-Dinitro- benzaldehyde	DNBA *	DNB **
			DNT				
13	0		75.8				
	10	76.5	17.8	trace	0.85	15.4	0.15
	20	83.9	12.2	trace	0.15	14.5	0.35
	30	98.2	1.4	0	0.15	5.9	0.70
	45	100	0	0	0	1.2	~ 0
	60		0	0	0	0.9	0
	90		0	0	0	0.3	0
26	0		75.8				
	5	67.7	24.5	trace	1.1	10.8	trace
	10	86.8	10.0	trace	0.6	10.8	0.2
	21	99.3	0.5	~ 0	trace	1.6	trace
	30	99.7	0.2	0	0	1.6	~ 0
	45	100	0	0	0	0.45	0
52	0		75.8				
	6	72.2	21.1	trace	1.3	14.6	0.07
	10	93.7	4.8	~ 0	0.15	5.5	0.15
	20	99.7	0.22	0	trace	1.4	trace
	33	~ 100	0	0	0	1.2	0
	45	100	0	0	0	0.2	0
104	0		75.8				
	10	89.2	8.2	trace	0.6	10.2	0.15
	20	96.8	2.4	trace	trace	3.9	0.15
	30	97.1	2.2	~ 0	trace	0.3	0.35
	45	~ 100	--	--	--	--	--
	60	~ 100	0	0	0	0.2	0
44	0		192.6				
	10	69.9	58.0	0.29	2.6	44.0	0.5
	20	94.1	11.3	0.29	0.4	24.3	0.6
	30	97.7	4.4	~ 0	trace	9.9	0.35
	60	99.6	0.8	0	0	3.7	trace
	90	~ 100	trace	0	0	1.7	0
	120	100	0	0	0	1.4	0
	180		0	0	0	1.0	0

* DNBA 2,4-dinitrobenzoic acid

** DNB 1,3-dinitrobenzene

Several experiments were also done by exposure the aqueous $\text{H}_2\text{O}_2/\text{DNT} = 26$ mixture to the same UV lamp equipped with a Pyrex or a Vycor filter in order to block out or partially block out light in the far UV region (to reduce the energy of the incident light). With Pyrex filter (to block out light $< 280 \text{ nm}$), after 14 hours of exposure, it was found that only about 92% of the original DNT was eliminated and lots of solid byproducts were produced. While with Vycor filter, which only partially blocked out the far-UV region light, it was found that the degradation of DNT was comparable with the same solution when exposed to the same UV light without filter, except that it took a much longer time to completely eliminate the same amount of DNT. Thus it appears the presence of light in the far UV region is also a very important factor to degrade DNT in aqueous solution completely.

Under the conditions of molar ratio of $\text{H}_2\text{O}_2/\text{DNT} = 26$ to 52, and in the presence of unfiltered UV light, the intermediates found after short reaction times (2 to 10 minutes) were 2,4-dinitrobenzyl alcohol, 2,4-dinitrobenzaldehyde, 2,4-dinitrobenzoic acid (dominant), 1,3-dinitrobenzene, 3-nitrophenol, 2,4-dinitrophenol, maleic acid derivatives, oxalic acid, glyoxylic acid, glyoxal, and formic acid. The finding of dinitrobenzyl alcohol, dinitrobenzaldehyde, dinitrobenzoic acid, and dinitrobenzene produced at short time probably indicates that a major part of the degradation in the beginning is sidechain oxidation, that is:

The large amount of 2,4-dinitrobenzoic acid and relatively small amount of dinitrobenzyl alcohol and dinitrobenzaldehyde revealed that the rates of oxidation of the alcohol and aldehyde derivatives were faster than the rate of decomposition of the dinitrobenzoic acid. Table 14.1 also gives the rate of formation and decomposition of these intermediates.

The sidechain oxidation was probably induced by hydroxyl radicals which were formed by photolytic cleavage of hydrogen peroxide¹⁻⁶. The presence of 3-nitrophenol and 2,4-dinitrophenol suggested that, after the sidechain oxidation, ring hydroxylation reactions proceeded as in eqns. (2) and (3).

