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CHEMISTRY DIVISION ANNUAL PROGRESS REPORT
for Period Ending January 31, 1983

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1. INTRODUCTION AND DIVISIONAL OVERVIEW

Since our last Annual Report of a year and a half ago, a number of especially important contributions have been made by the Staff. Some illustrative highlights are:

1. Measured preliminary cross-sections to indicate that the HFIR neutron spectrum when hardened by filtration with cadmium, boron-10, or lithium-6 will increase the production of $^{254}\text{Es}$ ($T_{1/2} = 276$ d) over conventional HFIR/TRU yields of ~6 ug per campaign by a factor of 3 to 5. The long-lived einsteinium isotope is needed as the highest Z, highest N target at accelerators to allow studies in the $Z = 101$ to 109 region of known elements and to attempt to reach the $Z = 110$-120 region of the superheavy elements search.

2. Employed ~100 ug of 20 d $^{253}\text{Es}$ alloyed with Yb metal to obtain the vapor pressure of einsteinium as a function of temperature. The results confirm our earlier results (based on the crystal structure) that einsteinium metal is divalent.

3. Measured hydrolysis and carbonate complexation constants for $\text{Np(V)}$. These constants are of use in modeling of environmental migration.

4. Determined the hydration number in concentrated aqueous solution for $\text{Nd}^{3+}$ in preparation for work on actinides. A technique based on neutron diffraction using two isotopes of Nd in otherwise identical solutions allowed a definitive, model free result to be obtained for the hydration number.

5. As part of our investigation of coal structure, counted benzylic carbon-hydrogen groups in coal by "titrating" Illinois No. 6 vitrain with carbanions of varying basicity and then capping the coal carbanions produced with $^{14}$C methyl iodide.

6. Investigated the reduction of coal model compounds with solvated electrons to elucidate the pathways of carbon-carbon bond breaking.

7. Under Chemical Energy funding, developed high resolution solid state $^{13}$C NMR techniques. These techniques were employed during the year in a DuPont funded study to successfully correlate a variety of coals with ethylene feedstock yields under pyrolysis conditions. The important underlying structural feature appears to be the long chain aliphatic units in coal. A paper from DuPont and ORNL authors has been submitted to Fuel.

8. Determined positions of oxygen and carbon adatoms on a clean Mo(100) surface with low-energy angle-resolved alkali metal ion scattering. Also, in the case of oxygen, its distance above the Mo surface could be estimated from the data.

9. Discovered a new, simple two parameter relationship that accurately reproduces the vaporization properties of dissimilar inorganic and organic liquids over wide ranges of temperature.

10. Demonstrated that the short range contribution to the excess partial molal free energy is a linear function of the reciprocal of the cation radius using a correlation based on ORNL isopiestic measurements of alkali metal chlorides above 200°C.

11. Observed, using the new high temperature flow calorimeter, unusually large heats of dilution for concentrated CaCl$_2$ solutions. These results indicate an unusual change in hydration of the ions in the solutions.
(12) Modeled the thermodynamics and kinetics of iodine hydrolysis reactions to obtain information needed to stabilize non-volatile forms of iodine under nuclear reactor accident conditions.

(13) Developed stopped-flow cell and fast optical multichannel spectrometer for the study of fast organic reactions catalyzed by molten salts.

(14) Combined methods of single-crystal and liquid x-ray diffraction to determine the structures of complexes formed in uranyl nitrate/organophosphorus systems of interest in solvent extraction mechanisms.

(15) Formulated new synthetic routes for the preparation of titanium diboride powders at relatively low temperatures. The submicron particle size and high purity of these new powders is allowing a controlled study of their hot pressing characteristics.

(16) Developed a method for calculating elastic constants from atmospheric pressure to 50 kilobars of crystalline materials. The method has been successfully applied to mantle materials, such as olivine and diopside, of interest in geologic processes.

(17) Employed photoacoustic spectroscopy to correlate the formation of titanium dioxide film on a titanium electrode with applied potential in a new approach to the study of corrosion mechanisms.

(18) Developed techniques to calculate exactly the number of modes participating in the unimolecular decomposition of certain polyatomic molecules.

(19) Explained theoretically the experimentally observed bimodal energy distribution of electrons collisionally detached from highly energetic (MeV) H atoms. The explanation provided a needed test of theories of H structure and dynamics which had been puzzling theorists for several years.

(20) Established the aqueous speciation of tungsten(VI) to 300°C by potentiometric titration and demonstrated that normal hydrothermal fluids can carry 1-10 ppm tungsten, as $\text{HWO}_4^{2-}$, at saturation with scheelite ($\text{CaWO}_4$).

(21) Demonstrated slow high temperature (1243°C) iron redox kinetics in rhyolitic melts (no observed reaction in 96 hours) which indicates that the redox state of natural silicic volcanic rocks may reflect redox conditions in parent magma chambers.

(22) Participated in ORNL programs for the NRC to provide technical assistance in geochemistry and to conduct confirmatory experimental studies relative to nuclide migration from nuclear waste repositories.

(23) Obtained the ionization behavior of aqueous hydrochloric acid to 600°C and 4,000 atmospheres pressure from electrical conductances, for evaluating acidity in steam generator fluids and for fundamental applications in geochemistry.

(24) Produced experimental data and semi-theoretical evaluations of sodium sulfate solubilities in $\text{H}_2\text{SO}_4-\text{NaCl-H}_2\text{O}$ solutions at high temperatures and pressures of basic interest and immediate need for operating behavior of steam generator fluids.
(25) Simulated the permeability of bedded salt to brine with a model based on experimental measurements of brine flow through interfaces between stressed salt crystals. These results are important in nuclear waste isolation studies related to a salt based repository.

(26) Employed synchrotron radiation to experimentally study a wide variety of gaseous molecular and atomic metallic species from which two new areas of photoelectron spectroscopy were opened up: (1) the evaluation of the Cooper minimum and (2) the use of constant final state transitions. These experimental results allow the application of new critical tests to quantum mechanical calculations of molecular structure and of molecular and atomic photoelectron dynamics.

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

Visiting scientists and students from universities, industry, and research institutes continue to enrich the work of the Division. In the last four years, the Division has had 20 Visiting Scientists from foreign institutions (2 publications), 33 Visiting Professors from American universities (20 publications), along with a number of graduate students (6 Ph.D. and 2 M.S. degrees awarded). Collaboration with students of the Great Lakes Colleges Association, Oak Ridge Associated Universities, various co-op programs, and the Southern Colleges and University Union resulted in 16 publications.

Legal and institutional barriers to industrially funded projects in the Laboratory continue to ease, and such collaborative research, which is driven by international industrial competition, should continue to increase slowly over the next few years. Another area, cooperation in weapons related research, is driven by the perceived need by the nation for defense preparedness and probably also will increase.
2. COAL CHEMISTRY

The ongoing work described in Section 2.1 is aimed at gaining improved understanding of the chemical structure and reactivity of coal. Structural studies are carried out both by spectroscopic and chemical degradation approaches. Solid-state $^{13}$C NMR is our chief spectroscopic tool for study of both native and chemically modified coals. Organic reactions which selectively break C-C bonds are emphasized in the degradation work on coals and appropriate model compounds. Studies of reactivity are centered on thermal reactions of model compounds in the coal liquefaction temperature range. Research in Section 2.1 is sponsored by DOE/Basic Energy Sciences.

The work described in Section 2.2 was sponsored by DOE/Fossil Energy and has been more closely focused on the chemistry of coal liquefaction. Support for work of this type has at the moment been terminated.

2.1 Organic Chemistry of Coal and Model Compounds

2.1.1 Solid State $^{13}$C NMR Spectroscopy: Measurement of Proton Relaxation Times in the Rotating Frame and Implications for Carbon Counting Experiments

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

We have shown previously that the standard CPMAS-$^{13}$C-NMR experiment does not detect all carbons in coal with unit intensity response. The reasons underlying this quantitation problem have been examined in part by characterizing the time constants for the dynamic spin processes which yield the measured $^{13}$C magnetization in Illinois #6 vitrain. The requirement for quantitative intensity response in this experiment is $T_{CH} < CT < T_{1p}(H)$ where $T_{CH}$ is the time constant for $^{13}$C-H cross polarization, CT is the contact time during which cross polarization is allowed to occur, and $T_{1p}(H)$ is the time constant for the decay of proton magnetization from a spin lock r.f. field. The spin locked proton magnetization is that which is transferred, in part, to the $^{13}$C nuclei.

Measurements on a diverse array of coals have shown that optimum signal-to-noise in the experiment is achieved with a contact time of 1 ms. For an exponential cross polarization process: $T_{CH}$ of the longest cross polarization time should be $< CT$ in order for all carbon signals to be polarized equally (within 15%; $3 T_{CH} < CT$ will yield relative $^{13}$C intensities within 5% of each other). Cross polarization times for protonated aliphatic and aromatic carbons of Illinois #6 vitrain are less than 70 µs, and hence will all polarize completely in a 1 ms CT period. Non-protonated aromatic carbons which dominate the 145-155 ppm spectral region yield $T_{CH}$ values in the 300-500 µs range and will not polarize fully in a 1 ms CT period. The error introduced into the total integrated intensity of the aromatic resonance band is less than 3% for this coal.

Proton $T_{1p}$ is on the order of several ms. Long $T_{1p}$ relative to CT maximizes signal-to-noise in the experiment. However, if all carbon magnetization decayed with the same $T_{1p}(H)$, correct relative integrated intensities would be observed for all values of $T_{1p}(H) > CT$. In fact, $T_{1p}(H)$ of the aliphatic resonance band is 20% longer than $T_{1p}(H)$ of the aromatic band. The difference indicates that the protons of the coal do not form a single spin system connected to each other by spin diffusion. Thus, this coal contains some degree of predominantly aromatic and predominantly aliphatic domains which are isolated from each other.

For $T_{1p}(H)$ times greater than CT a 20% variation in $T_{1p}$ (aromatic) and $T_{1p}$ (aliphatic) will induce a negligible error in relative integrated intensity. For Illinois #6 vitrain an underestimation of aromatic resonance area will approach 20% as the average $T_{1p}$ approaches CT. $T_{1p}(H)$ is dependent on the field strength of the spin locking r.f. field and is under experimental control. Strong r.f. fields that yield $T_{1p}(H)$ of several milliseconds are adequate to keep errors arising from minor differences in $T_{1p}(H)$ small.

2.1.2 Solid State $^{13}$C NMR Spectroscopy: Correlations of Oil Yield with Oil Shale Spectra

(E. W. Hegaman)

An investigation of a series of related oil shale samples taken as a function of depth from an oil shale bed at a single location in the Mahogany Zone of the Green River formation demonstrated that relative aliphatic carbon areas from CP/MAS-$^{13}$C-NMR spectra can be used to predict oil yield. These samples were provided by D. C. Cronauer, Gulf Oil Corporation, who determined the oil yields.

Using a single set of time variables, Maciel et al. have established a linear relationship between aliphatic carbon content of an oil shale and Fischer Assay oil yield, given by Eq. (1), where $f_{al}$ is the ratio of aliphatic carbon area to total carbon area determined from the NMR measurement and $P$ is the weight percent organic carbon (measured independently as total carbon minus carbonate and bicarbonate).

$$f_{al}(P) = K \cdot \text{oil yield}$$  \hspace{1cm} (1)

The correlation of Maciel, et al. was obtained from a series of oil shales of worldwide origin representing a variety of geologic ages and depositional environments. In their sampling, the aliphatic carbon fraction of the organic material and the weight percent organic carbon of the oil shale spanned the ranges 0.27-0.85 and 11-81%, respectively. Hence, within the error of the linear fit, the general result emerges that the sp$^2$/sp$^3$ area ratios measured in the CP/MAS-$^{13}$C-NMR experiment are insensitive to the composition and concentration of the mineral matter in the oil shale matrix. This conclusion has been experimentally supported in the limiting case where in equal $f_{al}$ values were measured from the intact oil shale and from the kerogen concentrate obtained from the same sample. Subsequent reports have shown that the aromatic carbon content of a series of oil shales is unchanged following retorting. This work suggests that the aromatic carbon fraction in the oil shales is largely responsible for the carbonaceous residue obtained during retorting and supports the thesis that it is the aliphatic carbon in the oil shale which is largely responsible for the oil retorted from the shale.

The successful correlation of fractional carbon area from CP/MAS-$^{13}$C-NMR measurements with process yields for a diverse array of oil shale specimens implies that $T_{CH}$, $T_{IPH}$, $T_{IH}$ distributions in these materials are similar enough to permit the use of a unique set of experimental time parameters in the experiment and maintain quantitative capability. This apparent uniformity in relaxation behavior, insensitive to the inorganic matrix of the shale, underlies the tremendous potential of CP/MAS-$^{13}$C-NMR spectroscopy in rapid evaluations of oil yield from oil shale.

Table 2.1 lists the weight percent organic carbon and Fischer assay oil yield for ten oil shale specimens which are arranged in order of increasing depth of the sample source in a vertical sampling of the oil shale formation. For each sample, the aliphatic carbon fraction, $f_{al}$, and a relative aliphatic carbon area are also tabulated. The $f_{al}$ value is nearly constant for all samples ($0.79 \pm 0.03$) with a slight indication of increased carbon aromaticity as sample depth increases. This criterion suggests the formation is rather homogeneous and

<table>
<thead>
<tr>
<th>Sample</th>
<th>Wt. % Org. C</th>
<th>Oil Yield (gal/ton)</th>
<th>$f_{al}$</th>
<th>C-sp$^3$ area$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10.92</td>
<td>21.2</td>
<td>.80</td>
<td>8076</td>
</tr>
<tr>
<td>2</td>
<td>16.03</td>
<td>30.4</td>
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<td>25.0</td>
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<td>9</td>
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<td>18.7</td>
<td>.78</td>
<td>7019</td>
</tr>
<tr>
<td>10</td>
<td>7.08</td>
<td>13.1</td>
<td>.77</td>
<td>5384</td>
</tr>
</tbody>
</table>

$^a$Ratio of aliphatic carbon area to total organic carbon area.

$^b$Relative areas of the aliphatic carbon resonance envelope.
within the approximation of constant $f_{al}$; Eq. (1) indicates oil yield should be directly proportional to $P$. Plots of $f_{al}$ vs oil yield and $(P)(f_{al}) \times$ oil yield are linear with correlation coefficients of 0.96 and 0.95, respectively. Hence, in the limiting case in which $f_{al}$ is constant, $P$ suffices as a measure of potential oil yield. The uniformity of the oil shale bed with respect to $f_{al}$ found in this study may prove not to be a general feature of this or other formations. In the general case where oil shales from different sources must be compared, oil yield evaluations by Eq. (1) require the measurement of $f_{al}$ and $P$.

The product, $f_{al}(P)$, has the meaning of weight percent aliphatic carbon, a quantity which is simply proportional to the NMR aliphatic area for constant number of acquisitions, spectrometer sensitivity, and weight of the sample. These areas are given in Table 2.1. When plotted vs oil yield, the linearity of the data, $r = 0.94$, is comparable to that obtained using Eq. (1). In contrast to correlations using $f_{al}$, direct area integrals are a function of spectrometer sensitivity and data reduction constants.

The requirement of constant sensitivity may, in general, impose unrealistic demands on the spectrometer, e.g., probe sensitivity will be difficult to hold constant between samples which possess large variations in mineral matter concentration and composition since this material will detune the coil to differing extents. The spectrometer noise figure may also vary with ambient conditions. These limitations may be circumvented by returning to area ratio measurements—not $f_{al}$—but with a suitable internal standard: $Csp^3$ area/standard area. Operation in this mode should allow, in the general case, rapid oil shale-oil yield estimation solely from a single CP/MAS-$^{13}$C-NMR determination.

2.1.3 Solid State $^{13}$C NMR Spectroscopy: Correlations of Pyrolysis Products with Coal Spectra

(H. Zeldes, E. W. Hagaman)

This work represents a joint effort between ORNL and W. H. Calkins of E. I. duPont de Nemours and Co. The coals and their respective ethylene yields were supplied by Dr. Calkins; the NMR data collection and correlation at ORNL was supported by duPont.

When coal is pyrolyzed at various temperatures as reported by Tyler, the yield of tar produced goes through a maximum. At the maximum, around 600°C for most coals, little gas is evolved except perhaps carbon dioxide in low-rank coals, and some carbon monoxide and methane. At higher temperatures, many other gases and volatile liquids are evolved, including the olefins—ethylene, propylene and butadiene. The yields of the hydrocarbon gases produced vary greatly depending on the particular coal.

The ethylene yields are related to the propylene and butadiene yields, suggesting that these gases have a common precursor. The methane and benzene, however, show no obvious relation to the ethylene yields. These products are apparently derived from other components in the coal.

To try to relate these yield differences to structural differences in the coals themselves, several coals whose pyrolysis behavior had been studied were examined by CP/MAS-$^{13}$C-NMR spectroscopy. Fractional areas and ethylene yields for these coals are collected in Table 2.2.

Two trends emerge from inspection of the spectra for all seventeen coals studied; (1) aliphatic carbon fraction, $f_{al} \equiv (\text{aliphatic carbon area})/(\text{total carbon area})$, generally increases with ethylene yield, and (2) all coals with an ethylene yield $> 4.7$ wt % possess a distinctive peak at 31.0 ppm which becomes more pronounced as ethylene yield increases. The invariance of this singular resonance and its chemical shift suggest it arises from the highly degenerate carbon chemical shift of the internal methylene carbons of $n$-paraffinic material. Since the resonance does not become

Table 2.2. CP/MAS-\(^{13}\)C-NMR Fractional Areas and Ethylene Yields for Coals

<table>
<thead>
<tr>
<th>Coal</th>
<th>(f_{ai})</th>
<th>(f_{31.0} \times 10^3)</th>
<th>(f_{43.8} \times 10^3)</th>
<th>(y^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSOC-124</td>
<td>.436</td>
<td>17.78</td>
<td>9.10</td>
<td>15.71</td>
</tr>
<tr>
<td>Lovelady L-2</td>
<td>.489</td>
<td>17.36</td>
<td>10.66</td>
<td>15.78</td>
</tr>
<tr>
<td>Blind Canyon</td>
<td>.396</td>
<td>12.38</td>
<td>8.63</td>
<td>6.72</td>
</tr>
<tr>
<td>PSOC-435</td>
<td>.337</td>
<td>11.12</td>
<td>7.23</td>
<td>6.58</td>
</tr>
<tr>
<td>Emery</td>
<td>.306</td>
<td>10.74</td>
<td>6.65</td>
<td>6.11</td>
</tr>
<tr>
<td>Con Paso Blue 2</td>
<td>.325</td>
<td>10.96</td>
<td>7.00</td>
<td>9.39</td>
</tr>
<tr>
<td>Con Paso Yellow 4</td>
<td>.330</td>
<td>10.24</td>
<td>6.52</td>
<td>9.07</td>
</tr>
<tr>
<td>Wyodak</td>
<td>.322</td>
<td>11.11</td>
<td>7.27</td>
<td>6.28</td>
</tr>
<tr>
<td>Con Paso Blue 4</td>
<td>.327</td>
<td>11.72</td>
<td>6.95</td>
<td>7.54</td>
</tr>
<tr>
<td>Alcoa Texas Lignite</td>
<td>.333</td>
<td>10.55</td>
<td>6.96</td>
<td>7.20</td>
</tr>
<tr>
<td>PSOC-181</td>
<td>.261</td>
<td>7.19</td>
<td>5.54</td>
<td>4.31</td>
</tr>
<tr>
<td>Con Paso Yellow 6</td>
<td>.300</td>
<td>9.01</td>
<td>5.99</td>
<td>4.40</td>
</tr>
<tr>
<td>Pittsburgh 8</td>
<td>.252</td>
<td>6.53</td>
<td>5.84</td>
<td>4.65</td>
</tr>
<tr>
<td>PSOC-1016</td>
<td>.253</td>
<td>7.24</td>
<td>5.87</td>
<td>2.98</td>
</tr>
<tr>
<td>Illinois #6 Burning Star</td>
<td>.237</td>
<td>6.21</td>
<td>5.17</td>
<td>3.17</td>
</tr>
<tr>
<td>Sewickley</td>
<td>.237</td>
<td>5.58</td>
<td>5.10</td>
<td>2.60</td>
</tr>
</tbody>
</table>

\(a_f_{ai} = \) (aliphatic resonance area)/(total area of the spectrum).

\(b_f_{31.0} \times 10^3 = \) [area under the spectral curve in a 1 ppm wide increment, centered at the frequency of interest]/(total area of the spectrum) \(\times 10^3\).

\(c_y = \) ethylene yield, as wt % of organic carbon in MF coals.

degenerate until the carbon is three bonds removed from the chain end, this resonance provides no information on terminal group functionality. This chemical shift is ca. 1.5 ppm downfield of the well characterized resonance of the degenerate resonance position of long chain \(n\)-alkanes measured in solution (29.5 ppm). This latter shift is an average shift value which reflects the equilibrium conformational distribution of trans and gauche conformers along the chain, and is not, a priori, applicable in the solid state. In fact, the degenerate resonance of the non-crystalline component of linear polyethylene (LPE) appears at 32 ppm; the crystalline component which has an all-trans conformation appears 2.4 ppm downfield of the non-crystalline component (34.4 ppm).\(^2\) The 31.0 ppm resonance in the coal spectra is very similar. Small differences may arise from a difference in the mode of referencing chemical shifts in this work and in reference 2. In order to evaluate in a more quantitative fashion the relationship of ethylene yield and features within the aliphatic resonance envelope, the quantity \(f_{ppm}\) was defined as the fractional area of the spectrum per ppm, i.e., the area under the spectral curve in a 1 ppm wide increment, centered at the frequency of interest, divided by the total area of the spectrum. These fractional areas (see Table 2.2) were investigated for possible linear relationship with ethylene yield according to

\[ y = m(f_x) + b \]

where \(f_x = f_{ppm}\) and \(y\) is ethylene yield as wt % of MF coal divided by the organic carbon fraction of the coal (MF basis). Defined in this way, \(y\) is the ethylene yield as wt % of
organic carbon for all coals. Area fractions, \( f_{\text{ppm}} \), were measured at five frequencies which span the aliphatic resonance envelope; the extreme chemical shifts, 15.9 and 56.6 ppm, correspond to frequencies which determine the width at half height of the aliphatic resonance envelope in the low-yielding coal, Pittsburgh 8. This procedure was followed to assure that all fractional areas would be large in comparison to possible baseline distortions that enter from the uncertainty in correct phase adjustment. Correlation coefficients, \( r \), for \( y \) vs \( f_{\text{ppm}} \) at 15.9, 23.5, 31.0, 43.8 and 56.6 ppm are 0.26, 0.53, 0.94, 0.89 and 0.78, respectively. Thus the area fraction at 31.0 ppm shows the best and remarkably high correlation with ethylene yield, and implicates normal paraffinic structural moieties in coal as likely precursors of ethylene in this coal pyrolysis.

Linear regression analysis of Eq. (1) with \( f_x = f_{31.0} \) yields a slope and intercept of 1.03 = 0.10 and -3.6 ± 1.1, respectively. In this model, the line would pass through the origin if all the area under \( f_{31.0} \) represented one kind of carbon which is the only precursor to ethylene. The occurrence of area at this frequency associated with carbon that does not yield ethylene would account for the negative intercept. Conversely, fractional area at other frequencies representing carbon that yields ethylene would displace the least squares line upward, giving a positive intercept. The physical interpretation of Eq. (1) is not likely a good reflection of reality since it specifies that each coal has a constant fractional area at 31 ppm representing carbon that does not yield ethylene.

Though the area fraction at 31.0 ppm is the best predictor of ethylene yield, the correlation coefficient of \( y \) vs \( f_{31.0} \) is 0.91 and that for \( y \) vs \( f_{43.8} \) is only marginally degraded to 0.89. These results suggested that a linear combination of fractional areas might predict with higher accuracy. Linear regression was not used to fit \( y \) to an equation of the form

\[
y = m_1 f_{31.0} + m_2 f_{43.8}
\]

since it became apparent that \( f_{31.0} \) and \( f_{43.8} \) are themselves highly correlated quantities with \( r = 0.95 \). This surprising result, not apparent on casual inspection of the spectra, seems to imply that a basic structural similarity is present among the coals examined. The significance of this observation is under study; its existence defeats the application of Eq. (2) which requires independent \( f_{\text{ppm}} \).

The chemical shift of 43.8 ppm does not correspond to a unique carbon type but is the general shift area for many methylene and methine carbons in varied structural moieties. Inspection of the series of coal spectra reveals that the spectral curve connecting points at 31.0 and 43.8 ppm can be closely approximated by a straight line segment. It follows that ethylene yield will be predicted using the fractional area between 31.0 and 43.8 ppm with a correlation coefficient intermediate between those of \( f_{31.0} \) and \( f_{43.8} \); i.e., \( r = 0.91 \), the value determined for \( y \) vs \( f_{31.0} \).

The high correlation of \( f_{31.0} \) vs \( f_{43.8} \) prevents a precise mathematical determination of ethylene precursor within the band from 31 to 44 ppm. Lack of correlation of ethylene yield vs fractional area above 23.5 ppm and below 56 ppm suggests that carbon with these shifts, i.e., predominantly methyl carbons at high field and quaternary and hetero-substituted carbons at low field, are in fact poor precursors for the formation of ethylene. The fact that ethylene/propane and ethylene/butadiene ratios are produced in constant proportion in the pyrolysis strongly supports a common precursor with \( (\text{CH}_2)_n > 4 \). It may prove true that the best ethylene yield predictor in the solid \(^{13}\text{C} \) NMR spectrum, fractional area measured at the resonance position of \( (\text{CH}_2)_n \), is monitoring the actual precursor of these hydrocarbon gases.

2.1.4 Displacement of Retained Pyridine from Coal by Aqueous Tetrahydrofuran

(R. R. Chambers, Jr., D. Mckamey)

Solvent extraction of coal represents one of the most common methods for obtaining coal-derived materials whose structure closely resembles that of the entire coal. These extracts are ideal for further study since they are soluble in at least one solvent and they lack a high mineral content which can interfere with some analytical techniques such as NMR.

Within the coal community, pyridine has been the solvent of choice for extraction because of its ability to dissolve a substantial portion of the coal, as much as 30% for a bituminous vitrain. In addition, the excellent swelling properties of pyridine make it an ideal medium for performing various chemical transformations on coal such as acylation and trimethylation of phenolic hydroxyls. The major disadvantage, however, associated with the use of pyridine is the difficulty in completely liberating the coal of residual amine which clings tenaciously even after extended periods under high vacuum.

Collins, et al. demonstrated that large quantities (12-20% by weight) of \(^{14}\)C-pyridine are retained both by the pyridine extract and residue from an Illinois #6 vitrain after 48 h under high vacuum. And, although all but 0.2-1.7% of the labeled amine could be exchanged with unlabeled pyridine, repeated benzene extractions removed only 20-25% of the \(^{14}\)C-pyridine from the solutes.

Two recent reports from the Ames Laboratory describe a method, using supercritical carbon dioxide, for the removal of retained pyridine from Illinois #6 and Kentucky #9 extracts. The amount of pyridine removed by this method agrees well with the amount of reversibly bound pyridine as found by Collins. Of interest is the finding that water is an essential co-solvent for complete extraction.

We have developed a useful alternative to supercritical CO\(_2\) extraction for producing pyridine-free coals which avoids the use of high pressure equipment. The method involves repetitive washing with a dilute aqueous THF solution. For this study, an Illinois #6 vitrain and its O-methylated derivative were used. The O-alkylated coal was prepared according to the general procedure outlined by Liotta in which phenolic hydroxyls and carboxylic acids are converted to methyl ethers and esters by treatment with tetrabutylammonium hydroxide and methyl iodide.

The pyridine-retained coal samples were prepared by refluxing coal and \(^{14}\)C-pyridine under argon. The excess pyridine was distilled off and the sample placed under vacuum. Carbon-14 assay revealed that Illinois #6 and the O-methylated derivative retained 10.7% and 7.9% (^/W) pyridine, respectively. The decrease in retained pyridine upon O-methylation is consistent with the notion that hydrogen bonding contributes to the affinity of coals for amine solvents.

A portion of the labeled coals was placed on a funnel, stirred with a 5% aqueous THF solution and then filtered. This was repeated a total of ten times. After drying, the samples were assayed for their carbon-14 content. The Illinois #6 vitrain retained only 1.3% pyridine while the O-methylated derivative retained 1.9% pyridine, in agreement with Collins' finding that most of the pyridine is not bound irreversibly to coal.

To rule out the incorporation of large quantities of THF during this procedure, the two coals were treated as above with an aqueous \(^{14}\)C-THF solution and dried. Neither coal retained more than 1.2% THF.

The same extraction process was carried out on a larger (1 g) amount of coal containing a known amount of unlabeled pyridine to monitor weight losses. At most, 3% of the coal is lost during this procedure.

An explanation for the effectiveness of aqueous THF at removing retained pyridine was found by varying the amount of THF initially in solution. An Illinois #6 coal containing 10% pyridine and an O-methylated sample containing 5.1% pyridine were treated for 1 h.
with aqueous solutions of varying THF concentration. After centrifugation, an aliquot of the mixture was titrated for its pyridine content and a plot made of percent pyridine released vs volume percent THF. The results are illustrated in Figures 2.1 and 2.2. As is clearly evident, the amount of pyridine released increases curvilinearly with an increase in percent THF which is consistent with a displacement role for THF (Eq. 1).

\[
\text{Coal--Pyridine}_{\text{adsorbed}} + \text{THF} \rightleftharpoons \text{Coal--THF}_{\text{adsorbed}} + \text{Pyridine}
\]  

(1)

In addition, 2-methyl-THF was found to be somewhat more effective than THF (Figure 2.1) in removing pyridine from Illinois #6, suggesting that part of the driving force for the displacement is a favorable equilibrium between coal and THF in aqueous medium.


2.1.5 Reductive Carbon-Carbon Bond Cleavage by Sodium-Potassium Alloy
(R. R. Chambers, Jr.)

As part of a program to delineate structural changes that occur when coal is treated with electron transfer agents, we have investigated the reduction of various coal model compounds by an Na-K alloy. C. J. Collins, et al. reported that Na-K in a 50/50 mixture of glyme:triglyme (V/V) cleaved the central bond in dibenzyl at 0°C to give, upon protonation, toluene plus smaller (10%) amounts of
CO

products derived from reaction with solvent. Under similar conditions, diphenylmethane yielded toluene but now accompanied by 3-benzylbiphenyl. The proposed mechanism involved an ipso aromatic substitution process with benzyl anion as a leaving group (Eq. 1).

\[
\text{C}_8\text{H}_8 + \text{C}_6\text{H}_6 \rightarrow \text{C}_8\text{H}_8\text{C}_6\text{H}_5 \quad \text{(1)}
\]

Schanne and Haenel\(^2\) reported similar products from diphenylmethane when subjected to reduction by K in gl. we/octaglyme (5:1), but suggested that attack by phenyl radical on diphenylmethane accounts for the observation of benzylbiphenyl.

To improve our understanding of the bond breaking processes, we have investigated the reaction of \(\text{CH}_2\text{CH}_2\text{A} \quad \text{(x = 1, 2, 3, 4)}\) with Na-K. This series of hydrocarbons constitutes the simplest models for coal. In order to accurately mimic the situation where coal is reduced, we decided to use a large excess of alloy (6-fold) relative to hydrocarbon. Since under these conditions extensive reduction can occur during work-up, this requires that an oxidative quench be employed. We considered that an ideal quenching agent should be capable of protonating anions but accepting electrons from radical anions. Two candidates were tested: tert-butyl bromide and iodide.

When \(\text{CH}_2\text{CH}_2\text{A} \quad \text{(x = 1, 2, 3, 4)}\) was reduced with Na-K (6 equivalents, 0°C, 15 min) followed by reaction with \((\text{CH}_3)_2\text{CBr}\), the products were toluene (83%), bibenzyl (11%), and hydrogenated dibenzyl (6%). A parallel quench with ethanol led to toluene (45%), dihydrotoluene (40%), bibenzyl (2%), and hydrogenated dibenzyl (9%). The success with \((\text{CH}_3)_2\text{CBr}\) can be rationalized as follows:

\[
\text{ArCH}_2(\text{ArCH}_2\text{Ar}) + (\text{CH}_3)_2\text{CBr} \rightarrow \text{ArCH}_2 + (\text{CH}_3)_2\text{CBr} (\text{Proton Transfer})
\]

\[
\text{ArCH}_3 + (\text{ArCH}_2\text{Ar}) + (\text{CH}_3)_2\text{C} \rightarrow \text{ArCH}_3 + \text{CH}_2 + \text{Br}^- (\text{2})
\]

\[
2 \text{Ar}^+ + (\text{CH}_3)_2\text{C} \rightarrow 2\text{Ar} + (\text{CH}_3)_2\text{C}^+ + \text{Br}^- (\text{3})
\]

In contrast to the bromide, using \((\text{CH}_3)_2\text{C}^-\) resulted in larger amounts of unretracted \(\text{CH}_2\text{CH}_2\) than expected, which suggested that resynthesis of bibenzyl was occurring. This conclusion was verified, for the same methodology yielded bibenzyl, 4-methylbibenzyl and 4,4′-dimethylbibenzyl from Na-K reduction of 4-methylbibenzyl.

A similar treatment of diphenylmethane (6 equiv. Na-K, \((\text{CH}_3)_2\text{CBr}\)) gave toluene (8%), diphenylmethane (61%), hydrogenated diphenylmethanes (29%) and benzylbiphenyl (2%). Likewise, 2,2-diphenylpropane yielded cumene (7%), unretracted diphenylpropane (78%), and hydrogenated diphenylpropenes (15%). Clearly, structural units such as \((\text{Ar})_2\text{C}^+\) \((\text{Ar} = \text{phenyl}, \text{R} = \text{H, alkyl})\) are comparatively stable towards bond breaking by Na-K.

The relative cleavage aptitude of \(\text{CH}_2\text{CH}_2\) vs \(\text{CH}_2\) was determined by reacting 1,1,2-triphenylethane with Na-K. As shown in Eq. (4), the only products detected were derived from fission of the weaker 1,2-diarylethane bond and not the 1,1-diarylethane bond.

Both 1,3-diphenylpropane and 1,4-diphenylbutane were found to be inert towards Na-K with respect to carbon-carbon bond fission. These results suggest that the formation of methyl groups when coal is reduced by alkali metals derive primarily from cleavage of weak sp\(^3\)-sp\(^3\) type bonds in 1,2-diarylethanes.\(^1\)

2.1.6 Selective Functionalization of Benzylic Carbon Atoms in Coal

(R. R. Chambers, Jr., O. R. McKeaney)

The development of improved methodology for converting coal resources into fuels and useful chemical feedstocks requires a better understanding of the fundamental structure of coal. The currently accepted view of the coal "molecule" is that of a diverse cluster of aromatic nuclei cross-linked by various aliphatic carbon and oxygen linkages. Studies by Reggel, et al. on the dehydrogenation of coals and related materials strongly implicate a hydroaromatic structure for coal.1 To further our knowledge of coal's structure, we have been interested in probing the nature of the carbon atoms comprising the aliphatic carbon linkages.

One approach has been to differentiate among the various aliphatic carbon cross-links by the difference in acidity of the benzylic C-H groups. It is well established that the $pK_a$ of a carbon acid is quite sensitive to the number of attached aromatic groups. As a general rule, the $pK_a$ decreases as the number of resonance-stabilizing groups increases.2 Furthermore, the change in $pK_a$ is quite dramatic, there being a decrease of some 22 $pK$ units as one goes from benzylic anion to 9-phenylfluorenyl anion.

Work at Exxon has established the presence of approximately 5 weakly acidic phenolic hydroxyl/carboxylic acid ($pK_a < 16$) functionalities per 100 carbon atoms in an Illinois #6 vitrain.3 To simplify data interpretation, it is necessary to first protect these groups. We chose to do so by conversion of the phenols and acids to their respective methyl ethers and esters using the phase transfer conditions ((nBu)$_4$N$^+$HOT/CH$_3$I) outlined by Liotta, et al.4 We proceeded to treat this demethylated coal with a series of carbanions followed by capping with carbon-14 labeled methyl iodide. The radioactive label was used as a quantitative measure of extent of reaction. By varying the initial carbanion concentration, a series of titration curves were obtained which provide information regarding the number of accessible acidic C-H groups present in Illinois #6. The carbanions used thus far are 9-phenylfluorenyl, fluorenyl, and trityl anion.

The results from this series of carbanions are presented in Table 2.3. Several trends are evident from the data. First, for a given base, there is a gradual increase in the number of alkyl groups incorporated as the amount of base is increased. This leads to a series of characteristic "titration curves" which reflect the maximum number of coal anions that can be generated by a given base. To rule out the retention of B$^{14}$CH$_3$ (B = base) as a major contributor to the observed carbon-14 activity, a portion of coal from a trityl anion experiment (Table 2.3) was stirred with triphenylmethane, extracted with THF and reassayed. The C-14 content was diminished only slightly (4%) after this treatment, suggesting that the methyl groups added are covalently attached to the coal. Secondly, as expected, we note that the maximum number of methyl groups added increases with an increase in base $pK_a$.

A comparison of columns 2 and 3 (Table 2.3) reveals that a high concentration of base is required to introduce a small number of methyl groups. This may reflect the problem of diffusing a large anion into the inner structure of a negatively charged coal "molecule".

In conclusion, our preliminary data have shown it possible to introduce under mild conditions a small but significant number of alkyl groups on carbon by the two step process.

\[
\begin{align*}
\text{CH}_3 & \quad 1. B^- \quad \text{CH}_3^+ \quad \text{OCH}_3 \\
\text{Coal}^- & \quad \text{OCH}_3 \\
2. \text{CH}_3 & \quad \text{Coal}^- + \text{CH}_3 \\
\end{align*}
\]

This study will be extended to include stronger bases and then to determine the possibility of introducing other functional groups into coal by a similar sequence of steps.
Table 2.3. Alkylation of Carbon in Illinois
No. 6 Coal

<table>
<thead>
<tr>
<th>Base</th>
<th>Moles $^{14}$CH$_3$</th>
<th>Moles $^{14}$CH$_3$ added/g coal</th>
<th>C Alkylated/100 C</th>
</tr>
</thead>
<tbody>
<tr>
<td>9-phenylfluorenyl</td>
<td>3</td>
<td>0.07</td>
<td>0.2</td>
</tr>
<tr>
<td>$pK_a$ 18.5</td>
<td>4.2</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.0</td>
<td>0.13</td>
<td></td>
</tr>
<tr>
<td></td>
<td>9.0</td>
<td>0.15</td>
<td></td>
</tr>
<tr>
<td></td>
<td>12.0</td>
<td>0.15</td>
<td></td>
</tr>
<tr>
<td>fluorenyl</td>
<td>4.2</td>
<td>0.08</td>
<td>0.9</td>
</tr>
<tr>
<td>$pK_a$ 22.7</td>
<td>6.0</td>
<td>0.55</td>
<td></td>
</tr>
<tr>
<td></td>
<td>9.0</td>
<td>0.57</td>
<td></td>
</tr>
<tr>
<td></td>
<td>12.0</td>
<td>0.50</td>
<td></td>
</tr>
<tr>
<td>trityl</td>
<td>6.0</td>
<td>0.53</td>
<td>3</td>
</tr>
<tr>
<td>$pK_a$ 31.5</td>
<td>9.0</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>15.0</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(1.54)$^a$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>18.0</td>
<td>1.7</td>
<td></td>
</tr>
</tbody>
</table>

(a) The number of $^{14}$CH$_3$ groups remaining after exchange with triphenylmethane.

2.1.7 Thermolysis of Model Coal Structures:
Experimental and Thermochcmical Kinetic Evaluations of Radical Chain Decompositions of a,a-Diphenylalkanes
(M. L. Poutsma)

Studies of the thermolysis (-400°C) of the set of compounds Ph(CHOH)$_n$Ph ($n = 2-4$) as models for the aliphatic bridging units in coal have been described in previous reports. The observed rate for $n = 2$ agreed with that predicted from the dissociation energy of the weakest C-C bond. However, that for $n = 3$ and $n = 4$ was significantly accelerated. Kinetic evidence was presented to support a free-radical chain mechanism rather than a unimolecular retroene mechanism. The key step was $a$-scission of substrate-derived benzylic radicals which is kinetically accessible at 400°C only for $n > 3$. These conclusions have now been elaborated and strengthened by additional data.