Such ring hydroxylation by hydroxyl radicals has been suggested by many researchers⁷⁻¹². In reaction (2), addition to an unsubstituted position of the benzene ring gives a hydroxycyclohexadienyl radical^{10,11} which is oxidized further to the phenol derivative. In reaction (3), addition to an ipso position again achieves ring hydroxylation but now with loss of the nitro substituent.

In order to investigate the reaction pathway subsequent to the formation of 2,4-dinitrobenzoic acid and 1,3-dinitrobenzene, photooxidations of several of the identified intermediates, such as 2,4-dinitrobenzoic acid, 1,3-dinitrobenzene, 3-nitrophenol, and 2,4-dinitrophenol, etc., were studied. Based on intermediates identified after each photooxidation of the degradation products of DNT, the following

reaction pathway for photooxidation of aqueous DNT solutions with UV/H_2O_2 is suggested: (1) sidechain oxidation, which converts DNT to 1,3-dinitrobenzene; (2) hydroxylation of the benzene ring, which converts 1,3-dinitrobenzene to hydroxynitrobenzene derivatives; (3) benzene-ring cleavage of these hydroxynitrobenzenes, which produces lower-molecular-weight carboxylic acids and aldehydes; and (4) further photooxidation, which eventually converts the lower-molecular-weight acids and aldehydes to CO_2 , H_2O , and HNO_3 .

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14.3 Mercury Removal from Effluent Streams

(J. S. Johnson, Jr.¹, K. A. Kraus,² C. G. Westmoreland)

The Y-12 Plant has encountered some problems with contamination by mercury of some waters that it desired to discharge into streams. Maximum concentrations allowed were of the order of a part per billion. They were successful in meeting these requirements by passage through beds of organic ion exchangers in which ferrous sulfide had been precipitated. Mercury was removed by metathesis to highly insoluble HgS ³. Incorporation into the anion exchanger obviated the dispersion of the metal sulfides into the treated solution by peptization⁴.

Although the materials used were adequate, the low content of FeS attainable meant low capacity and relatively high cost for resin and its disposal after use. We have investigated alternative materials for removal of mercury and other toxic ions of interest to Y-12.

For mercury, activated carbon and several adsorbents based on it--carbon on which sulfide ions had been adsorbed, carbon on which adsorbed sulfide had been converted to FeS, and carbon containing elemental sulfur--seemed better than the modified organic exchanger. Elemental sulfur was incorporated by treating carbon on which thiosulfate or polysulfide had been adsorbed with HCl from the gas phase. A commercial product containing sulfur (trade name "Mersorb") was also found to be available; it is marketed for removal of mercury from the gas phase. When ground and sized, removal properties for mercury were found to be similar to, perhaps a little better than, those we prepared.

Of these, carbon filled with elemental sulfur was best, both with respect to uptake (Table 14.2) and distribution coefficient (D) (Table 14.3). In removal from very dilute streams (< one ppm), as here, high distribution coefficients are probably of more

Table 14.2

Removal of Hg(II) by Various Adsorbents
Adsorbent   Uptake, moles Hg(II)/kg solid

Charcoal, as-received	0.6
Above, sulfide-filled	1.4
Above, FeS-filled	1.7
Sulfur-filled activated carbon	1.8

Table 14.3

Distribution Coefficients of Hg(II) on Various Adsorbents

<u>Adsorbent</u>	<u>Loading of Adsorbents</u>			
	<u>Tracer</u>		<u>0.001 moles Hg/kg</u>	
	<u>pH(eq)</u>	<u>D (l/kg)</u>	<u>pH</u>	<u>D (l/kg)</u>
From 0.05 M NaNO ₃ :				
Charcoal, as-rec + sulfide	7.7	62500	NM	13600
	7.3	5695	NM	43700
Charcoal + FeS	7.3	7035	NM	8070
Mersorb	7.5	1.65x10 ⁵	NM	76200
From 0.05 M NaCl:				
Charcoal, as-rec + sulfide	8.0	99500	NM	38700
	8.4	19000	NM	83700
Charcoal + FeS	7.8	40800	NM	34000
Mersorb	7.7	~1x10 ⁶	NM	1.75x10 ⁵

concern, because these are an index to the number of bed volumes which may be processed with complete removal in ideal chromatographic operation.