The mechanism for PhCH$_2$CH$_2$CH$_2$Ph (I) is more complex because two intermeshed chains result from the existence of two substrate-derived radicals 2 and 3. An observed variation of the PhCH$_3$:PhCH$_2$H product ratio with the concentration of 1 revealed that these two radicals were kinetically connected by a bimolecular hydrogen transfer (step 7, -7). The following set of chain steps was proposed:

$$
\text{PhCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph} \xrightarrow{k_1} \text{PhCH} = \text{CH}_2 + \text{PhCH}_2\text{CH}_2^* \\
\text{PhCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph} \xrightarrow{k_2} \text{PhCH}_2\text{CH} = \text{CH}_2 + \text{PhCH}_2^* \\
\text{PhCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph} \xrightarrow{k_3} \text{PhCH}_2\text{CH} = \text{CH}_2 \text{CH} = \text{CH}_2 + \text{PhCH}_2^* \\
\text{PhCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph} \xrightarrow{k_4} \text{PhCH}_2\text{CH} = \text{CH}_2 \text{CH} = \text{CH}_2 \text{CH} = \text{CH}_2 + \text{PhCH}_2^* \\
\text{PhCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph} \xrightarrow{k_5} \text{PhCH}_2\text{CH} = \text{CH}_2 \text{CH} = \text{CH}_2 \text{CH} = \text{CH}_2 \text{CH} = \text{CH}_2 + \text{PhCH}_2^* \\
\text{PhCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph} \xrightarrow{k_6} \text{PhCH}_2\text{CH} = \text{CH}_2 \text{CH} = \text{CH}_2 \text{CH} = \text{CH}_2 \text{CH} = \text{CH}_2 \text{CH} = \text{CH}_2 + \text{PhCH}_2^* .
$$

The steady-state solution for the network given above is:

\[
\frac{\text{PhCH}_3}{\text{PhC}_3\text{H}_5} = \frac{(k_4/k_3 + k_4) \cdot (k_7/k_1)}{(k_5/k_6) \cdot (k_7/k_2)}.
\]

The solid line in Fig. 2.3 is drawn for the values: \(k_4/(k_3 + k_4) = 0.16; k_5/(k_5 + k_6) = 0.90; k_7/k_1 = 0.75; \) and \(k_7/k_2 = 0.65\). Independent estimates of each of the 8 rate constants from reported values for analogous cases modified for the particular structures involved here by thermochemical kinetic methods led to rate constant ratios completely compatible with those suggested in Fig. 2.3 within the accuracy expected for such estimation procedures.


2.1.8 Thermolysis of Model Coal Structures: Effect of Surface Immobilization

(M. L. Poutsma, E. C. Douglas, J. E. Leach)

All studies of the mechanisms of thermolysis of model compounds for coal by ourselves and others have been carried out in the liquid or gaseous state where reactive intermediates, such as free radicals, are free to diffuse and interact. In contrast, in the early stages of coal decomposition when much of the macromolecular framework is still intact, there will be major restrictions to diffusion. The present study has been initiated to model the effects of mobility by carrying out thermolysis studies of model compounds which have been immobilized by covalent attachment to an inert surface.

The first task was to find a surface and mode of attachment which would be both relatively stable at 400°C and amenable to quantitative analysis of surface-bound products. This has been achieved by the reaction of phenols with the surface hydroxyl groups of silica. The resulting solid product can be assayed for the extent of surface coverage by dissolution in aqueous base to regenerate the starting phenol. For example, refluxing

\[
\text{PhCH}_2\text{CH}_2\text{CH}_2\text{Ph} + \text{H}_2\text{O} \rightarrow \text{PhCH}_2\text{CH}_2\text{CH}_2\text{OH} + \text{Ph}
\]

...
(182°C) fumed silica (Cab-O-Sil MS; 200 ± 25 m² g⁻¹) with phenol followed by removal of excess phenol in vacuum at 320°C gave a free-flowing white powder whose phenyl content was 0.90 mmol g⁻¹, corresponding to 2.7 surface phenyl groups m⁻². Thermolysis under vacuum at 400°C for 3.5 h evolved only 7% of these groups as phenol, presumably by reaction with residual surface hydroxyls. Assay of the residue accounted quantitatively for the remaining phenyls.

The first model compounds chosen were the \( \alpha, \omega \)-diphenylalkanes whose thermal behavior in fluid media we understand² in detail. Each of the five phenols, \( \text{C}_n\text{H}_5(\text{CH}_2)_n\text{C}_6\text{H}_4\text{OH} \) \( (n = 0-4) \), has been successfully attached to the fumed silica by heating at ~225°C followed by evacuation at 300°C. Surface coverages are typically 0.4 mmol g⁻¹. Exploratory thermolyses have been carried out for \( n = 0-2 \) in sealed evacuated tubes in a configuration where the solid sample was held at 400°C but volatile products could migrate to a cold zone as they were formed. For \( n = 0 \) and \( n = 1 \), \( \text{Ph}(\text{CH}_2)_n\text{Ph} \) are completely stable at 400°C in the fluid state. The surface-attached analogs were similarly stable. Hence, as hoped, new reaction pathways were induced by the surface. For \( n = 2 \), where thermal reactivity for \( \text{Ph}(\text{CH}_2)_n\text{Ph} \) is first observed, the surface-attached analog was also comparably reactive but major perturbations in product composition were found.

In a specific case, \( \text{SiO}_2\text{-OC}_6\text{H}_4\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5 \) was heated at 400°C for 4 h. In addition to slow evolution of \( \text{HOC}_6\text{H}_4\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5 \), several products were formed, only the major of which will be discussed here because analysis is not yet complete. Evidence for initial C-C homolysis, as in the fluid phase, is provided by the formation in equal amounts of \( \text{PhCH}_3 \) and surface-attached \( \text{HOC}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_5 \). The rate of formation of \( \text{PhCH}_2 \) corresponds closely to that seen in fluid media.²,³ Hence, we conclude that C-C homolysis is still rate-determining and that the resulting "free" \( \text{PhCH}_3 \) and surface-attached \( \text{SiO}_2\text{-OC}_6\text{H}_4\text{CH}_2 \) radicals both abstract hydrogen from \( \text{SiO}_2\text{-OC}_6\text{H}_4\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5 \) units to give surface-attached \( \text{SiO}_2\text{-OC}_6\text{H}_4\text{CHCH}_2\text{C}_6\text{H}_5 \) (and its positional isomer). The major products which apparently arise from these radicals are surface-attached \( \text{SiO}_2\text{-C}_6\text{H}_4\text{CH}(\text{Ph})\text{CH}_3 \) and, to a lesser extent, \( \text{SiO}_2\text{-CH}_3 \).

In the fluid phase,²,⁴ \( \text{PHCHCH}_2\text{Ph} \) radicals disappear almost totally by bimolecular self-combination and disproportionation. Unimolecular skeletal isomerization to form \( \text{Ph}_2\text{CHCH}_3 \) is, at best, a minor pathway, and cyclization-dehydrogenation to form phenanthrene is essentially absent, although the possibility of such a process has been considered.⁴ Our current hypothesis to rationalize these unusual products in the surface-immobilized case is that bimolecular radical-radical interactions are severely inhibited by the inability of surface-attached radicals to diffuse and that therefore inherently somewhat slower unimolecular radical reactions are observed by default. In addition to the relevance to modeling coal thermolysis, we feel that the present experimental approach may have broader utility to observe unimolecular decay pathways of reactive intermediates which, in fluid media, are not competitive with diffusion-controlled bimolecular decay pathways.

1. SCUU Science Semester Student from Centenary College.
2. References, 1 and 3, Sect. 2.1.7.

2.2 Chemistry of Coal Liquefaction
2.2.1 Use of Hydrogen-Deuterium Exchange to Identify Hydrogen Shuttlers in Coal Liquefaction Recycle Solvents
(B. M. Benjamin, E. C. Douglas)

Some insight into the chemical properties of the recycle solvents used in direct coal
liquefaction processes is necessary for understanding how these solvents function. Of particular interest here are those chemical properties which are associated with hydrogen transfer or "hydrogen shuttling" reactions. In the several processes the recycle solvents may vary in composition, particularly with respect to boiling ranges. Thus it is possible to operate with a distillate boiling in the 290-500° range. However, in some cases an improvement in yield or conversion is achieved by recycling vacuum tower bottoms while, in other cases, so-called fractionated heavy materials are added. In those solvents which contain heavy distillate or added light SRC it has been suggested that certain polynuclear aromatic components make a large contribution to hydrogen redistribution. If this is true, it is important to understand more about the exchange processes associated with the polynuclear aromatics, particularly for those compounds which undergo rapid exchange. In this regard it is not known whether a particular compound which undergoes rapid hydrogen exchange in the presence of solvent-coal reactions also undergoes rapid exchange in simpler chemical systems. Therefore it was necessary to select a series of compounds for further special study. Selection of appropriate compounds was based on known solvent composition; their hydrogen exchange abilities were assessed in simple chemical systems, and the results were reported earlier. The observed data were compared with exchange information for the same compounds and other similar compounds in the complex recycle solvent system and ultimately in coal-recycle solvent mixtures. This report deals principally with the results observed for the complex recycle solvent system in admixture with coal and without coal.

In the introductory work it was assumed that a compound's ability to take part in hydrogen redistribution is related in some way to its ability to undergo hydrogen exchange reactions. It was then considered possible to evaluate the effectiveness toward liquefaction of a compound by studying its behavior toward hydrogen-deuterium exchange. With this concept in mind, we investigated the degree of H-D exchange in a large number of aromatic compounds, both single ring and polynuclear. Experimental conditions for H-D exchange of the model aromatics consisted of heating at 400°C a mixture of the subject compound with enough 1,4-phenylmethane-d2 so that the number of exchangeable H's and D's were equal. To briefly summarize the results, it was generally observed that the hydrogens on the aromatic nuclei exchanged slowly. Rapid exchange occurred only when molecular decomposition took place and accelerated exchange took place in molecules which contained a substituent or other activating feature. It is interesting that certain compounds, such as pyrene, and phenanthrene, which are of particular interest in the recycle solvent system, were unexpectedly inert toward exchange in model systems. However, some of these same molecules freely participate in exchange in the presence of the coal decomposition reactions.

Turning attention now to the behavior of compounds in the coal-derived recycle solvent, we are interested in mapping the degree of exchange of as many as possible of the compounds present. A detailed list of compounds identified in our solvent sample is available. The solvent used here (referred to as Hydro-Solvent) was originally obtained from the Missionville Pilot Plant by Conoco Coal Development Co. where light SRC was added to it. The material was found to contain approximately 200 compounds, 132 of which were identified using capillary gc-m.s. The remainder were present in very small amounts or were components in overlapping gc peaks which in some cases gave ms data which defied interpretation.

In the ensuing discussion every compound cannot be dealt with individually because of space and technical difficulties. However, it is possible to focus on major components and principle classes or groups of components.

A summary of the composition of principle components is as follows: The solvent was rich in methylnaphthalenes, phenanthrene, biphenyl.
and diphenyl ether. The most abundant series of compounds were the methyl and polymethyl-naphthalenes, long-straight-chain aliphatic hydrocarbons, and methyl- and poly-methylenanthrenes. Methyl substituted bibenyls, indanes, acenaphthenes and dibenzofurans were also present.

Exchange experiments with the recycle solvents were attempted using three different deuterium sources: cyclohexylmethane-d_{2}, pyrene-d_{n}, and D_{2} gas. Even though key solvent components were found to undergo exchange in the runs with D_{2} gas, in the present report attention is focused mainly on results with pyrene-d_{n}.

In a typical experiment, pyrene-d_{n} (675 \text{ P}) was mixed with hydro-solvent or with coal and hydro-solvent in a stainless steel tubing bomb. A parallel experiment was run using ordinary pyrene so that gc-ms data could be sorted out in confusing areas and more easily compared. After thermolysis of the mixtures, fractionation of the product was necessary to concentrate solvent components and eliminate heavy coal derivatives. Data were gathered on a compound-by-compound basis in the recovered fractions using the capillary gc-ms and comparison was made with identical runs in which deuterium was not present. Isotopic compositions for selected components which occurred as unique peaks could be calculated. Examples of exchange data for these components are recorded in Table 2.4. Results are not conclusive for a large number of the remaining compounds because of high background or interference due to compounds present in low concentrations. However, inspections of the ms spectra of many of the compounds reveals a considerable degree of exchange occurred, particularly in the higher molecular weight polynuclear aromatics containing methyl substituents.

Conclusions. Inspection of the examples given in Table 2.4 reveals the following: [1] In general, exchange was more extensive in the experiment in which coal was present. The synergistic effect is probably a consequence of the thermally induced coal decomposition reaction. A higher degree of exchange than

<table>
<thead>
<tr>
<th>Compound</th>
<th>% D Content (a)</th>
<th>Coal Present</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphthalene</td>
<td>3.76</td>
<td>5.83</td>
</tr>
<tr>
<td>Methyl-naphthalene</td>
<td>5.94 (3.76 a)</td>
<td>5.89 (5.92 a)</td>
</tr>
<tr>
<td>Dimethyl-naphthalene</td>
<td>5.66 (5.64) (9.40) (7.44)</td>
<td>6.06 (6.01) (12.2)</td>
</tr>
<tr>
<td>Trimethyl-naphthalene</td>
<td>9.12</td>
<td>10.5</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>4.52</td>
<td>6.6</td>
</tr>
<tr>
<td>Methylphenanthrene</td>
<td>6.61 (5.33)</td>
<td>7.0 (9.0) (9.1)</td>
</tr>
<tr>
<td>Dimethyl-phenanthrene</td>
<td>(b) (5.58)</td>
<td>9.5 (10.5) (12.5)</td>
</tr>
<tr>
<td>Biphenyl</td>
<td>0.5</td>
<td>1.6</td>
</tr>
<tr>
<td>Diphenylether</td>
<td>1.9</td>
<td>2.0</td>
</tr>
<tr>
<td>Dibenzofuran</td>
<td>0.8</td>
<td>0.85</td>
</tr>
<tr>
<td>Methyldibenzofuran</td>
<td>12.1</td>
<td>16.91</td>
</tr>
</tbody>
</table>
expected was observed in the solvent without coal present. The result is probably caused by thermal reaction initiated in the light SRC present. (2) The straight chain aliphatic hydrocarbons (data not shown) did not undergo H-D exchange reactions and we conclude that they do not participate in hydrogen shuttling. (3) Single ring aromatic hydrocarbons as typified by biphenyl and diphenyl ether exchange slowly and therefore are not expected to be effective hydrogen shuttlers. The same is true of dibenzofuran. (4) Although naphthalene and phenanthrene exchange only reluctantly in model experiments, they exchange more rapidly in the presence of the coal decomposition reaction. (5) Polynuclear aromatics substituted with methyl groups undergo vigorous exchange, depending at least partly on the position of substitution, thus illustrating the importance of the structure-reactivity relationship demonstrated to be important in bond breaking reactions. The methyl-substituted aromatics are expected to be effective for coal conversion because of their ability to participate in hydrogen shuttling. (6) Other aromatics which contain α-hydrogens such as found in indane and fluorene, and their ethyl-substituted derivatives, are expected to function as hydrogen shuttlers.

Of the numerous compounds in coal process recycle liquids, the polynuclear aromatics substituted with one or more methyl groups appear to be the important constituents which take part in hydrogen exchange reaction affecting hydrogen redistribution and consequent solubilization of coal.


8. ORNL Fossil Energy Program Annu. Prog. Rep. March 31, 1982, ORNL-5877, p. 55. The solvent is a Wilsonville distillate V131, to which light SRC was added by Conoco Coal Development Corp. designated as "Hydro-Solvent, Product from Run 257, 12-8 Feed to S1T-1". The material is referred to as Hydro-solvent in this report.
9. The presence of excessive amounts of biphenyl and diphenyl ether was a result of a leak in the Dowtherm heat exchanger. The fact was discovered only after considerable effort was expended on the solvent, but results and conclusions are not affected.

2.2.2 Radiochemical Studies Related to the Kerr-McGee Critical Solvent Deashing Process (B. M. Benjamin)

This discussion is divided into two parts. The first part deals with Kerr-McGee critical solvent losses resulting from chemical reactions in the second stage of the CSD unit. The second part briefly describes the results of a validation study of Kerr-McGee analysis for deashing solvent in the various streams from the CSD unit.

Solvent Losses. Work was completed in 1981 to a project designed to determine the extent to which Kerr-McGee solvents are lost as a result of chemical reactions with coal-derived products under conditions typical of first
stage operation. When it was demonstrated that these losses are well within design limits, it became necessary to evaluate solvent losses under conditions employed in CSD second stage operation. Solvent balance under pilot plant operation has not been good and it has not been demonstrated whether losses originate from mechanical or chemical problems.

Carbon-14 tagged deashing solvent was prepared using known synthetic procedures. Other experimental and analytical procedures are similar to those used in the first study. Some differences between this experiment and previous experiments are evident. For the earlier work on first stage product fractions, the most soluble part of the SRC contained 53% of the total adsorbed and chemically reacted DAS compared to 98% in this work. The relative amounts for fraction 2, the least soluble part of the SRC, are 47% and 0.8% total adsorbed and reacted solvent, and for fraction 3, which consists of insolubles and ash, 0.4% and 1.6%. Based upon recovered solids, in the earlier work fraction 1 contained a sum of 1.19% of reacted and adsorbed solvent relative to 5.75% in this work. The relative amounts for fraction 2 are 4.98% and 0.20%, and for fraction 3, 0.009% and 0.12%, respectively. In the study on the first stage, the recovered solids contained a total of 0.22% of reacted solvent, whereas in this work the recovered solids contained a total of 0.58% of reacted solvents. The total reacted solvents cannot be recovered, but the adsorbed material must be recovered by steam stripping or other means to meet the design specifications.

Analytical Techniques. Two methods were used for analysis of deashing solvent retained in streams from the Kerr-McGee CSD process. Kerr-McGee used a gas chromatography method and the Wilsonville plant used a distillation method. Large differences in analytical results existed between the two methods. The objective of this work was to validate the Kerr-McGee analytical procedure using 14C-labeled DAS and a material equivalent to CSD first stage feed. A second objective was to evaluate the Wilsonville analytical method via the validated Kerr-McGee method. The Wilsonville method requires sample sizes too large for convenient and safe experimental operations using the 14C-labeled DAS technique.

In our laboratory, reference samples containing known amounts of DAS were prepared by reacting SRC with 14C-labeled DAS in tubing bombs under CSD first stage conditions. Samples of SRC and ash concentrate were prepared from the reaction product. The radio-labeled DAS content of the samples was adjusted approximately to predetermined levels and then accurately measured by burning weighed samples and monitoring the 14C-carbon dioxide in an ionization chamber. Separate samples of SRC and ash concentrate were analyzed for chemically reacted DAS after equilibration with unlabeled DAS. Total DAS assays were then adjusted to reflect only the adsorbed DAS content since the assay performed by Kerr-McGee recovers only the unreacted portion. The materials supplied for this work by Kerr-McGee were never exposed to non-radio-labeled DAS; they were stored in one-gram quantities in vials closed with caps containing a metallic vapor barrier.

The samples, containing a known amount of 14C-labeled DAS, were shipped to Kerr-McGee's Technical Center in Oklahoma City for analysis. Their results were compared with those of ORNL. Generally, the analyses reported by Kerr-McGee displayed a negative bias ranging from about -10 to -20%. Precision was quite good, ranging from relative standard deviations of 2.2 to 2.5% for multiple assays of an SRC and an ash concentrate sample. The radiolabeled samples were returned to ORNL immediately after their assay by Kerr-McGee. In order to ensure that no change in DAS content had occurred in transit, an SRC and an ash concentrate sample were reanalyzed at ORNL. These assays were within ±1.7% of the original assays, verifying that no loss in DAS content had taken place during transit.

The analytical results obtained by Kerr-McGee compare reasonably well with the DAS content by radiolabel assay. The small nega-
tive bias may reflect an inability of solvent extraction at 105°C by the Kerr-McGee method to recover 100% of the physically adsorbed DAS. However, deviations of the analyses from the reference values apparently are independent of DAS content and could be accounted for by assumption of an 86% recovery factor in the solvent extraction step.

The analytical method employed by Kerr-McGee to assay DAS in SRC and ash concentrate samples seems to be quite adequate. Precision as stated by Kerr-McGee is about 5% relative deviation from the mean. The precision obtained on two of these reference samples was much better than that, being 2.2 and 1.5%, respectively. The only possible recommendation for improvement in the method would be the inclusion of an internal standard in the trimethylbenzene solvent. Use of such an internal standard could compensate for minor variations in the flame ionization detector during the period of an analysis. Of course, such an internal standard is useful only if its elution position is close to that of the component being measured and if there is no interfering chromatographic peak produced by solvent extraction of the sample.

The procedure employed at Wilsonville to assay SRC products for their DAS content differs considerably from that of Kerr-McGee. As mentioned earlier, it consists of a distillation procedure. The distillate is caught in a dry ice-methanol trap and estimated by difference weighing and gas chromatography. A group of samples were assayed by the Kerr-McGee method and the Wilsonville method at their respective plants. In general, correlation between the assay was extremely poor. Even after conversations with personnel at both plants, the reasons for the deviation could not be ascertained. In view of the possibility of factors such as non-representative mass balance samples and changes in sample composition due to time lapse between sampling and assaying, the following recommendations were made: (1) At least three samples of each stream to be analyzed should be shipped directly to Kerr-McGee, and (2) the samples are to be portions of the identical homogenized samples which Wilsonville analyzes.
3. AQUEOUS CHEMISTRY AT HIGH TEMPERATURES

This program is directed toward the goal of a broad and detailed understanding of chemical processes occurring in aqueous systems to high temperatures and pressures. Such information relates to the safe and efficient operation of energy production, steam generation, fuel reprocessing, and waste disposal facilities as well as to the extraction of heat and materials from natural resources. Specialized techniques are employed in calorimetry, conductance, potentiometry, spectrophotometry, isopiestic and phase equilibrium studies at temperatures generally to 300°C and at modest pressures and sometimes to 800°C and 4000 bars.

Species identification, thermodynamic properties and equilibrium stability information are obtained but some new emphasis will be placed on structural and detailed quantitative information from neutron and Raman scattering results in collaboration with other programs at ORNL.

3.1 Thermodynamics of Solutions

3.1.1 The Enthalpy of Dilution of Aqueous NaCl to 673 K. Excess Thermodynamic Properties and Their Pressure Coefficients

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

A new high-temperature-high pressure heat and liquid flow calorimeter has been described that is suitable for precise thermal measurements on homogeneous solutions. The present enthalpy of dilution measurements on aqueous NaCl, the accuracy is about 2 per cent but this has been improved in later measurements. Pressure coefficients of reactions are readily measured to about 20 per cent.

The sensitivity of the calorimetric apparatus permits observations to be made on sufficiently dilute solutions that good extrapolations to infinite dilutions are possible. Such extrapolations are required for derivation of excess thermodynamic properties as well as standard state quantities. Excess thermodynamic properties of aqueous NaCl and their pressure coefficients have been derived from our enthalpy of dilution observations and compared with values from the literature. The agreement has been good to excellent except in certain cases at the high salt concentration.

Values of the excess thermodynamic properties of $L_0$, $\gamma$, and $L_2$ (apparent relative molal enthalpy, osmotic coefficient, activity coefficient, and relative partial molal enthalpy, respectively) to 5 mol-kg$^{-1}$ as a function of temperature have been extended into the supercritical region of water to 673 K and 41.5 MPa. Saturation values of $C_p$ (excess heat capacity) have been given to 523 K, and saturation values of $L_0$, $L_1$, $L_2$, $\gamma$, and $\gamma$ have been given to 623 K. No values of these thermodynamic properties above 573 K have been previously available. Pressure coefficients of $C_p$ to 5 mol-kg$^{-1}$ have been given to 522 K, and pressure coefficients of $L_0$, $L_1$, $L_2$, $\gamma$, $\gamma$, and $\gamma$ have been given to 623 K.

The excess thermodynamic properties above 573 K made available from this research show an extension of trends exhibited at lower temperatures. For a 3 mol-kg$^{-1}$ solution of sodium chloride at 673 K and saturation pressure, $L_0 = 188.8$ kJ-mol$^{-1}$, $\gamma = 0.079$, and $\gamma = 0.532$, which may be compared to the values 1.10 kJ-mol$^{-1}$, 0.714 and 1.046, respectively at 298 K. The absolute values of all the pressure coefficients of the excess thermodynamic properties increase with increasing temperature, the rate of increase accelerating above about 550 K.

In our application of the ion interaction model, we found additional terms ($i_2$ and $c^{(2)}$) were required to give a satisfactory fit of our enthalpy results at 573 and 623 K. We were able to obtain a satisfactory, analytical fit of the temperature dependence of the apparent relative enthalpy only to 523 K. Above this temperature graphical treatment of the results were used.

1.1.2 Ionic (Real) Activity Coefficients of NaCl from 30°C to 400°C

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

Aqueous sodium chloride has been shown by electrical conductance measurements to associate at high temperatures (400°-800°C). Stoichiometric activity coefficients of NaCl to 400°C (415 bars) have recently become available from high temperature enthalpy of dilution measurements by flow calorimetry. These two sets of results present an opportunity to estimate the ionic or real activity coefficients, $g^t$, of aqueous NaCl. Knowledge of these activity coefficients is important to geochemists and to theorists interested in testing theories of ionic solutions.

One may write for the association constant, $K$, of NaCl the expression

$$K = \frac{(1 - \alpha)Y_n}{a^2g^t_m^2m}$$

where $\alpha$ is the degree of dissociation, $Y_n$ is the activity coefficient of the neutral NaCl, $g^t$ is the ionic activity coefficient, and $m$ is the molality. For a 1:1 salt, $\alpha = \gamma_z/q_z^t$, where $\gamma_z$ is the stoichiometric activity coefficient. Making the latter substitution into the above expression leads to an equation for $q_z^t$: $1/q_z^t = 1/\gamma_z - km_z^t/\gamma_n$. $\gamma_n$ is assumed to follow the Setchenow relation, $0.01 \gamma_n = kI$, where $k$ is a constant and $I$ is the ionic strength ($I = \sum z_i^2/m_z^t$, $m_z$ is the molality of the $i$-th ion and $Z_i$ is its charge).

Figure 3.1 presents the results of the calculations assuming the Setchenow constant, $K$, to be 0, 0.5, and 0.10. At each temperature the solid curve represent $\gamma_z$ and the broken curves represent $q_z^t$. Below ~1 m the broken curves coalesce. The values of $K$ calculated from Qulst and Marshall were 0.4, 2, and 16 at 250°, 300°, 350°C and 207 bars, respectively, and 62 at 400°C and 415 bars. Reducing the values of $K$ cause the curves of $q_z^t$ to move closer to the curves of $\gamma_z$. A modest increase in the value of $K$, however, has a more dramatic effect. For example, if $K$ at 300°C is increased from 2 to 3, representing a change in log $K$ of only ~0.2, the value of $g^t$ at 5 m and $k = 0$ changes from 0.32 to 0.6. Similarly, the value of $g^t$ at 350°C (and $k = 0$) approximately doubles when $K$ is increased by 0.2 of a log $K$ unit. These much higher values of $g^t$ give curves which do not appear reasonable, suggesting that values of $K$
extrapolated from the results given by Quist and Marshall are probably upper limits.

These calculations demonstrate the extreme difficulty or impossibility of determining association constants from stoichiometric activity coefficients alone. The calculations also demonstrate that the association constants and stoichiometric activity coefficients employed are consistent with each other.


3.1.3 Excess Thermodynamic Properties of Aqueous Solutions of the Alkali Metal Chlorides: 0 to 250°C
(H. F. Holmes, R. E. Mesmer)

Alkali metal chlorides, the most common family of metal salts, have served as the basic model for theoretical and experimental studies of aqueous solutions of electrolytes. Reliable values for the thermodynamic properties of these solutions as a function of temperature have been scarce, particularly so for the less common members. Our recently completed isopiestic study has provided definitive excess free energy data for LiCl(aq), KCl(aq), and CsCl(aq) from 110 to 250°C. In principle other thermodynamic functions can be obtained from basic thermodynamic relationships provided that an adequate model is available for the mathematical operations.

Results from other types of thermodynamic measurements, including enthalpies and heat capacities, have been combined with the isopiestic data within the framework of the ion interaction model by assuming an arbitrary temperature dependence for the parameters of the model. The resulting mathematical description reproduces the experimental results essentially within experimental error over the temperature range of 0 to 250°C. Since the volumetric properties of these three solutions have not been determined in this temperature range it was necessary to neglect the pressure dependence of the thermodynamic functions—an adequate procedure at or below the saturation pressure of water at 250°C. General trends and features of the thermodynamic properties of aqueous solutions of the alkali metal chlorides can be seen from a comparison of the results for LiCl(aq), KCl(aq), and CsCl(aq) with the previously published description of NaCl(aq).

With the exception of the excess heat capacity, the thermodynamic properties of the alkali metal chlorides are in the order LiCl(aq)>KCl(aq)>CsCl(aq) at all temperatures with the individual character of LiCl(aq) being most noticeable in the case of the excess free energy. All of the thermodynamic properties uniformly become more temperature dependent as the temperature increases. Since the ion interaction model uses a fixed ion size parameter in the long range (Debye-Hückel) contributions to the excess thermodynamic properties, differences between members of the alkali metal chlorides are necessarily confined to short range interactions. Differences among the alkali metal chlorides are much more apparent if one examines the quantity \(\ln(\gamma - f^\gamma)\), where \(\gamma\) is the activity coefficient and \(f^\gamma\) is the Debye-Hückel contribution to the activity coefficient. Not only is \(\ln(\gamma - f^\gamma)\) larger for LiCl(aq) but also its temperature coefficient is, under most conditions, opposite to that of the other alkali metal chlorides. At all temperatures involved in this study \(\ln(\gamma - f^\gamma)\) is in the inverse order of the cation size (crystal). This dependence on size is demonstrated in a quantitative manner in Fig. 3.2 which shows the short range contribution to the activity coefficient as a linear function of the reciprocal of the cationic radius for three molalities at four temperatures: The straight lines in Fig. 3.2 are least-squares fits of the data with the
maximum standard deviation amounting to about 5 per cent in the activity coefficient (the maximum standard deviation is at 25°C and 6 mol kg⁻¹). For the cases shown in Fig. 3.2 the average standard deviation is 2.2 per cent.

Two trends are evident in Fig. 3. Dependence of \((\ln \gamma - f)\) on the cation radius decreases with increasing temperature and decreasing molality. The dependence of \((\ln \gamma - f)\) on temperature and ion size should be quite useful for extrapolations and predictions.

As a fitting function, the theoretical form of the Pitzer ion interaction model contains only one adjustable parameter—the hard core ionic diameter. Excess free energies of the four common alkali metal chlorides to 250°C and molalities to 6 mol kg⁻¹ can be modeled surprisingly well with the theoretical form of the ion interaction model, giving standard deviations of fit ranging from 2.5 to 0.3 per cent. Hard core diameters obtained from the fit are in the inverse order of the cation size at all temperatures and are temperature dependent. It is clear that the hard core diameters are physically realistic only if they refer to the hydrated ions. In this respect they are consistent with generally accepted trends in hydration. It is not possible to simultaneously fit free energies, enthalpies, and heat capacities with this theoretical framework.


3.1.4 Isopiestic Studies of Aqueous Solutions at Elevated Temperatures: Alkali Metal Sulfates
(H. F. Holmes, R. E. Wesmer)

The only family of metal sulfates in which all members are sufficiently soluble to permit a comparative study of the thermodynamic properties of their aqueous solutions is the alkali metal sulfates. The sulfate anion is divalent, stable at high temperatures, and plays an important role in natural processes—all significant reasons for inclusion in our isopiestic program. We have measured the isopiestic ratios (relative to NaCl(aq) which allows us to compute osmotic and activity coefficients) of the alkali metal sulfates to 225°C and saturation molalities (except for Cs₂SO₄ which is much more soluble).

General trends of the osmotic and activity coefficients of the alkali metal sulfates with temperature is similar to that seen with the metal chlorides we have studied, i.e., the coefficients decrease with increasing temperature and differences between members of the same family diminish. Under most conditions, the osmotic coefficient exhibits a minimum on passing from Li₂SO₄ to Cs₂SO₄.

However, at high temperatures (>150°C) and low molalities (<1.0 mol kg⁻¹) the osmotic coefficient monotonically increases on going from Li₂SO₄ to Cs₂SO₄. On an absolute basis, the
osmotic coefficients of the alkali metal sulfates are not as temperature dependent as those of the alkali and alkaline earth metal chlorides because they are considerably smaller than those of the chlorides at low temperatures (25°C).

Each set of isothermal osmotic coefficients was subjected to a least-squares fit to the ion interaction model. In contrast to the situation with the chlorides the resulting fits were not very satisfactory. The difficulty lies in the molality dependence of the contribution of binary ionic interactions (the second virial coefficient). This coefficient, $B$, is defined as

$$ B = B_0 + B_1 \exp(-\alpha \sqrt{I}) \quad (1) $$

where $B_0$ and $B_1$ are adjustable parameters, $I$ is the ionic strength, and $\alpha$ is a constant assumed to be $2.0 \text{ kg}^{1/2} \text{ mol}^{-1/2}$ for all electrolytes in which at least one of the ions is univalent. Mathematically, $\alpha$ determines the ionic strength at which the contribution of $B_1$ to the osmotic coefficient is a maximum. For aqueous solutions of the alkali metal sulfates at high temperatures we have found that a much better fit is obtained if $\alpha$ is taken to be 1.4 rather than 2.0. This is illustrated in Fig. 3.3 for the osmotic coefficients of Cs$_2$SO$_4$(aq) at 225°C. The standard deviations of fit are 0.0051, 0.0028, and 0.0139 for $\alpha$ values of 1.2, 1.4, and 2.0, respectively. There are several unfortunate aspects of this situation, not the least of which is the loss of generality and simplicity for the ion interaction model. With the exception of very dilute solution, $B_1$ makes a significant contribution to the activity coefficient at all molalities with the contribution being dependent on the value

![Figure 3.3 Osmotic coefficients, $\phi$, of Cs$_2$SO$_4$(aq) at 225°C as a function of molality, m. Lines are least-squares fits of the ion interaction model to the experimental results using the listed values for $\alpha$.](image-url)
assigned to $\alpha$. This dependence introduces considerable uncertainty into the activity coefficients derived from osmotic coefficient results. The situation at low temperatures (25°C) is less dubious as the goodness of fit of the model to osmotic coefficients is much less dependent on the value assigned to $\alpha$ and the contribution of $8_j$ to the activity coefficient is less significant. Physical reasons for the change in behavior with increased temperature are not clear at the present time but ion association is one possibility.

High temperature heat capacity and enthalpy measurements on $\text{Na}_2\text{SO}_4(aq)$ have recently been completed. These literature data are being combined with our isopiestic results to derive a model for $\text{Na}_2\text{SO}_4(aq)$ in much the same manner as we have done for the alkali metal chlorides. Since we are using the ion interaction model as a mathematical framework, the chosen value of $\alpha$ becomes a critical question. Fortunately, fitting of the heat capacity and enthalpy results is not very dependent on the specific value assigned to $\alpha$ within reasonable bounds. Our present work will result in some refinement to the current osmotic and activity coefficients for $\text{Na}_2\text{SO}_4(aq)$ at high temperatures as the published tables were calculated from a double integration using $2.0 \text{kJ mol}^{-1}$ as the value of $\alpha$.


3.2 Equilibrium, Kinetics, and Speciation Studies

3.2.1 New Relationship for the Vaporization of Liquids to the Critical Temperature

(W. L. Marshall)

In examining the vaporization ratio, $\Delta E/(P\Delta V)$, for liquids at the approach to the critical temperature, a simple relationship for this property over wide ranges of temperature has been observed. In this relationship, $\Delta E/(P\Delta V)$ is a straight line function of $(1 - T_r)^2$, where $\Delta E$ is the internal energy of vaporization, $P$ is the vapor pressure, and $\Delta V$ is the volume change upon vaporization. In the latter expression, $T_r$ is the reduced temperature and is equal to $T/T_c$ where $T$ is the temperature of observation in degrees Kelvin and $T_c$ is the liquid-vapor critical temperature. The straight line adherence was observed for approximately ninety liquids, including inorganic, organic, and those of the atmospheric gas, at values of $T_r$ from 1.0 to 0.6, and even to the freezing point if $T_r$ did not decrease below this range. The intercept ($B$) and slope ($C$) in the relationship,

$$R_E = B + C \cdot (1 - T_r)^2 \quad (1)$$

where $R_E$ equals $\Delta E/(P\Delta V)$, differ for each liquid but generally increase as $T_c$ increases. The wide agreement by dissimilar liquids suggests that the relationship is universal and fundamentally important.

Differentiation of Eq. 1 with respect to temperature shows that $dR_E/dT$ approaches zero at the critical temperature. The ratio $R_E$ asymptotically approaches $B$ at this limit, and $B$ is thus a property of a liquid at the limit of $T_c$ that is defined here as the critical vaporization ratio. Figure 3.4a shows separate values of $\Delta E$ and of $P\Delta V$ for water from the critical temperature of 647.31 K down to 373 K, calculated from values elsewhere and plotted against $(1 - T_r)^2$. In Fig. 3.4b, $R_E$ is plotted similarly against $(1 - T_r)^2$. Thus a combination of the two asymmetrical curves in Fig. 3.4a produces a straight line from $T_r$ equal to unity to a value of 0.59. A positive deviation for water occurs at temperatures below 373 K and reaches a maximum of 10% in $R_E$ at the freezing point.

Additional examples of the adherence to Eq. 1 are given in Fig. 3.5 as plots of $(R_E - B)$.
against \((1 - T_r)^2\) for thirteen dissimilar liquids (including water), with values of \(R_E\) determined from readily available properties.\(^2,3\) From Eq. 1, it can be shown the proportionality of \(\Delta E\) to P\(AV\) approaches independence with temperature at the limit of \(T_C\). This behavior is unique. An hypothesis is suggested that P\(AV\) approaches the numerical equivalence of \(\Delta E\) for a single interaction destroyed. With this supposition, \(B\) would represent the number of interactions destroyed, whether expressed as van der Waals or London forces, or structural bonds. The hypothesis will be supported by a later publication.

The simple relationship of Eq. 1 thus describes a vaporization property of liquids over wide ranges of temperature, and it produces for a liquid at the limit of the critical temperature a unique critical property: the critical vaporization ratio. The relationship is supported by its successful inclusion into the Clapeyron equation for calculating vapor pressures, and it may be significant in thermodynamics and its theory.

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1. Summary of paper submitted for publication. Details presentation in:
   W. L. Marshall, ORNL-5920 (September 1982).
2. International Formulation Committee 1967 Steam Tables; Committee established by Sixth International Conference on the Properties of Steam (New York, October, 1963).
3.2.2 Amorphous Silica Solubilities: Postulated Sulfate-Silicic Acid Solution Complex

(W. L. Marshall, C.-T. A. Chen)

Solubilities have been presented recently of amorphous silica in separate and combined aqueous solutions of sodium chloride, magnesium chloride, sodium sulfate, and magnesium sulfate at temperatures from 100°C to 350°C. These results show that, with the exception of sodium sulfate solutions at 150°C and above, amorphous silica at a constant temperature decreases in solubility with increasing concentration of added salt (a salting-out effect). Sodium sulfate decreases the solubility at temperatures below 150°C but progressively increases the solubility with increasing temperatures.

Although several factors may be involved in salting-in or salting-out, it seems that the formation of a complex between dissolved silicic acid and the sulfate ion might account for salting-in by Na₂SO₄. For example, we may write the equilibria:

\[ Si(\text{OH})_4 + n\text{Na}^+ + m\text{SO}_4^{2-} \rightleftharpoons Si(\text{OH})_4\text{·SO}_4^{2-} \cdot n\text{Na}^+ \]  

The increased solubility in a Na₂SO₄ solution over that in a NaCl solution containing an equivalent sodium molality would be expected to represent the molality of the complex described in Eq. (2).

The association constants for the proposed complex are obtained from behavior at the approach to infinite dilution although calculations at finite concentrations, using the determined constants, agree well with experiment. We may write:

\[ n_a = \frac{(s_1 - s_2)}{s_2 \cdot (m_1 - (s_1 - s_2))} \]  

where \( s_1 \) is the molal solubility in a given molality of Na₂SO₄, \( s_2 \) is the solubility in a NaCl solution of twice the molality of Na₂SO₄, and \( m_1 \) is the molality of Na₂SO₄.

Values of \( s_1 \) and \( s_2 \) at given values of \( m_1 \) are easily calculated from the mathematical equations published recently that describe the solubilities of amorphous silica in Na₂SO₄ and NaCl aqueous solutions as a function of concentration and temperature (from 0 to 300°C). By incorporating these several published equations into Eq. (3), together with the extrapolations to zero ionic strength, the following equation is obtained to describe the log of the association constant \( K_a \) of Eq. (3) for the postulated complex as a function of absolute temperature:

\[ \log K_a = \log(-9.016154 + 1.2727 \times 10^{-2} T - 8.8429 \times 10^{-7} T^2) \]  

Figure 3.6 shows \( \log K_a \) obtained from Eq. (4) plotted against \( 1/(T/K) \). A surprisingly straight line is obtained from which a stan-
standard molar heat of formation of +0.49 kcal mol\(^{-1}\) is evaluated from the slope. It is interesting to note that the equations that were combined to produce Eq. (4) were obtained independently of each other and before the present evaluation. The straight line (Fig. 3.6) simply results from this combination. Because of the abundance of silica in the natural environment, the possible existence of a silica-sulfate solution complex is very important. It could be useful in predicting silica solubilities in multicomponent aqueous systems of greater complexity than those already studied.