Elemental sulfur presumably is effective because the free energy of HgS is so low that S⁰ can be reduced to S²⁻ by reaction with water or other substances in the stream. However, even finely divided sulfur ("flowers") is ineffective w/in macro mercury concentrations, and only about 90% of Hg was removed by it from tracer concentrations. Apparently incorporation in activated carbon pores results in an enormous increase in surface area available for reaction with mercury ions.

The other adsorbents investigated appear to be better for removal of other ions of

interest. A comparison of uptakes for several is given in Table 14.4. Distribution coefficients for those ions which time allowed us to check also were favorable.

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Table 14.4

Removal of Various Ions
Uptake, moles/kg

	<u>Hg(II)</u>	<u>Ag(I)</u>	<u>Cd(II)</u>	<u>Cr(VI)</u>
Charcoal, as-received	0.6	0.80	0.35	0.71
Sulfide-filled	1.4	1.20	0.40	0.02
Sulfur-filled	1.8	0.50	0.20	0.04
FeS-filled	1.7	1.0	0.30	0.12

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1. Summer Research Participant, Notre Dame University, IN.
2. E. I. DuPont de Nemours Corp.
3. Environmental Sciences Division.
4. Department of Chemistry, University of Tennessee, Knoxville; part-time ORNL employee.
5. Gulf Oil Corporation.
6. SCUW Science Semester Participant.

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1. Retired.
2. Department of Chemistry, University of California, Lawrence Berkeley Laboratory, Berkeley, CA.
3. Arizona State University, Tempe, AZ.
4. Carleton College, Northfield, MN.
5. Department of Chemistry, Drury College, Springfield, MO.

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1. Health and Safety Research Division.
  2. Earth Sciences Laboratory, University of Utah Research Institute, Salt Lake City, UT.
  3. Dept. of Geosciences, The Pennsylvania State University, University Park, PA.
  4. Geophysical Laboratory, Washington, DC.
  5. Dept. of Geology/Geophysics, University of Alaska, Fairbanks, AK.
  6. Furman University, Greenville, SC.
  7. Retired.
  8. Materials Research Laboratory, The Pennsylvania State University, University Park, PA.
  9. University of Wisconsin.

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1. Chemistry Department, Rollins College, Winter Park, FL.
2. 1982 student participant from St. Olaf College, Northfield, MN.
3. Analytical Chemistry Division.
4. Student participant from Centenary College, Shreveport, LA.
5. Commission of the European Communities, European Institute for Transuranium Elements, Karlsruhe, FRG.
6. University of Tennessee, Knoxville; part-time ORNL employee.
7. Tennessee Technological University, Chemistry Department, Cookeville, TN.
8. University of Liege, Belgium.
9. Environmental and Occupational Safety Division.
10. Chemical Technology Division.
11. University of Tennessee, Knoxville, Physics Department.
12. Lawrence Berkeley National Laboratory, Berkeley, CA.
13. Los Alamos National Laboratory, Los Alamos, NM.
14. Florida State University, Department of Chemistry, Tallahassee, FL.
15. Centre de' Etudes Nucleaires, Fontenay-aux-Roses, France.
16. Laboratoire de Chimie des Metaux de Transition, Paris, France.
17. Solid State Division.
18. Gesellschaft fur Schwerionenforschung, Darmstadt, West Germany.
19. Institut fur Kernchemie, Universitat Mainz, Mainz, Federal Republic of Germany.
20. Lawrence Livermore National Laboratory, Livermore, CA.
21. Physics Division.
22. Anorganische-Chemisches Institute, University of Bern, Bern, Switzerland and Swiss Federal Institute for Reactor Research, Wurenlingen, Switzerland.
23. Health and Safety Research Division.