3.2.3 Calculation of Amorphous Silica Solubilities and Cation Hydration Numbers in Aqueous Salt Solutions using the Concept of Effective Density of Water\(^1,2\) (R. O. Fournier,\(^3\) W. L. Marshall)

There is a large need for reliable predictions of silica solubilities at temperatures up to 400°C in dilute and concentrated natural salt solutions. Geothermal power production, developing theories on the transport of minerals in hydrothermal solutions, neother-

monometry applying the quantitative measurements of silica solubility, and the recent discoveries of the deep ocean: hot springs have necessitated further knowledge in this direction.

In a fundamental approach, the solubility of amorphous silica in aqueous salt solutions at 25° to 300°C has been calculated from information on its solubility in pure water and a model in which the activity of water in the salt solution is defined to equal the density of effective water in the solution (\(\rho_e\)). At temperatures of 100°C and above, \(\rho_e\) closely equals the product of the density of the solution times the weight fraction of water in the solution. At 25°C, a correction parameter was applied to \(\rho_e\) that incorporates a term called the apparent cation hydration number, h. The numbers obtained are not necessarily real hydration numbers even though they do agree with some published values determined by activity and diffusion methods.\(^4\)

At temperatures of 100°C and above, the apparent hydration number for Na\(^+\) in aqueous NaCl and NaN\(_3\) solutions from this model is zero, and \(\rho_e\) reduces to the product of the density of the salt solution multiplied by the weight fraction of water in the initial salt solution. The above probably is true for most other salts above 100° to 200°C. Below about 100°C an activity coefficient or correction parameter must be applied that appears to be related to the tightly bound waters of hydration of the salt. At 25°C, if the solubility of amorphous silica in a salt solution and the density of that solution are known, an apparent cation hydration number can be calculated, provided dissolved silica does not form a complex with the salt.

Figure 3.7 shows the correlation at 25°C that is obtained by calculating values of the apparent hydration number from the published solubilities\(^5\) for several salts. In this figure, the logarithm of the molal solubility of amorphous silica is plotted against the logarithm of the effective density (\(\rho_e\)), where the slope shown is that extrapolated from
The use of the Setchenow equation with units of molarity allows the description of solubilities to the highest concentrations of a dissolved salt, with one parameter (the slope of the relation) needed for each salt. However, solubility behavior as a function of density (or pressure) in pure water cannot be described with the Setchenow equation. With given values of n from the solubility results in pure water, the present chemical model describes solubilities, with one parameter for each salt (the apparent hydration number), both in salt solutions and in pure water as a function of density of "free" water. At temperatures of 100°C and above, a hydration parameter is unnecessary for NaNO₃ and NaCl, and may not be needed for most other salts, except those of smaller ionic radius or higher charge such as Li, Mn, and Ca. This study provides a chemical model for describing amorphous silica solubilities that should have both fundamental and practical applications.


1.2.4 Sodium Sulfate Solubilities in High Temperature (250-374°C) Aqueous Solutions of Sodium Chloride and Sulfuric Acid; Experimental Measurements, Theoretical Predictions, and Applications to Corrosion in Steam Generators¹ ²

(M. H. Lietzke³, W. L. Marshall)

A major problem in the operation of steam generators for both nuclear and fossil fuel plants is that of intergranular attack, tube wastage, and pitting and crevice corrosion in steam generator tubes. Because of temperature gradients, boiling concentration appears to occur at various locations including that within the tubesheet crevices, and thus corrosion is further enhanced. The saturation precipitation of sodium sulfate (Na₂SO₄) solid on the metallic surfaces, or within crevices of steam generator components caused by corrosion, for example, within steam generator tubes, has been perceived to be a possible cause for enhanced corrosion.

Experimental measurements on the solubility of Na₂SO₄ in aqueous solution mixtures of NaCl and H₂SO₄ were obtained at temperatures from
250 to 374°C, the temperature range of interest for existing steam generator cycles. The technique used was developed earlier at ORNL. The solute compositions, other than Na$_2$SO$_4$, were varied in mole ratio, NaCl/H$_2$SO$_4$, from NaCl only to H$_2$SO$_4$ only, and the total solute concentrations were varied from very dilute solutions to 3-4 molal.

Figure 3.8 shows isothermal plots of the solubility of Na$_2$SO$_4$ in the aqueous NaCl solutions at temperatures from 250 to 350°C. We observe the decrease in solubility in H$_2$O along with increasing temperature and the reversal of solubility behavior in NaCl solutions (decreasing solubility as m$_{NaCl}$ increases at temperatures below 315°C, and the reverse behavior at higher temperatures).

Figure 3.9 shows one example of some of the solubility measurements obtained in this study, in solutions with a mole ratio, H$_2$SO$_4$/NaCl, of 3.

The measurements, together with some earlier published solubilities of Na$_2$SO$_4$, and values for several ionization constants, were used in obtaining parameters for some semi-theoretical equations whereby calculations of solubility could be made and compared with the experimentally obtained values. Figure 3.10 gives plots at several constant temperatures of the calculated values of $Q_{sp}$ shows the Nernst-Möckel limiting law slopes. From the several observations, the behavior shown in Fig. 3.8 is now understood. At the lower temperatures, the decreasing solubility (with...
increasing $m_{NaCl}$) is due to the mass action or common ion effect. With increasing temperature, the Debye-Hückel calculated slopes (as shown in Fig. 3.10) increase and subsequently the ionic strength outweighs the mass action effect. The solubility then increases with increasing NaCl.

Although bulk water in the steam cycle may contain only ppm or ppb impurities, these impurities may concentrate in crevices under the conditions cited above to produce as much as one to three molal $Na_2SO_4$, together with NaCl and $H_2SO_4$, in the highly concentrated solution before precipitation (of $Na_2SO_4$) would occur. The pH (acidity) therefore could approach values of 2 or even 1 (0.01 or 0.1 molal $H^+$), resulting in a highly corrosive solution. Computer programs included in the full report should be useful in determining the extents of concentration of solutes in crevices resulting from the temperature gradients within the tubes together with the vapor pressures of the concentrated solutions formed during a plant operation.

This study demonstrates the practical knowledge and wide predictability that can be obtained from a fundamental approach to the study of properties of aqueous electrolytes at high temperatures.

2. Sponsored by the Electric Power Research Institute, Menlo Park, CA.
3. Present address: Dept. of Chemistry, University of Tennessee, Knoxville, TN.

3.2.5 Two-Liquid-Phase Boundaries and Critical Phenomena at 275-400°C for High Temperature Aqueous Potassium Phosphate and Sodium Phosphate Solutions

(W. L. Marshall)

Two-liquid phase boundaries and liquid-vapor critical temperatures for aqueous solutions of potassium phosphates have been obtained, together with analogous measurements, in addition to those reported previously, on the sodium phosphate system. This work was motivated because of its potential application to the chemistry and possible reduction of corrosion in steam generator cycles by the
addition of very small amounts (in the ppb range) of phosphates to the circulating fluid. The experimental procedures were the same as those used for studying the sodium system and earlier for the first study of the potassium system.

Figure 3.11 shows the plots of boundary temperatures of two-liquid-phase formation for aqueous solutions of potassium phosphates for the several constant mole ratios, K/PO₄. Above the critical temperature of the dilute phase, as described by the horizontally dashed lines, the composition of concentrated phase depends upon the relative volume of supercritical fluid, which may be varied by changing the pressure on the system.

It is of much interest to know the phase behavior of potassium phosphate solutions of mole ratio, K/PO₄, greater than 2.12. A plot of the minimum temperature of immiscibility for the several series of curves (Fig. 3.11) against the mole ratio, K/PO₄, for each series shows an initially rapid decrease in temperature of immiscibility with increasing K/PO₄ ratio, which reaches zero chance at the composition K₂HPO₄, and then increases with a further increase in ratio. With a minimum temperature of immiscibility reached for K₂HPO₄-H₂O solutions, it would appear that increasing the mole ratio, K/PO₄, from 2.0 toward 3.0 and even toward infinity (that is, for KOH-H₂O) will simply increase the immiscibility temperature or eliminate immiscibility entirely.

Figure 3.11. Two-liquid-phase boundaries for condensed aqueous solution mixtures of potassium phosphates for mole ratios, K/PO₄, from 1.00 to 2.12, 360-400°C.

Figure 3.12. Two-liquid-phase and solution-solid boundaries for aqueous solution mixtures of sodium phosphates for mole ratios, Na/PO₄, from 1.00 to 3.00 at 200 to 400°C.
Figure 3.12 shows the experimentally determined values for liquid-liquid immiscibility and the estimated compositions and liquid-vapor critical temperatures for dilute liquid phases for the several series of solution compositions of constant mole ratios, Na/PO₄. Also shown are values of liquid-liquid immiscibility reported by Broadbent et al.⁵ and some interpolated values from the very recent work of Wetton⁶, from Panson et al.⁷, and from Ravich and Shcherbakova.⁸ Included also are the solid-liquid equilibrium values of Schroeder, et al. Agreement of the present measurements with these values appears to be excellent.

Conclusions. In this study comparative immiscibility boundaries and liquid-vapor critical temperatures were made for aqueous potassium phosphate and sodium phosphate solutions of mole ratio, alkali metal/phosphate, varying from 1.7 to 2.17 and 2.16, respectively, and at temperatures between 275 and 399°C. Potassium phosphate solutions show higher solubilities and higher temperatures of phase homogeneity than comparable sodium phosphate solutions. Aside from the strongly fundamental interest in the phenomenon of liquid-liquid immiscibility in aqueous-inorganic systems at high temperatures, there are potential applications to problems of steam power generation.


3.2.6. The Kinetics of Iodine Hydrolysis

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

The kinetics of iodine hydrolysis, including a number of side reactions, have been modelled from existing literature data using a computer program based on the L-SNOE subroutine which utilizes the Gear method to solve tight differential equations.¹ This model allowed the limited data base to be expanded to incorporate conditions that may be encountered after a nuclear accident. The ranges of conditions covered are: 25 to 125°C, pH values from 5 to 11, and initial iodine concentrations of 10⁻⁴ to 10⁻⁵ M.

The reactions considered are as follows:

\[

t_1: I_2 + H_2O \rightleftharpoons HOI + I^- + H^+ \quad (1)
\]

\[
k_1^{-1}
\]

\[
k_2
\]

\[
t_2: I^- + I^- + 2H^+ \rightleftharpoons I_3^- \quad (2)
\]

\[
k_2^{-1}
\]

\[
k_3
\]

\[
t_3: 3HOI \rightleftharpoons I_3^- + 2I^- + 3H^+ \quad (3)
\]

\[
k_3^{-1}
\]

\[
k_4
\]

\[
t_4: HOI + H^+ \rightleftharpoons H^+ \quad (4)
\]

\[
k_4^{-1}
\]

\[
k_w
\]

\[
t_5: H_2O \rightleftharpoons OH^- + H^+ \quad (5)
\]

Reaction (1) is very fast and experiments with temperature-jump relaxation techniques carried out in cooperation with Dr. R. van Eldik at the University of Frankfurt, F.R.G., have indicated that the mechanism is more complex than was reported in the literature. Work is continuing to resolve this dilemma with measurements being made at 20°C over the pH range of 3 to 6.

Equation (3) is central to this reaction scheme and studies of the reverse reaction (Dushman Reaction), characterized by rate constant k$_{-3}$, have been completed using stopped-flow spectrophotometry. The results substantiate$^4$ that a fifth-order rate law is operative over the entire range of conditions studied, viz. pH range 1.3 to 4.2; initial iodate concentrations of 5 x 10$^{-5}$ M; ionic strengths of 0.1 to 1.0 M; temperatures of 14 to 67°C; and iodide concentrations of 0.005 to 0.05 M. For example, at 25°C and I = 1.0 (NaClO$_4$), k$_{-3}$ = 2.62 x 10$^{8}$ M$^{-4}$ s$^{-1}$ and the activation energy is 26.2 ± 0.8 kJ mol$^{-1}$.

The rate of the forward reaction in Eq. (3) was studied by the pH stat technique with able assistance from a summer student, Leslie Lyons of Colgate University. The nature of this method restricted the pH range that could be studied effectively to ca. 8 to 10.4. Nevertheless, these data established that a two-term rate law is in effect under these conditions, with the observed second-order rate constant, $k_{obs}$, being represented by the expression:

$$k_{obs} = k_1[H0I]^2 + k_2[0I^-](HOI)$$  \hspace{1cm} (6)

Ongoing spectrophotometric measurements at high pH (ca. 12-13) indicate a third term exists, corresponding to $k_3[0I^-]^2$. The latter term is naturally much smaller as it is derived from the interaction of two similarly charged ions. Conversely, the rates determined by the two terms in Eq. (6) are similar, i.e., $k_1$ = 1.6 ± 0.4 M$^{-1}$ s$^{-1}$ and $k_2$ = 7.34 ± 0.4 M$^{-1}$ s$^{-1}$ at 25°C and I = 0.2.

The data from the pH stat and spectrophotometric measurements were fitted to a model involving Eqs. (1)-(5) which were solved using the Newton-Raphson method. By extrapolating the pH stat data to zero time using a quadratic equation the value of $K_4$ was determined under reaction conditions. Values of $K_1$ and $K_2$ were determined independently by spectrophotometric methods under the same pertinent conditions.


3.2.7 A Comprehensive Review of Metal Carbonato Chemistry$^1$

(D. A. Palmer, R. van Eldik$^2$)

This review pertains essentially to the period from 1969 to 1982, but does include pertinent references to earlier studies. In excess of one thousand references are cited. The treatise is structured as follows:

I. Introduction
   The Chemistry of Carbonates
II. Physical Properties of Carbonates
   A. Spectroscopic characterization
   B. Solubility characteristics
   C. Thermodynamic and related properties
   D. Thermal decomposition of CO$_2$
III. Carbonic Acid, Bicarbonate and Carbonate Hydrolysis Equilibria
   A. Carbon dioxide dissolution equilibria
   B. Carbonic acid ionization
   C. Aqueous carbon dioxide ionization
   D. Bicarbonate ion ionization
   E. Isotopic exchange equilibria
IV. Kinetics of Carbon Dioxide Hydrolysis and Carbonic Acid Dehydration
The Chemistry of Metal Carbonato Complexes

V. Preparation and Characterization
   A. Preparation and spectroscopic data
   B. Structure

VI. Solid State Thermal Decomposition
   A. Transition metal complexes
   B. Lanthanide complexes
   C. Actinide complexes

VII. Equilibria

VIII. Kinetics and Mechanisms
   A. Formation reactions
   B. Aquation reactions
   C. Exchange, substitution and isomerization reactions
   D. Miscellaneous reactions

The Chemistry of Metal Carbon Dioxide Complexes

IX. Preparation and Characterization

X. Carbon Dioxide Fixation Reactions
   A. Rh-CO₂ complexes
   B. Ir-CO₂ complexes
   C. Cu-CO₂ complexes
   D. Ni-CO₂ complexes
   E. Other metal-CO₂ complexes

XI. Carbon Dioxide Insertion Reactions
   A. Insertion into M-H bonds
   B. Insertion into M-C bonds
   C. Insertion into M-N bonds
   D. Insertion into M-O bonds
   E. Other insertion reactions

Applied Metal Carbonate Chemistry

XII. Geochemistry and Oceanography
   A. Mineralization and Transport
   B. Exchange processes
   C. Oceanography

XIII. Biochemistry
   A. Carbonic anhydrase
   B. Other enzymes

The applied sections on geochemistry, oceanography and biochemistry are not meant to provide researchers active in these areas with a comprehensive review of the literature, but rather to give research chemists an insight into some of the applied aspects and implications of carbonate metal chemistry in these areas.

1. Submitted to Chemical Reviews.
2. University of Frankfurt, F.R.G.
4. GEOSCIENCES

This program provides basic geochemical information on hydrothermal and magmatic processes involving both homogeneous and heterogeneous systems emphasizing the high temperature and high pressure regimes that are conducive to promote transport and redistribution of materials in the crust. Special facilities are employed in experimental studies including a hydrogen service, internally heated vessel for studies to 1400°C and 500 MPa. Dickson-type gold cell apparatus, emf cells, conductance, calorimetric and isopiestic facilities are utilized in hydrothermal work to conduct speciation, equilibrium and kinetics studies. Detailed thermodynamic and kinetic information on well chosen specific systems is needed to provide the data base for quantitative modeling of complex mixtures in natural rocks and fluids. The important geochemical questions addressed are magmatic and volcanic processes, element cycling, petrogenesis, alteration, ore deposition, waste storage and geothermal energy.

In Section 4.3 the role of the oceans in the carbon cycle is discussed and a two-dimensional model is described which simulates the processes that control the exchange of CO2 with the atmosphere.

4.1 High Temperature-High Pressure Silicate Studies

4.1.1 New High Pressure/High Temperature Facility for Simulation of Conditions to 18.5 Km in the Earth's Crust (M. T. Maney)

High pressure/high temperature oxidation and reduction reactions strongly affect evolutionary changes in rocks of the Earth's crust. A new facility in use at ORNL enables study of such reactions under conditions simulating depths to 18.5 km. The main component of the facility is an internally heated pressure vessel capable of operating at hydrogen pressures of 500 MPa and temperatures up to 1400°C (see Fig. 4.1). High pressure gas mixtures used in the vessel contain hydrogen to control oxidation-reduction reactions in studies of natural and analog geologic materials. In the past, use of hydrogen containing atmospheres to study these reactions was limited and hazardous because hydrogen embrittlement weakened the vessels. Our novel design utilizes a vented liner and two alloys that are not subject to hydrogen-embrittlement (austenitic stainless steel and copper-beryllium alloy). The hydrogen content of the high pressure atmosphere is manipulated by osmotic diffusion above 500°C using an internally supported platinum membrane. The ability to control the amount of hydrogen in the high pressure gas mixture allows the experimenter to impose a wide range of desired oxidation-reduction conditions on the assemblage of minerals under investigation, since they are also encapsulated in a hydrogen permeable alloy. An example would be the control of ferrous/ferric ratios in iron-bearing phases. Initial studies using the new facility will be made on uranium partitioning among oxidation-reduction sensitive iron-bearing phases, and on methane stability under conditions simulating deep crustal environments.

4.1.2 Iron Redox Equilibrium and its Effect on Crystallization of Silicate Liquids

Results of experiments recently conducted at 100 kPa to investigate iron redox reactions in silicate melts indicate that assumptions about
the kinetics of these reactions made in recently published reports by others have been too optimistic, with regard to silica-rich compositions. An important consequence of underestimating the time required for silicate melts to reach redox equilibrium is that ferrous-ferric iron ratios obtained from such samples are non-equilibrium values. These non-equilibrium data have subsequently been used to formulate functional relationships to calculate equilibrium oxygen fugacity of natural magmas in terms of temperature, bulk composition, and Fe\(^{2+}/Fe^{3+}\) ratios.

The results summarized below pertain to the widely used "platinum loop method" developed to minimize sample-crucible chemical interaction and simultaneously promote rapid interaction between sample and a \(f_0_2\) controlling furnace atmosphere. Sample preparation methods which fully encapsulate a specimen require greater times to reach redox equilibrium under otherwise similar conditions.

A series of timed experiments with each of three silicate liquids derived by melting natural volcanic rocks of widely varying composition (basalt, andesite and rhyolite) were conducted at 1243°C and two redox conditions: \(\log f_0_2 = -6.05\) and \(-7.03\) (quartz-fayalite-magnetite buffer) in a \(CO/CO_2\) gas mixing vertical tube-furnace. The time required for redox equilibration was established by the shortest experiment duration required to attain a constant \(Fe^{2+}/Fe^{3+}\) ratio. Total Fe and Fe\(^{2+}\) were determined colorimetrically (Fe by difference). Minimum equilibration times determined by this method are 900 and 1000 for the basalt and andesite respectively. The rhyolite showed no indication of reaching equilibrium in experiments of up to 5000 minutes duration. Equilibrium times reported here are 20% longer than durations cited in the literature for experiments with andesite, and suggest that no data reported for rhyolite represent equilibrium. Results of this study may be used as a guide to iron redox kinetics, in studies of silica-rich magmatic liquids employing the platinum wire loop experimental technique.

Additional studies of silicic calc-alkaline melts, using the previously obtained kinetic data, are in progress to investigate the influence of redox conditions on crystallization. The goal of these studies is to understand the influence of redox conditions on chemical fractionation and crystallization of magmas in the crust.

This investigation is designed to test the influence of Fe\(^{2+}/Fe^{3+}\) ratios in silicate melts and the presence or absence of coexisting iron oxide phases, on subsequent development of crystallization texture upon cooling. Research work to date (with an andesitic melt) indicates that a more oxidized melt, containing an iron oxide phase, when subjected to moderate undercooling produces a fine grained mass of plagioclase and pyroxene similar to the ground mass texture of the natural rock. A more reduced silicate melt (containing no oxide phase) subjected to the same moderate undercooling produced a sparse number of larger plagioclase spherulites (somewhat analogous to natural porphyritic volcanic rock textures).

Petrologists have long recognized the tendency for more reduced volcanic rocks to be glassy and their oxidized counterparts in the same flow to be more crystalline (e.g., Washington, 1920, Am. J. Sc., 50, 446-462). Our results suggest that this phenomenon may be controlled by the absence or presence, respectively, of an iron oxide phase, that acts as a nucleating agent for crystallization of other silicate minerals from the silicate liquid upon cooling. Experiments are being conducted to test this hypothesis and to further investigate the influence of the redox state of homogeneous silicate liquids on crystallization.

4.1.3 Olivine Nucleation and Growth Kinetics in Synthetic Basalt Magmas

Results of crystal nucleation and growth experiments conducted at 100 kPa to investigate nucleation delay and the crystal growth
rate of olivine (Mg$_2$SiO$_4$) precipitating from two Fe-free model basaltic liquids indicate that: (1) increased viscosity reduces the predictability of crystal nucleation, (2) initial growth rates are 2 to 3 orders of magnitude greater than "average" growth rates observed in this study (experiment duration > 24 hours) and reported for olivine in the literature, and (3) nucleation delay phenomena can significantly influence growth rate values as calculated from isothermal crystallization experimental data.

Synthetic iron-free basaltic liquids having contrasting viscosities (B1 - quartz dolerite, T$_{liq}$ = 1352 ± 3°C, n = 237 poise; B3 - high alumina basalt, T$_{liq}$ = 1375 ± 3°C, n = 36 poise) were subjected to undercoolings of 10 to 90°C and maintained at the subliquidus temperature for times ranging from 0 to 5000 minutes before quenching. A time-temperature region of unpredictable nucleation was observed for both compositions studied, but for a given undercooling greater periods of unpredictable nucleation were observed in experiments with the more viscous quartz dolerite (B1). Crystal growth rates in both compositions (corrected for nucleation delay times) parallel to the c crystallographic direction decreased linearly from initial values as high as 10$^{-3}$ cm/sec for experiment durations less than 1 minute to growth rates in the range 10$^{-7}$ to 10$^{-6}$ cm/sec for experiments of 24 hours duration subjected to small undercoolings (<30°C). Crystal growth rate values changed by a factor of up to 200 when nucleation delay time corrections were applied to the data. This study has provided kinetic data needed for development of a quantitative model of basaltic magma flow and consolidation.

4.1.4 Stability of "Magmatic" Epidote in Granitic Rock Systems

The recently installed hydrogen-service internally heated pressure vessel is being used to investigate the stability of epidote [Ca$_2$Al$_3$Si$_3$O$_{12}$(OH)$_2$], a common accessory mineral of silicic plutonic rocks. Experiments are being conducted to define the coexistence of epidote with hydrous granitic melts as a function of temperature (500-700°C), pressure (200-800 MPa), bulk composition, and oxygen fugacity. A pressure dependence for this coexistence has been demonstrated (Naney, 1983) that may provide a single point "geobarometer" under favorable geologic conditions. This study will quantify the pressure dependence of epidote-melt coexistence in granitic systems and provide phase stability data that will be needed in a subsequent study of uranium and thorium chemical partitioning among coexisting silicic liquids, aqueous vapor, and crystalline phases.


4.1.5 Theoretical Evaluation of Diffusion-Controlled Oxygen Isotopic Exchange between Silicates and Fluids at Elevated Temperatures (D. R. Cole)

Stable isotopic exchange accompanying the interaction of minerals and fluids is controlled by one of two major processes, diffusion or surface reactions. Diffusion involves the transport of oxygen-bearing species through phases either along lattice planes or crystal imperfections. Self-diffusion coefficients for oxygen or oxygen-bearing species measured in feldspars and micas range from 10$^{-18}$ to 10$^{-12}$ cm$^2$ sec$^{-1}$ in the temperature range of 400° to 800°C.

Detailed examination of diffusion equations indicates that the time required to attain a given fraction of equilibrium (1-F) can be evaluated as a function of grain radius, grain geometry, fluid/solid mass ratio and rate at a particular temperature (See Fig. 4.2).
Calculations using these equations demonstrate that the time required to attain isotopic equilibrium increases with an increase in the fluid/solid mass ratio and/or grain radius, or a decrease in temperature. The rates of isotopic exchange involving diffusion are, however, several orders of magnitude slower than isotopic exchange accompanying surface reactions (Cole, et al., 1993).

These calculations suggest that in natural systems, stable isotopic exchange may proceed in two very different directions. One involves a two stage process where the first stage is surface-controlled (alteration reactions), with partial attainment of isotopic equilibrium occurring between mineral and solutions as the mineral alters to some new equilibrium phase. Diffusion of oxygen-bearing species from the solution into the unaltered, residual portion of the mineral controls the second stage of isotopic equilibration with the fluid.

Isotopic data from several types of natural systems (hydrothermal, diagenetic, subsolidus igneous plutons) suggest that in addition to a coupling of the two mechanisms, they may also be mutually exclusive (Cole, 1980). Based on the calculations given by Cole (1983) and Cole et al. (1983) diffusion is likely to dominate in many systems at temperatures in excess of 350°C to 400°C, whereas surface exchange is dominant below these temperatures. The distinction is not necessarily clear cut and the coupling of both mechanisms is probably widespread between 300°C and 400°C.

Application of diffusion equations to selected geologic problems has demonstrated the power these equations have in quantifying important geologic variables such as grain radius, fluid/solid mass ratio and time. For example, the relationship between the degree of $^{18}$O depletion in plagioclase and grain radius observed in some igneous plutons was explained by the use of the diffusion equation for spheres interacting with a well-mixed solution of limited volume. It is hoped that these and other geologic estimates can be tested by integration of isotope kinetic data with mass transfer and fluid flow modeling.


4.2 Hydrothermal Geochemistry

4.2.1 Electrical Conductances and Ionization Constants of Acids and Bases in Supercritical Aqueous Fluids: Hydrochloric Acid from 100 to 700°C and at Pressures to 4000 Bars$^1$2

(W. L. Marshall, J. N. Frantz$^3$)

The quantitative determination of the electrical conductances of aqueous electrolytes and their ionization behavior at high
temperatures and pressures is of basic and practical interest to several disciplines: hydrothermal geochemistry, including chemical oceanography (for example, understanding the behavior of deep ocean hot springs), pressurized water reactors and associated steam generators, geothermal energy processes, and basic chemistry and physics. One electrolyte of considerable interest is HCl.

The electrical conductances of 0.002, 0.005, and 0.010 m HCl solutions have now been measured at 100°C intervals up to 700°C and at pressures between 500 and 4000 bars. The results for one molality (0.002 m HCl) are shown in Fig. 4.3 as plots of molar conductance (A) vs. density (dH₂O, g·cm⁻³) at several high temperatures. The initial increase in the equivalent conductance with increasing temperature and decreasing density reflects the increased mobility of the ions resulting from the reduced viscosity of the solvent. The decrease in the equivalent conductance with increasing temperature above 400°C and decreasing density below 0.75 g·cm⁻³ reflect increased association of HCl.

By using the Debye-Hückel-Onsager equations, the equivalent conductances of HCl (A) can be extrapolated to infinite dilution to yield the limiting equivalent conductances (A₀). For each integral temperature below 450°C and density above 0.70 g·cm⁻³, the limiting equivalent conductance of HCl was computed with a least-squares fitting program in conjunction with equivalent conductance values of this study.

As shown earlier, limiting equivalent conductances appear to follow straight lines with respect to density. At low temperatures, they increase rapidly as a function of temperature but tend to become temperature dependent and linear with respect to density above 400°C. Experiments on 1:1 salts (MgCl₂ and CaCl₂) resulted in nearly identical functional relationships between the limiting equivalent conductances and the density of H₂O.¹⁻⁷

\[
\begin{align*}
A_0(K(\text{HSO}_4)) &= 1740 - 1100 d_{\text{H}_2\text{O}} \\
A_0(\text{NaCl}) &= 1876 - 1160 d_{\text{H}_2\text{O}} \\
A_0(\text{NaBr}) &= 1880 - 1130 d_{\text{H}_2\text{O}} \\
A_0(\text{MgCl}_2) &= 1980 - 1230 d_{\text{H}_2\text{O}} \\
A_0(\text{CaCl}_2) &= 2100 - 1370 d_{\text{H}_2\text{O}}
\end{align*}
\]

It can be inferred from the above results that the mobilities of K⁺, Na⁺, Ca²⁺, Mg²⁺, Cl⁻, Br⁻, and HSO₄⁻ are approximately equal at temperatures above 400°C. The acid HBr, while providing approximately the same value for the intercept (1840) as above, yields a slope approximately one-half of the above values (560).¹ In the present study, A₀(HCl) is shown to follow the relationship.

\[
A_0(\text{HCl}) = 1850 - 500 d_{\text{H}_2\text{O}}
\]

Thus, the acids show considerably higher limiting molar conductances at the higher densities, which may be reasonable in view of a proposed proton-jump mechanism for the mobility of H⁺ ions in aqueous solutions.

From the limiting equivalent conductances and values of equivalent conductances (as shown in Fig. 4.3) for several molalities of HCl, together with application of conductance
theory, ionization constants of HCl at several densities and temperatures were calculated. These results in logarithmic form are plotted vs. log density in Fig. 4.4 to show the rectilinear straight lines that result. All previous studies in this program have provided similar straight line behavior. This observation makes it easy to describe the ionization behavior as a function of temperature and density. The equation for log $K$ for HCl is given as,

$$\log K_{\text{HCl}} = -5.405(\pm 0.127) + 3874.9(\pm 8.7)/T^\circ \text{K} + 14.93(\pm 0.16) \log d_{\text{H}_2\text{O}}$$

(3)

where the values in parentheses represent uncertainties of one standard deviation for the constants. The lines in Fig. 4.4 are plotted from Eq. 3. It is interesting to note that the slopes of the lines are 14.92, which is within three tenths of a logarithm unit of the slopes of the high temperature HBr data. The ionization constants of HBr, however, are greater than those of HCl indicating that HBr is a stronger acid than HCl. This is reasonable considering the smaller radius of the chloride ions.

In earlier pioneering work, Franck obtained ionization constants of HCl from one molality of HCl. The present values of log $K_{\text{HCl}}$ with additional molalities of HCl, approach those of Franck at the highest density but are believed to provide greater accuracy over most of the range of measurement.

1. Summary of paper submitted for publication in Amer. J. Science. This paper will also be summarized in the Annual Report of the Director of the Geophysical Laboratory (Carnegie Institution of Washington, Yearbook). Earlier parts of this study are summarized in Chem. Div. Annu. Prog. Reps. ORNL-5917 (p. 72) and ORNL-5665 (p. 43), and in earlier annual reports.

2. Work co-sponsored by the Carnegie Institution of Washington, Geophysical Laboratory, Washington, D.C. A portion of this study was sponsored by the Earth Sciences Section, National Science Foundation, NSF-Grant EAR 80-08798.

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


4.2.2 Hydrolysis Equilibria of Tungsten(VI) in Aqueous Sodium Chloride Solutions to 300°C
(S. E. Drummond, O. Wesolowski\textsuperscript{1}, R. E. Mesmer)

Formation constants for the protonated mononuclear and polynuclear forms of tungstate have been measured by means of a hydrogen electrode concentration cell from 95 to 290°C in 0.10 to 5.1 m NaCl media over a pH range of 2 to 8 and tungsten concentrations from 5 \times 10^{-4} to 10^{-2} m. Polytungstates \((6,7), (6,10)\) and \((12,18)\) dominate the speciation in the 10^{-2} m solutions below a pH of 5, particularly at the lower temperatures (Fig. 4.5). Monomers \(((1,0), (1,1)\) and \((1,2)\)) become increasingly stable at low tungsten concentrations, high temperatures and high ionic strengths (Fig. 4.6) and were the only form of tungsten detected above 200°C in 5.1 m NaCl.

\[
\log Q_{1,1} = -28.577 - 49.1^2 / T + 0.350701 + 1.7499 \times 10^{-7} \ln T
\]

\[2 \ \text{T} \ \text{K}, \ I = \text{ionic strength}, \ a_{H^2O} = \text{activity of water, and } F(1), \ \Omega(w) \text{ are given in Busey and Mesmer (1975).} \]

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4.2.3 Hydrothermal Transport and Deposition of Tungsten in Skarns
(S. E. Drummond, O. Wesolowski\textsuperscript{1})

Recent experimental hydrolysis studies have shown that \(WO_4^{2-}\) and \(HWO_4^-\) are the dominant tungsten species at most geologically reasonable values of pH, \(F(1)\), ionic strength and tungsten concentrations below 300°C. Extrapolations of these results to 500°C and 1 kilobar indicate that these two species are predominant over the entire pressure-temperature-composition range of crustal fluids. These experimental data and extrapolations thereof were combined with data from the literature on the solubility of scheelite to examine the mobility of tungsten in the hydrothermal fluids derived from cooling granitic intrusions as well as likely deposition mechanisms for tungsten in skarns commonly associated with these plutons. Fluid inclusion data from such skarn deposits suggest 400°C-500°C fluids with an ionic strength of ~6 m, total potassium ~1 m, and total cal-

Figure 4.5. Speciation-pH diagram for 0.01 m W(VI), 150°C, I = 1.0.

Figure 4.6. Speciation-pH diagram for 0.001 m W(VI), 290°C, I = 1.0.
ciun -0.1 m. If these fluids are assumed to have a pH in equilibrium with the ubiquitous potassium feldspar-muscovite-quartz assemblage, the 500°C solution would have a tungsten concentration of about 10 ppm (±5 × 10^−5 m) in equilibrium with scheelite. This value is quite reasonable since the average tungsten concentration of most granites is 1-2 ppm. Reaction of such a fluid with calcite would shift the solution pH by two units, the tungsten speciation from dominantly MnO_4^- to MnO_4^- and deposit 90% of the tungsten as scheelite. Conversely, cooling the solution is a relatively ineffective depositional mechanism. These results are compatible with the geological, physical and chemical constraints that can be imposed on the analysis of the genesis of tungsten skarn deposits and suggest that the mobility of tungsten in the environment is now well understood.

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4.2.4 Kinetics of the Thermal Decarboxylation of Acetic Acid and the Effects of Catalysis
(S. F. Drummond, D. A. Palmer)

Carothers and Kharaka argue that natural gas migrates as acetate from the source in a sedimentary basin and that the acetate decomposes at or near the reservoir to form N_2 and CO_2. The idea is attractive because acetate, unlike CH_4, is completely miscible in water and consequently is more mobile in water laden sediments. The hypothesis is plausible if the time required to decompose acetate is compatible with the fluid migration time from source to reservoir. In order to address this point, experiments on the effects of temperature, composition, and catalysis on the thermal decomposition rates of acetate are in progress.

The rates of decomposition of acetic acid in aqueous solutions have been studied as a function of concentration, pH, temperature and the rate of the containment vessel. The product distribution was also determined at the conclusion of each experiment.

Experiments with 1 m acetic acid in stainless steel vessels at 351 and 359°C yielded rates which were consistent with values reported by Kharaka et al. at lower temperatures. However, subsequent experiments in silica and quartz tubes at 340°C showed that the reaction is surface catalyzed. In fact, in silica tubes containing 10 m acetic acid at 340°C, the change in concentration with time was observed to increase after an induction period of ca. 3 weeks which also corresponded to a marked increase in the etching of the tubes. At 359°C, 1 m acetic acid decomposes most rapidly in silica where, after a short induction period, the reaction was 90% complete after 5.7 days. This compares to the slowest rates observed in gold-lined and titanium vessels where 90% reaction required 70 years under the same conditions.

Several solution compositions (0.1, 1.0 and 10 m HAc, 1 m NaAc, and 0.5 m HAc-0.5 m NaAc) were studied in titanium vessels at 359°C and each manifested a different rate with no clear trend observable. The slowest rate was measured for 1 m HAc where k = 1.33 × 10^-4 hr^-1, while the fastest was observed for the HAc-NaAc mixture for which k = 2.43 × 10^-7 hr^-1, corresponding to the almost exclusive decomposition of the HAc component. The latter result can be rationalized in terms of complexation of titanium by acetate at approximately neutral pH values. These experiments will be repeated in the “gold bath” vessels to test this idea.

The reaction products are predominantly CO_2 and CH_4, particularly for the “catalyzed”, faster reaction systems. For the slower processes, higher hydrocarbons were formed together with appreciable quantities of H_2 and CO. The reaction in stainless steel was characterized by the formation of copious amounts of magnetite on the vessels walls. All of these findings provide strong circumstantial evidence for a dominant surface-catalyzed reaction mechanism with minimum
catalysis in gold and titanium at 1 m concentrations.

Preliminary data from the decomposition rates of 1 m HAc in titanium vessels over the temperature range, 340-400°C, indicate that the enthalpy of activation is ca. 37 kcal mol⁻¹ and that the entropy of activation is strongly negative. A smaller enthalpy and an even larger negative entropy were reported by Kharaka et al.² for the reaction in stainless steel. The negative entropy provides particularly strong evidence in favor of a reaction at the surface of the vessel, implying that catalysis is still operative in titanium. Nevertheless, the results in titanium and gold provide a minimum or background rate which may then be compared to results for other "systems" where catalysis is more apparent. Kharaka et al.² suggested a half-life for acetic acid decomposition of 12.6 and 1.2 years at 100° and 200°C respectively, from experiments in stainless steel vessels. These results differ markedly from the present results in both gold and titanium which suggest a half-life of 4 × 10⁶ and 1 × 10⁴ years at these temperatures. These differences point out the enormous catalytic effects possible in acetate-water systems and are critical to the hypothesis of methane migration. Fluid migration times from source to reservoir are probably on the order of 10⁵-10⁶ years. Ages of these reservoirs range from >10⁶ to >10⁸ years. This evidence is compatible with the concept of natural gas migration as acetate if the half-lives for the decomposition are in the range 10⁴-10⁸ years. However half-lives of 1-13 years are totally nonsensical within the framework of this hypothesis. Accordingly, the present results lend feasibility to the hypothesis but must be extended to other temperatures and pH conditions in the presence of geologically available catalysts before the hypothesis and its implications for the localization of natural gas can be evaluated.


4.2.5 Kinetics of the Reactions of Quartz with H₂O, 1 M NaCl, and Saturated 1 M NaCl Solutions from 125 to 250°C at 20 MPa (200 Bars)

(F. W. Dickson)

Equilibria and kinetics of quartz aqueous solution reactions are being studied with the use of double-ended 58 ml titanium reaction vessels, from 125°C to 250°C at 20 MPa (200 bars). One hundred g of coarse sand grains with low surface area (0.00415 m²/gram) plus about 20 g of interstitial fluid were heated in cylindrical furnaces. Some experiments were done by rocking the furnace-reaction vessel assembly through 180 degrees 3 times per minute. Most experiments were quiescent. These conditions were chosen as an attempt to avoid difficulties encountered by other researchers, who found anomalous and irreproducible behavior in reactions of silica solid phases with various kinds of aqueous solution. The difficulties have been ascribed to: (1) excessively small grain size of some powders, of 200 mesh and smaller; (2) strained quartz surfaces; (3) the production of small fragments by abrasion during vigorous stirring; and (4) the appearance of other solid phases, probably on quartz surfaces.

Liquid samples, removed from the top of the reaction vessel while fresh fluid was being pumped to the opposite end, were passed through an external filter (millipore, 0.22 μm and 0.45 μm) into a sampling syringe that had been previously loaded with 2 g of colorimetric reagent of pH 3.10. Generally 0.6 to 2.0 grams were taken. Weighed aliquots of the samples were diluted with colorimetric reagent to 20 g, and allowed to stand for 1 hour before analyzing. The analytical method was spectrophotometric (Rausch and Lomb, Spectronic 710), using the yellow color (390 nanometers) of the silico-molybdate complex. The colorimetric reagent was made at about weekly intervals, from analytical grade NH₄Cl, monochloracetic acid, ammonium molybdate, ammonia and HCl according to the procedures described by Marshall¹. Standard solutions in the range 5-20 ppm SIV₂ proved to be stable and to be within the linear response
of the Spectronic 710. Analyses were generally reproducible to ± 1 ppm: 500 ppm levels. Experimental solutions were made up of distilled \( \text{H}_2\text{O} \) and reagent grade \( \text{NaCl}, \text{Na}_2\text{HPO}_4, \) and \( \text{HCl} \), to about 1 molal total ionic strength of the salt solutions. The NaCl-borate buffered solution was made by mixing \( \text{NaCl} \) and \( \text{Na}_2\text{HPO}_4 \) in proportions that resulted in 0.90 m \( \text{NaCl} \) and 0.1 m boron (as \( \text{Na}_2(\text{OH})_2 \) and \( \text{B}(\text{OH})_3 \). The ratio of \( \text{B}(\text{OH})_3 \) to \( \text{B}(\text{OH})_2 \) was adjusted to 1/4 by the addition of \( \text{HCl} \). The pH was 9.2. The pH at elevated temperatures reflected the various equilibria that changed with temperature. At 200°C, for example, the calculated pH of the stock solution was 7.7. The experimental solutions were delivered to the reaction vessel by a 22 ml hand operated pressure generator. Little pressure or temperature variations resulted from the sampling. Temperatures were controlled to ±1°C by commercial regulators. Temperatures at the top, middle and bottom of the reaction assembly were measured within ±0.5°C by alunel-chromel thermocouples bound tightly to the outer surfaces of the reaction vessels, which were enclosed in aluminum foil wrappings used to smooth temperatures. Temperatures along the reaction vessel were constant to ±1°C. A total of 58 experiments were done, each requiring 6 to 12 samplings over times from 1 day to 1 month, at constant temperature and pressure; of the 58, about 32 proved useful for kinetic analyses. The solubilities were reversed at each temperature (approached from supersaturation and undersaturation).