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1. Chemistry Department, University of Tennessee, Knoxville, TN.
2. L. Eötvös University, Budapest, Hungary.
3. International Atomic Energy Agency, Vienna, Austria.
4. CSIRO, Lucas Heights Research Laboratories, Sutherland, Australia.
5. Babes-Bolyai University, Cluj-Napoca, Romania.
6. Comenius University, Bratislava, Czechoslovakia.
7. Nuclear Research Centre, Cairo, Egypt.
8. Rockwell International, Golden, CO.
9. Shizuoka University, Hamamatsu, Japan.
10. Fuel Recycle Division.
11. Computer and Telecommunications Division.
12. Department of Nuclear Engineering, Arizona State University, Tempe, AZ.

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-
1. Department of Chemistry, University of Tennessee, Knoxville, TN.
  2. Present address: Dow Chemical Company, Midland, MI.
  3. Department of Chemistry, Northwestern University, Evanston, IL.

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-
1. Retired.
  2. Free University of Berlin, West Germany.
  3. Health and Safety Research Division.
  4. Science Research Council, University of Bristol, Bristol, UK.
  5. Kanazawa Medical University, Ishikawa-ken, 920-02, Japan.
  6. Permanent address: Department of Physics & Measurements Tech., Linköping Inst. of Technology, Linköping, Sweden.
  7. On leave from Royal Institute of Technology, S-10044, Stockholm, Sweden.
  8. Department of Chemistry, University of Tennessee, Knoxville, TN.
  9. University of Wisconsin, Madison, WI.
  10. Department of Chemistry, University of Georgia, Athens, GA.
  11. Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, CA.
  12. Department of Chemistry, Texas A&M University, College Station, TX.
  13. Department of Chemistry, University of Arizona, Tucson, AZ.

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-
1. Oxford University, Oxford, UK.
  2. Los Alamos National Laboratory, Los Alamos, NM.
  3. Duke University, Durham, NC.
  4. College of William & Mary, Williamsburg, VA.
  5. North Texas State University, Denton, TX.
  6. University of Waterloo, Ontario, Canada.

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-
1. Chemical Technology Division.
  2. Metals and Ceramics Division.
  3. Health and Safety Research Division.
  4. Department of Chemistry, Florida State University, Tallahassee, FL.
  5. Environmental Sciences Division.

CHEMICAL APPLICATIONS OF ARTIFICIAL INTELLIGENCE

- C. K. Johnson, W. E. Thiessen, M. N. Burnett,¹ P. Condran,² A. Ronlan,² M. Yanaka² and W. T. Wipke,²
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-
1. Postdoctoral Research Associate, University of Tennessee, Knoxville, TN.
  2. Department of Chemistry, University of California, Santa Cruz, CA.

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-
1. Y-12 Development Division.
  2. Participant from Lawrence University in the Great Lakes College Association/Associated Colleges of Midwest Science Semester, Fall 1980.
  3. Undergraduate Cooperative Education Student from University of Tennessee, Knoxville, TN.
  4. Department of Chemistry, University of Tennessee, Knoxville, TN.
  5. Istituto di Chimica Fisica, V. Archirafi 26, Palermo, Italy.
  6. Present Address: Babcock & Wilcox, 1562 Beeson St., Alliance, OH.
  7. Massachusetts Institute of Technology School of Chemical Engineering Practice, Oak Ridge Station.

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Funding source	Funding (in thousands)	Direct scientific and technical person-years
DOE PROGRAMS		
Basic Energy Sciences	\$7,327	52.0
Fission Energy	150	1.0
Carbon Dioxide Research	60	0.5
Energy Conservation	69	0.5
TOTAL DOE PROGRAMS	\$7,606	54.0
WORK FOR OTHERS PROGRAMS		
Nuclear Regulatory Commission	\$ 408	3.0
US Air Force	68	0.5
NASA	118	1.0
US Army	263	2.0
US Navy	58	0.5
US Treasury	45	0.3
Savannah River Laboratory	60	0.5
Miscellaneous	25	0.2
TOTAL WORK FOR OTHERS	\$1,045	8.0
TOTAL FINANCIAL PLAN	\$8,651	62
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