**Results**

Table 4.1 presents a summary of the solubility data. Solubilities of quartz in the three solution types increased with rising temperature. The \( \text{H}_2\text{O} \) solubilities at 200 bars are somewhat higher than solubilities from the literature at the vapor pressures of the solutions (Rimstid and Barnes, 1980). At low temperatures the solubilities in 1 m \( \text{NaCl} \) were lower than solubilities in \( \text{H}_2\text{O} \), but with rising temperatures they became essentially equal at 225°C. Above 225°C, the solubilities continued to diverge; at 250°C, the solubility of quartz in 1 m \( \text{NaCl} \) is about 5% higher than solubility in \( \text{H}_2\text{O} \). At all temperatures, the solubility in the more alkaline NaCl-borate buffer was consistently higher than in \( \text{H}_2\text{O} \) or 1 m \( \text{NaCl} \). The higher solubilities reflect the reaction of Si(OH)\(_4\) with OH\(^-\) to form SiO(\(\text{OH})_3\)^- anions. At 200°C, the ratio

Table 4.1 Solubility (millimolal) and rate constants (\( k_{\text{SS}}, \) supersaturation, \( k_{\text{US}}, \) undersaturation, hour\(^{-1}\)) calculated on first-order assumption for standard area (1 m\(^2\)) and mass of \( \text{H}_2\text{O} \) (1 kg).

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>( \text{H}_2\text{O} )</th>
<th>1 m ( \text{NaCl} )</th>
<th>NaCl-buffer (1:1)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( k_{\text{SS}} )</td>
<td>( k_{\text{US}} )</td>
<td>( k_{\text{SS}} )</td>
</tr>
<tr>
<td>125</td>
<td>7.87</td>
<td>2.69</td>
<td>2.06</td>
</tr>
<tr>
<td>150</td>
<td>3.76</td>
<td>1.93</td>
<td>3.29</td>
</tr>
<tr>
<td>175</td>
<td>4.76</td>
<td>-0.00070</td>
<td>5.21</td>
</tr>
<tr>
<td>200</td>
<td>6.03</td>
<td>-0.0067</td>
<td>-0.0073</td>
</tr>
<tr>
<td>225</td>
<td>7.64</td>
<td>-0.0019</td>
<td>-0.0019</td>
</tr>
<tr>
<td>250</td>
<td>8.28</td>
<td>-0.0028</td>
<td>-0.0028</td>
</tr>
</tbody>
</table>

*Log C as functions of t(T°C)*

- \( \text{H}_2\text{O} \): \( 0.004100t - 3.147 \)
- 1 m \( \text{NaCl} \): \( 0.004776t + 3.779 \)
- NaCl-buffer: \( 0.008056 - 3.503 \)
of anion to silicic acid is about 0.78; this ratio will probably continue to increase at temperatures above 200°C.

The reactions of quartz with aqueous solutions under the conditions of the present experiments appears to be more complex than previously thought. The reaction generally is written:

\[ \text{SiO}_2 + 2\text{H}_2\text{O} \rightleftharpoons \text{Si(OH)}_4, \ K_{eq} = a_{\text{Si(OH)}_4} \]

with \( k_f \) being the forward reaction rate and \( k_r \) the reverse. If the reaction is single step and symmetrical, the relationship of the two rates to \( K_{eq} \), the equilibrium constant, is:

\[ \frac{k_f}{k_r} = K_{eq}, \text{ with } n = \text{molality} \]

Rimstidt and Barnes\(^2\) in their exhaustive study of the reactions of several kinds of silica solid phases of various grain sizes with \( \text{H}_2\text{O} \), reported that the reaction was first order and symmetrical. They did some experiments with quartz sand, which are directly comparable with the experiments of this report. They determined one of the rate constants from experiments that approached equilibrium from undersaturation, and calculated the other from the above relationship with the known \( K_{eq} \). Data from the present work cannot be treated similarly. The reaction probably involves the production of a solid phase, probably metastable, as surface coatings, that must disappear before quartz can interact directly with solutions. The reactions can be written:

\[ \text{SiO}_2 + n\text{H}_2\text{O} \rightleftharpoons \text{SiO}_2+n\text{H}_2\text{O}^n \]

\[ \text{SiO}_2+n\text{H}_2\text{O} + (2-n)\text{H}_2\text{O} \rightleftharpoons \text{Si(OH)}_4 \]

The formation of the postulated solid phase, \( \text{SiO}_2+n\text{H}_2\text{O} \), is rapid; it forms in contact with all solutions and at all temperatures in this work. The kinetic steps in this reaction have not been fully worked out. Rates calculated for first order assumptions are included in Table 4.1. They show that a strong difference exists between experiments that approached equilibrium from undersaturation compared to those from supersaturation. This lack of symmetry probably reflects a greater production of the postulated metastable solid by reaction with supersaturated solutions as compared to undersaturated. Stöber\(^3\) on the basis of studies of reactions of nearly all known solid forms of silica with alkaline NaCl solutions at 25°C, worked out the kinetic pathways on the basis of surface coatings that appeared during the initial stages of the reactions. He came to the interesting conclusion that only for quartz and \( \text{SiO}_2 \) glass (fused quartz) are the rates consistent with the disappearance of the intermediate phase. All other silica solids developed permanent coatings that prevented the true determination of solubilities. Stöber speculated that the surface coatings on quartz would not form under the more energetic conditions of higher temperatures. The present studies suggest that they form and persist, even on quartz exposed to undersaturated solutions.

Rates for the reactions of quartz with 1 m NaCl are slightly higher than with \( \text{H}_2\text{O} \). Rates are much higher for NaCl-borate buffered solutions. Rates calculated for experiments using undersaturated solutions are consistently higher by nearly an order of magnitude than for supersaturated solutions, for all solution types. Reasonable agreement was obtained with Rimstidt and Barnes\(^2\) rates for solutions initially undersaturated. The time dependencies of quartz reactions with the different solution types is being processed by computer programs to determine kinetic steps, orders, and rate constants.

4.3 Carbon Cycle

4.3.1 The Role of the Oceans in the Carbon Cycle

(C. F. Baes, Jr.)

The oceans are the ultimate sink for most of the carbon dioxide that may be released to the atmosphere by the use of fossil fuels. In order to decide how rapidly we may safely use this fuel, it will be necessary to predict how rapidly the oceans will take up the excess CO$_2$ from the atmosphere. For this purpose, ocean models are essential. But what features of the ocean should be included in such models?

The circulation of the ocean, which to a great extent will determine how rapidly it can respond to increasing atmospheric CO$_2$, is largely advective, i.e., occurring along nearly horizontal contours of constant density called isopycnals that reach the surface at locations where the water, through contact with the atmosphere, acquires a temperature and salinity that produces a matching density. Such advective circulation, along with some so-called diffusive mixing across isopycnal surfaces, has produced an ocean of fairly uniform chemical composition except for the elements (principally carbon, nitrogen, phosphorous, and silicon) that are involved in the biological processes.

Carbon dioxide is an acidic gas and its distribution between the ocean and atmosphere has been determined to a large extent by its reaction with basic minerals. Reactions producing the dissolved products H$_2$CO$_3$, HCO$_3^-$, and CO$_3^{2-}$ are rapid and their equilibrium behavior accurately predictable. As a consequence, the partial pressure of CO$_2$ generated in the surface waters is usually fairly close to that in the atmosphere.

Less generally recognized is the strong influence exercised by the biological processes in the ocean on the atmospheric content of CO$_2$. This comes about because these processes, largely confined to the upper ocean, alter the distribution of the inorganic forms of carbon in this region. Photosynthesis lowers the total inorganic carbon (TC) and increases somewhat the titration alkalinity (TA). At the same time, calcium carbonate is precipitated largely under biogenic control, lowering both TC and TA. The organic matter and the calcium carbonate fall from the surface waters as detritus and the organic portion is oxidized almost completely back to CO$_2$ in the first 1000 m, consuming oxygen and increasing TC in this region. The calcium carbonate does not redissolve until greater depths are reached.

A two-dimensional (latitude x depth) model of the oceans is required in order to simulate in a meaningful way these processes of circulation, ocean-atmosphere CO$_2$ exchange, photosynthesis, decay, and calcium carbonate precipitation and dissolution. Only then can the temperature, latitude, and depth dependencies of these processes be adequately represented. Thus far, most models of the ocean intended to predict the uptake of CO$_2$ have been one-dimensional (depth) and have not included the effect of the biologically controlled processes on the distribution of carbon.

Inclusion of the biological processes in a suitably constructed CO$_2$-ocean model is desirable for several reasons. It would permit use of the large body of oceanographic data (e.g., data from the GEOSecs and Transient Tracer Programs) on the distribution of TC, TA, nitrate, phosphate and oxygen for purposes of model validation. Such a model that could simulate the distribution of all these chemical tracers would be much more compelling than one that does not. In paleoclimatic studies, simulation of the ocean-atmosphere system will require the inclusion of the biological processes since they have such a strong effect on the atmospheric content of CO$_2$. It has been suggested, for example, that the event at the beginning of the Tertiary period leading to mass extinction involved first the extinction of life processes in the ocean and a consequent large release of CO$_2$ to the atmosphere. Similarly, there should be feed-
back effects resulting from future CO$_2$-induced climatic warming because of changes in patterns of ocean circulation. The principal driving force for this circulation is the latitudinal temperature gradient, and it is generally agreed that a warming climate will reduce this gradient. Hence a decrease in ocean circulation rate may be expected. This could have an appreciable effect on patterns of biological productivity, altering TC and TA in the surface waters, and the CO$_2$ content of the atmosphere.


4.3.2 A Two-Dimensional CO$_2$-Ocean Model (C. F. Baes, Jr. and G. Killough)

In order to simulate the ocean processes discussed in the previous section, a two-dimensional (latitude x depth) ocean model is being developed (Fig. 4.7). It consists of an array of boxes, each of which is assumed to be homogeneous in composition and at a specified temperature. The grid points defining the boxes are located to simulate approximately the observed variation of temperature with depth and latitude. Water is assumed to flow between adjacent boxes in such a way as to maintain the specified temperature of each subsurface box.

In the surface boxes, heat, CO$_2$, and oxygen are exchanged with the atmosphere. Within the surface boxes organic carbon is generated by photosynthesis and calcium carbonate is precipitated biogenically. (The concentration of carbon present as these suspended forms is denoted by CO and CI, respectively.) These biogenic processes change by predictable amounts the concentrations of dissolved nutrient (N) and total inorganic carbon (TC), as well as the titration alkalinity (TA), and the dissolved oxygen concentration (O$_2$) in the surface boxes. Similarly, the fallout of organic detritus and calcium carbonate and their oxidation and dissolution will alter these six quantities in the subsurface boxes.

The rate processes that affect each of these concentrations is summed for each box and equated to zero, and the resulting system of equations is solved in order to determine the steady-state concentrations as a function of the adjustable parameters. These parameters include the water flow rates, and parameters in rate functions for net photosynthetic productivity, for re-oxidation of organic matter, and
and for the precipitation and dissolution of calcium carbonate. The strategy will be to simulate in the steady-state case the observed distribution of the six quantities CO, CI, N, TA, TC, and O2 in the real ocean, using rate functions that employ the adjustable parameters. If this can be done with a suitably small number of parameters, we will proceed to study the time-dependent behavior of the model as a function of changes in such quantities as the water-circulation rate and the atmospheric CO2 content.

1. Health and Safety Research Division.
The program involving studies of the permeation of tritium through candidate steam generator materials is being concluded. The final experiments consist of measurement of tritium permeabilities through specimens undergoing oxidation by high-pressure steam (up to 10 MPa) at temperatures up to 1000 K. A major new thrust is focused on the synthesis of high purity covalent structural ceramic compounds. Novel reactions for the synthesis of ceramics such as TiB₂, ZrB₂ and HfB₂ have been identified, and are being tested experimentally. Emphasized are reactions that directly yield powders of very small particle size, a feature desirable for effective sintering of the powders. Exothermic homogeneous (i.e., gas-phase) reactions and heterogeneous (i.e., gas-solid) reactions that proceed via several steps appear to yield products of the desired particle size. Initial synthesis of TiB₂ powders consisting of extremely fine amorphous particles and microcrystalline particles with sizes up to 100 nm has been successful. Our studies are concentrated on chemistry of the reaction sequences. Compaction and sintering studies are being conducted in collaboration with the Metals and Ceramics Division. Thermodynamic calculations are identifying new reactions for preparing other metal borides and nitrides of potential technological interest. Raman spectroscopy is being used to characterize a wide variety of materials. Of special interest are SiC-coated nuclear fuel particles, nuclear waste-containing glasses, and species present in chloroaluminate melts.

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

(J. D. Redman)

Prevention of tritium loss from fusion power reactor systems is extremely important from an ecological standpoint. Probably the most vulnerable area of the system is the steam generator since tritium permeating into the generator would be irrevocably lost to the environment. We have been studying the possibility of utilizing the oxide formed in situ by steam oxidation of the base alloy to retard permeation rates. During this report period, we have completed construction of an apparatus that permits measurement of tritium permeation rates through candidate steam generator materials which are undergoing steam oxidation by high-pressure steam (up to 10 MPa) at temperatures up to 1000 K.

The first experiment in the new apparatus involved determination of the tritium permeation through Incoloy 800 exposed at 793 K (520°C) to steam at a pressure of 5.5 MPa (54.5 atm). The permeability constant at zero time was \(18 \times 10^{-6} \text{[cm}^3\text{T}_2\text{-mm/min-cm}^{-2}\text{-torr}^{1/2}]\), in excellent agreement with the value of \(23 \times 10^{-6}\) obtained previously in a system in which the steam pressure was only 95 kPa (0.96 atm). With the high steam pressure, the permeability decreased with time, as expected, as an oxide film formed on the surface of the alloy. After 38 days' exposure, the permeability had decreased by a factor of 44, only slightly lower than the decrease of 30 obtained with 0.96-atm steam. We have not yet obtained enough data at high steam pressures and high temperatures for a comprehensive analysis.

In addition to the work with the high-pressure, high-temperature system, we concluded our measurements of tritium permeability through high strength steel alloys during long-term in situ oxidation with sub-atmospheric steam. The last alloy to be studied, a ferritic 430-Ti stainless steel, was found to produce an oxide coating at 933 K and 95 kPa steam pressure which reduced the tritium permeability by a factor of 9000 after 310 days of oxidation. This reduction in permeability is the greatest found among the alloys that we have studied.

5.2 Direct Chemical Synthesis of Titanium, Zirconium and Hafnium Diborides in the Amorphous to Submicron Size Range


Because of the outstanding refractory properties of certain borides, especially titanium diboride, zirconium diboride and hafnium diboride, they are highly desirable materials for use in the fabrication of equipment and apparatus for application in harsh process situations such as those where physical erosion, chemical corrosion and very high temperatures are involved. Because those borides are anisotropic, it is desirable that components fabricated from them are made from submicron particles of high purity in order to avoid their structural failure when in use.

Presently, one of the more widely used commercial processes for preparing titanium diboride is the carbothermic process or modifications thereof. In this process, titanium dioxide (TiO₂), boron oxide (B₂O₃), and carbon are heated in an electric arc or high frequency furnace to form titanium diboride. A variation of this process is to use boron carbide, B₄C, instead of B₂O₃ as the boron source. The titanium diboride products obtained from these aforementioned processes are mechanically ground and milled. To obtain a finely divided product, extensive milling is required. However, even very lengthy milling does not reduce the particle size of the product to less than about 2000-10,000 nm (2-10 microns).

Moreover, such a product is usually contaminated with impurities abraded from the construction materials of the mill and grinding machine, as well as oxides of titanium and of boron formed by particle surface oxidation by oxygen from the ambient atmosphere.

A direct powder preparation method has been reported that consists of reacting in the vapor phase a titanium tetrahalide and a boron source (boron hydride or a boron halide) in the presence of a hot hydrogen gas stream produced by a hydrogen plasma heater in the absence of oxygen. The solid boride formed is quenched and recovered in fine particle collection equipment. This method yields products where substantially all, at least 90%, of the particles have a nominal section diameter of less than one micron; the predominant number (greater than 50%) of the particles less than one micron are in the particle size range of between 0.05 and 0.7 microns (50-700 nm). Powder products can be obtained containing less than 0.25 weight percent oxygen and less than 0.20 weight percent chlorine. Because this process is highly endothermic requiring energy input at very high temperatures, the TiB₂ particles formed have a tendency to grow and this results in a lower limit in obtainable particle size which appears to be about 0.05 microns.

In our search for alternative preparative methods that circumvent the drawbacks of the methods described above, we identified and demonstrated experimentally two new approaches. The first employs exothermic reactions in the gas phase, the metal boride being formed by homogeneous nucleation from reactants in the gas phase by a sequence of exothermic reactions. For example, gaseous titanium trichloride and boron trichloride undergo the overall net reaction:

$$\text{TiCl}_3(g) + 2\text{BCl}_3(g) \rightarrow \text{TiB}_2(s) + 9\text{TiCl}_4(g)$$

The gaseous titanium trichloride was brought into contact with gaseous boron trichloride in a graphite reactor at a temperature between 900°C and 1300°C, and the reaction went virtually to completion. The titanium trichloride gas was produced by the reaction:

$$3\text{TiCl}_4(g) \rightarrow \text{Ti}(s) + 4\text{TiCl}_3(g)$$

This reaction takes place smoothly at temperatures in the temperature range -1200°C to -1300°C; lower temperatures are avoided to
prevent the formation of titanium dichloride which can plug the exit lines.

The basis of the second approach is heterogeneous reactions involving a gaseous boron trihalide and a solid such as titanium, zirconium or hafnium metals; the net reaction can be represented by

$$2.5M(s) + ZBCl_3(g) \rightarrow 600-1100^\circ C \rightarrow Nb_2(s) + 1.5MC_4(g), \quad (3)$$

where M is Ti, Zr or Hf.

Experiments with Ti in which reaction (3) was not allowed to go to completion indicated that the overall reaction is comprised of a sequence of intermediate reactions involving titanium subhalides, some of which we have identified.

The powders obtained were characterized with regard to crystal structure, morphology, dimensions, impurity content, and sinterability. This was as a collaborative effort with members of the Structural Ceramics Group of the Metals and Ceramics Division (P. F. Becker, P. Angelini, C. B. Finch).

Representative products resulting from reactions (1) and (3) are shown in Fig. 5.1 as transmission electron microscopy (TEM) views of the powders in bright and dark field and

**Fig. 5.1.** Bright and dark field TEM, and SAD or TiB_2 powders by reaction (1) [left] and reaction (3) [right].
selected area (electron) diffraction (SAO). The bright field pictures give an idea of the agglomeration and shape of the particles, while those in dark field give an indication of the crystallite sizes. The nominal par- 
ticle size (average) of the powder obtained by reaction (1) at 1250°C was ~20 nm, and for the powder obtained by reaction (3) at 650°C was ~5 nm. The SAO pictures confirm the identity of the TiB$_2$; additionally, the broadening of the diffraction lines from TiB$_2$ made at 650°C confirms the small dimensions of the particles.

Representative samples of the powders produced are compacted by sintering in parametric studies geared to determine the effect of particle size, oxygen, and halide content on the physico-mechanical properties of the resulting monoliths. Early results from this effort are very promising in that 96% of the theoretical density has been achieved by sintering at 1600°C, a relatively low temperature for covalent borides such as TiB$_2$.

1. Metals and Ceramics Division.  

5. Removal of Oxide Contamination from TiB$_2$ Powders

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

Commercially available TiB$_2$ powders are commonly contaminated with oxides; their presence is due either to traces of unreacted oxides used as starting materials (e.g., from carbothermic reaction) or to the handling of finely dispersed TiB$_2$ in air or gaseous environments containing oxygen, even at trace levels. Because it is suspected that the presence of oxide has deleterious effects on the sintering properties of the powders as well as on the properties of the resulting compact solids, we sought to remove the oxide contamination by chemical reaction.

Free energy of reaction estimates at 1000 K for the following reactions involving the oxide phases most likely to be present indi-
cated that these reactions are thermodynamically feasible:

\[
\begin{align*}
\text{TiO}_2(s) + 2\text{BCl}_3(g) + \text{TiCl}_4(g) + 2/3 (\text{BOCl})_3(g) & \rightarrow (1) \\
\text{B}_2\text{O}_3(l) + \text{BCl}_3(g) + (\text{BOCl})_3(g) & \rightarrow (2) \\
5\text{Ti}_2\text{O}_3(s) + 17\text{BCl}_3(g) + 9\text{TiCl}_4(g) + 5(\text{BOCl})_3(g) + \text{TiB}_2(s) & \rightarrow (3) \\
\text{Al}_2\text{O}_3(s) + 3\text{BCl}_3(g) + 2\text{AlCl}_3(g) + (\text{BOCl})_3(g) & \rightarrow (4) \\
3\text{SiO}_2(s) + 6\text{BCl}_3(g) + 3\text{SiCl}_4(g) + 2(\text{BOCl})_3(g) & \rightarrow (5)
\end{align*}
\]

To determine if these reactions were also kinetically feasible, they were tested experimentally with as-received commercial TiB$_2$ powders. The powders, contained in a vertical nickel tube, were exposed to an upward flow of BCl$_3$ for four hours at 650°C. The powders were analyzed for oxygen content, before and after the BCl$_3$ treatment, by nuclear activation (NAA). Table 5.1 gives the experimental results for two commercial powders, one from Herman C. Starck, Berlin FRG, [Lot S2156A, 14.9 \text{nm} average particle size] (No. 1), and one from Kawecki Berylco Industries, Boyertown, Pa, [Lot B190 (finely ground), 3.37 \text{nm} average particle size] (No. 2).

<p>| Table 5.1 Oxygen content of TiB$_2$ powders before and after treatment with BCl$_3$ at 650°C |
|----------------------------------|----------------|
| Wt % oxygen (by NAA)           |                |</p>
<table>
<thead>
<tr>
<th>No.</th>
<th>As received</th>
<th>After treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.58</td>
<td>0.37</td>
</tr>
<tr>
<td>2</td>
<td>1.80</td>
<td>0.30</td>
</tr>
</tbody>
</table>

The results demonstrate that the oxygen content can be substantially reduced by the treatment with BCl$_3$. The results for powder No. 2 indicate that the oxygen contamination is mainly due to surface oxidation during grinding.
5.4 Raman Spectral Characterization of Silicon Carbide Nuclear Fuel Coatings

(G. M. Begun, P. Angelini, P. Krautwasser)

Chemically vapor-deposited silicon carbide (SiC) coatings deposited by thermal decomposition of methyltrichlorosilane in a fluidized bed of nuclear particles are used as a barrier for gaseous and metallic fission products in High-Temperature Gas-Cooled Reactor (HTGR) fuels. Quality control of the SiC coatings has previously been accomplished by means of density measurements and visual inspections of polished ceramographic sections. To improve the characterization and, consequently, the quality control of SiC, various investigative methods were evaluated at the Oak Ridge National Laboratory (ORNL) and the Kernforschungsanlage (KFA), Jülich. At ORNL, Raman spectroscopy was found to offer a rapid non-destructive method of characterizing the coated microspheres.

The changes in Raman spectra of SiC coatings produced by variations of production parameters such as deposition temperature, coating rate, and carrier gas, as well as the effect of accumulated fluence of fast neutrons, irradiation temperature, and heat treatment of unirradiated and irradiated SiC coatings have been studied.

The particles examined consisted of a nuclear fuel kernel (UO₂ or UC₂, and ThO₂), low density and high density inner pyrocarbon layers, a layer of SiC, and an outer layer of high density isotropic pyrocarbon. The SiC layers were 300-500 μm in outer diameter. Coatings were produced by successive chemical vapor depositions upon the fuel kernels in fluidized bed coaters. Pyrocarbon coatings were produced by thermal decomposition of ethylene, acetylene and methane or mixtures of these hydrocarbons. The silicon carbide layer was deposited by thermal decomposition of methyltrichlorosilane (CH₃SiCl₃). In order to study the Raman spectra of the SiC layer, the outer pyrocarbon layers were burned off by heating the samples in air at 1000°C for 10 hours. Single SiC-coated microspheres were held by suction on the tip of a horizontally held hypodermic needle. Using a long focus microscope to observe the microsphere, light from an argon-ion laser was then focused at the equator of the sphere and the sphere positioned to give maximum Raman scattering observed at 90° to the exciting laser light.

Fig. 5.2 shows a series of Raman spectra of SiC coatings deposited at different temperatures. The spectra show the two strong Raman
lines of cubic (\(\beta\)) SiC. In the cubic crystal the threefold degenerate Raman and infrared active \(F_2^+\) phonon vibrational mode splits into two vibrations - one transversely polarized (TO) mode at 796 cm\(^{-1}\) and the other longitudinally polarized (LO) at 972 cm\(^{-1}\). In addition to these peaks, our spectra show several other bands. We attribute a broad peak centered at 480 cm\(^{-1}\) to the presence of amorphous silicon and peaks at 1350-1370 cm\(^{-1}\), and 1575-1595 cm\(^{-1}\) to glassy or graphitic carbon contained in the sample. In Fig. 5.2 we see that the spectrum showing the purest SiC was obtained from a coating deposited at 1650°C. As the coating temperature was varied from 1500-1700°C the amount of amorphous silicon present in the coating decreased and the amount of excess carbon increased. Studies of the spectra of particles produced at various coating rates and constant temperatures showed that the strongest SiC spectra showing the least excess carbon were found in coatings produced at high coating rates.

Schlichting has reviewed a number of publications which discuss the thermodynamics of the chemical vapor deposition of SiC from methyltrichlorosilane. In agreement with our spectral observations, thermodynamics predicts silicon-rich SiC should be formed at low deposition temperatures whereas SiC with excess carbon should be formed at high formation temperatures. Intermediate temperatures should yield pure \(\beta\)-SiC (as clearly shown by the Raman spectra).

Heat treatment of various unirradiated SiC coatings produced very different changes in their Raman spectra. The spectrum of stoichiometric SiC was, in general, unchanged by heat treatment although in several cases a very thin layer of graphitic carbon was produced on the surface by decomposition of the SiC. Removal of a few micrometers of the surface by buffing restored the original SiC spectrum. Fig. 5.3 shows the Raman spectrum of a sample with excess carbon before and after heat treatment. In the untreated sample the carbon line at 1360 cm\(^{-1}\) was more intense than the carbon line at 1582 cm\(^{-1}\). After heat treatment at 1500° and 2000°C the latter line became much stronger indicating a crystallization of the carbon during heat treatment.

A number of different batches of particles were irradiated with fast neutron fluxes (>29 \(f \cdot 0.18\) MeV) at 900° and 1250°C. Fig. 5.4
Fig. 5.4. Raman spectra show a decrease in SiC line intensities with fast-neutron irradiation.

shows the spectra of one series of samples. The strong decrease in SiC line intensity agrees with the reported results of ion bombardment of SiC. The decomposition of SiC by fast neutrons leads to a higher concentration of amorphous silicon in a sample irradiated at 900°C than that irradiated at 1250°C. Clearly, a higher neutron induced lattice defect recovery rate exists at the higher temperature. Subsequent heat treatment of neutron irradiated SiC coatings at 1500°C for 5 hours resulted in the partial recovery of the SiC spectra. After heat treatment at 2000°C for 1 hour no SiC lines were found until the removal of the graphitic surface layer when the Raman spectrum was fully recovered except for the SiC line at 966 cm⁻¹. The low intensity of this LO line compared to the TO line at 796 cm⁻¹ still indicated distortions in the long range order of the SiC microstructure. A detailed description of this work has been accepted for publication in the Journal of the American Ceramic Society.

1. Metals and Ceramics Division.
6. Raman Spectral Study of WCl₆ in Al₂Cl₆ and Chloroaluminate Melts

(G. M. Begun, K. Tanemoto and G. Mamantov)

Several Raman spectral studies of solute species in chloro and fluoroaluminate melts have been previously undertaken at ORNL in cooperation with members of the Chemistry Department of The University of Tennessee, Knoxville. The chemical and electrochemical behavior of such species in chloroaluminate melts depends on the acid-base properties of the solvent which, for the AlCl₃-NaCl system, are determined by the AlCl₃/NaCl ratio and temperature. The electrochemical reductions of Nb(V), Ta(V), and W(VI) are very complex processes and result in the formation of clusters. Previous Raman spectral studies of pentavalent niobium² and tantalum³ showed that these species exist as XCl₆⁻, XCl₅⁻ or X₂Cl₁₀⁻ (X = Nb, Ta) depending on the melt composition and temperature. A similar
study for hexavalent tungsten has been carried out.

Tungsten hexachloride has an octahedral (O₆) structure with six normal modes of vibration. Of these vibrations, \( \gamma_3 \) (polarized), \( \gamma_2 \) and \( \gamma_5 \) are Raman active, \( \gamma_3 \) and \( \gamma_4 \) are infrared active and \( \gamma_6 \) is inactive. Raman spectra for WCl₆ dissolved in molten Al₂Cl₆, AlCl₃/NaCl (63/37), AlCl₃/NaCl (52/48), AlCl₃/NaCl sat. and WCl₆ in CHCl₃ were recorded. A tuneable dye laser was used to excite the spectrum using 602 nm radiation. The frequency of the strongest band of WCl₆(\( \gamma_1 \)) was essentially the same (c. 410 cm⁻¹) regardless of the medium or physical state (solid or liquid). The relative constancy of the \( \gamma_1 \) frequency of WCl₆ compared to the spectral shifts with melt composition of 15-40 cm⁻¹ for the Ta(V) and Nb(V) species, provides evidence that WCl₆ is present as a molecular entity and does not interact significantly with molten Al₂Cl₆ or chloroaluminate melts. The intensity of the 409 cm⁻¹ band of WCl₆ in chloroaluminate melts was found to increase with temperature and with melt acidity similar to the behavior observed for S₂ and I₂ in molten chloroaluminates.⁴,⁵ A complete account of this work has been published.⁶

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6. CHEMISTRY OF TRANSURANIUM ELEMENTS AND COMPOUNDS

The main thrust of this program is the study of the chemical and physical behavior of actinide elements and compounds, from uranium to einsteinium. As discussed in this section, fundamental information is obtained pertaining to several important questions: e.g., the role of 5f electrons in chemical bonding as reflected, for example, in values of magnetic moments; thermodynamic properties; the occurrence and stability of unusual oxidation states in solution and in solid compounds; and interactions in solutions, such as complexation, hydrolysis and solvation. Many of the solution properties that are determined in this program are relevant to the question of the long-term storage of nuclear waste. In particular, the speciation of the actinides is being investigated in very dilute solutions at near-neutral pH values in the presence of various complexing ligands. Furthermore, the sorption behavior of actinides on oxides and representative minerals is being studied. An important aspect of the program is the use of state-of-the-art experimental techniques such as Raman spectrometry, high-temperature determinations of enthalpies of sublimation, measurements of magnetic properties with superconducting devices at low temperatures, and X-ray and neutron scattering. In support of the DOE program of production of transuranium elements at HFIR-TRU, the possibility of the enhanced production of *Es in multimicrogram amounts is being investigated by measurements of the neutron cross sections of *Es and *Es.

6.1 Chemistry and Physics of Solids

6.1.1 Preparation and Properties of Transplutonium Metals
(R. G. Haire)

The metals of the first five transplutonium elements have been prepared on the micromgram to multimilligram scale. The metals are usually prepared in conjunction with specialized experiments, with either the major portion or the entire preparation being used in the particular experiment. The transamericium metals are prepared using Cm-248, Bk-249, Cf-249 and Es-253. The normal supply of the first three isotopes limits each product to 5-20 mg, while the amount of einsteinium metal that could be prepared is limited to less than one milligram. Although larger quantities of americium isotopes are available, the capacity of our equipment and the radiation levels encountered have kept our preparations of americium metal to the 100 mg level.

The transplutonium metals are prepared by two different procedures. The first method consists of reducing the transplutonium oxide with either lanthanum or thorium metal, followed by the volatilization and subsequent condensation of the transplutonium metal. The second method consists of reducing an anhydrous transplutonium fluoride with lithium metal, followed by volatilization of the excess reductant and lithium fluoride. Each procedure has advantages and disadvantages. The method of choice depends on several factors, the most important being the volatility of the transplutonium metal. Normally, americium, californium, and einsteinium are prepared by the distillation procedure, while curium and berkelium are made by reduction of their fluorides. During this report period, about 150 mg of americium-243 metal, 10 mg of curium-248 metal, 5 mg of californium-249 metal and 130 μg of einsteinium metal (as an alloy and as deposits on substrates) were prepared for several research projects.

The americium metal was used for two different collaborative investigations with LANL, one involving the specific heat of both crystal forms of the metal, and the second dealing with superconductivity and magnetism of plutonium-americium alloys. The interest in the plutonium-americium alloys arises from the fact that a sharp transition in electronic behavior occurs when progressing from pure plutonium to pure americium metal. Plutonium is known to possess itinerant f (bonding)
electrons, whereas its neighbor, americium, has localized (non-bonding) f electrons. In principle, forming alloys of these two metals should permit a gradual transition of f electron involvement in the metallic bonding by gradually altering the overlap of the electron's wavefunctions. A sensitive method of monitoring such an overlap is to look for the presence of superconductivity. Our preliminary data on several americium-plutonium alloys indicate a slow depressor of the superconducting temperature for americium with the addition of plutonium. This depression signifies that atom-atom interactions have been perturbed in these alloys. Such a perturbation is also apparent from the crystal form of the alloys (face center cubic) as compared to other crystal structures observed for the pure metals. Additional experiments are in progress to fully elucidate the bonding interactions in alloys of these two metals.

The curium-248 metal was primarily used for a collaborative low-temperature physics measurement (critical field, electronic heat capacity coefficient, etc.) with LAM. These low temperature measurements can only be made using the curium-248 isotope, as the self-heating due to radioactive decay is too great for the other curium isotopes. The experiments were carried out on a single, mg piece of curium-248 metal in the form of a thin disc about 3 mm in diameter. The measurements encountered experimental difficulties which led to large uncertainties in the specific heat and heat capacity coefficient (\( C_p \)). The results suggested that curium has a much larger specific heat than previously anticipated. New measurements on curium-248 metal are scheduled for mid-1983.

The largest single piece of californium-249 metal ever made (5 mg) was prepared and used for three research projects. One of these was an x-ray diffraction study of the metal under high pressure, which is part of an ongoing collaboration with the European Institute for Transuranium Elements in Germany. The initial results of this work have provided compressibility data for californium metal up to 16 GPa of applied pressure, but the data do not show a phase change indicative of partial 5f bonding as found for americium metal. Portions of the californium metal product were also used in magnetic studies (see section 6.1.4) and in measurements of its enthalpy of solution (see section 6.1.2).

The preparation of pure einsteinium metal free of a supporting substrate has not been reported. The limited studies on the metallic state of this element have been carried out using deposits on supporting material or alloys with other metals. The scarcity of einsteinium, together with the very high specific heat and alpha activity of the available 253Es isotope, prohibit the preparation of a pure bulk form of einsteinium metal. The infrequent availability (few weeks duration once or twice per year) also limits the number of experiments that can be attempted with einsteinium. Experiments on the metallic state of einsteinium during this report period consisted of electron diffraction and magnetic measurements of the metal deposited on supporting substrates, and vapor pressure measurements of einsteinium metal using an einsteinium-ytterbium alloy (see section 6.1.3). The diffraction and magnetic data are pending further analyses. The einsteinium-ytterbium alloy (0.2 mole % einsteinium) was prepared by simultaneously reducing a mixed oxide \([(Es, Yb)_{2}O_{3}]\) with lanthanum metal, and subsequently co-distilling/co-condensing the vapor of both metals. Ytterbium metal was chosen for the alloy preparation for several reasons, one of which was the similarity of its vapor pressure to that of einsteinium metal. Previous attempts to prepare an alloy with a higher einsteinium content encountered difficulties of partial sublimation in vacuum due to the self-heating of the einsteinium.\footnote{1. K. G. Haire, 'Preparation of Transplutonium Metals and Compounds', in Actes des 11èmes Journées Internationales d'Actualité du Transurane, ed. N. M. Edelstein, Pergamon, New York, 1982, pp 309-342.}


6.1.2 Enthalpy of Solution of Californium Metal 1

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

The solution microcalorimeter designed for use with the transplutonium elements has been used previously to determine the heats of solution of americium, curium, berkelium, and californium metals.⁴ The previous value for the enthalpy of solution of californium metal was a preliminary value determined with three small samples of metal foil.⁵ These data for californium metal indicated that the value for berkelium metal was more positive (less exothermic) than the values determined for americium, curium and californium. Since californium is the highest actinide element for which such measurements can be considered feasible, it became necessary to repeat the enthalpy of solution measurements on californium metal to firmly establish its value.

The enthalpy of solution of californium metal in 1 M HC¹ at 298 K was re-measured using larger quantities of well-characterized metal. Seven samples ranging in size from 168 to 370 micrograms were measured and yielded an average value of -576 kJ/mol.⁶ This value is lower than the previously determined enthalpies of solution in 1 M HC¹ at 298 K for dhcp californium (-617 ± 11 kJ/mol)⁵ and dhcp berkelium (-600.2 ± 5.1 kJ/mol)⁷ metals. This new value for californium metal now establishes a clear trend for the enthalpies of solution for the first four transplutonium metals (smaller enthalpy with increasing Z), which parallels the changes in the enthalpies of solution for lanthanum through dysprosium metals (excluding divalent europium metal). The values for the actinide metals are less exothermic than their lanthanide counterparts. The trend of less exothermic values for the higher members of the transplutonium elements may reflect the increasing stability of the divalent state in progressing across the actinide series.

1. Supported in part by DOE contract, DE-AS05-76ER04447 with The University of Tennessee, Knoxville.

2. Visiting Scientist from University of Liege, Belgium.

3. Chemistry Department, University of Tennessee, Knoxville.


6.1.3 Enthalpies of Vaporization and Vapor Pressures of Actinide Metals¹

(R. G. Haire, P. D. Kleinschmidt,² J. W. Ward²)

A collaborative program exists between ORNL and LANL for measuring the vapor pressures of actinide metals. The Knudsen effusion technique is used to obtain the vapor pressure of the metal as a function of temperature, and these data are used to calculate the enthalpy of vaporization via the second or third laws of thermodynamics. Previous vapor pressure
measurements on the transplutonium metals through einsteinium have been reported. These data have yielded a complete characterization of the metals through californium but have only permitted an estimate for the enthalpy of vaporization of einsteinium metal.

Recent efforts have been made to re-measure the vapor pressure of einsteinium metal and determine its enthalpy of vaporization by using an einsteinium-ytterbium alloy (0.2 mole % Es; see Section 6.1.1). The scarcity and the very high specific activity of einsteinium-253 preclude the preparation and direct study of pure einsteinium metal. Ytterbium metal was chosen as the metallic host for the einsteinium based in part on the similarity of its enthalpy of vaporization and vapor pressure with the corresponding extrapolated values for einsteinium metal. Previous studies have demonstrated that valid enthalpies and vapor pressures of an element can be obtained from alloys.\textsuperscript{3,4}

The vapor pressure of einsteinium in equilibrium with the solid alloy was measured over the temperature range of 455 to 855 K. A mass spectrometer in the system identified the volatile species as being monomeric metal atoms of einsteinium and ytterbium; a target collection device permitted calibrations (mass transferred per unit time) for the pressure measurements. A plot of the vapor pressure of einsteinium over the alloy as a function of $1/T$ is shown in Fig. 6.1, where excellent linearity is seen over seven orders of magnitude of pressure. From these data, a value of 31 kcal/mol was derived for the enthalpy of sublimation at 298 K. This einsteinium result compares with values of 39 and 36 kcal/mol for europium and ytterbium, respectively, which are both divalent metals. The trivalent lanthanide and transplutonium metals all have higher enthalpies of vaporization. The einsteinium pressures shown in Fig. 6.1 represent the pressures in equilibrium with the alloy, and must be corrected for the activity of einsteinium in the alloy to represent pressures that would be found over pure einsteinium metal. An activity coefficient for einsteinium can be calculated from the vapor pressure data and an estimated value for the entropy of the vaporization processes; such a calculation gives a value of about three, which is similar to activity coefficients known for other alloy systems. Other studies of einsteinium alloys and possibly pure einsteinium are planned to confirm our findings. However, these data for einsteinium together with previous diffraction data\textsuperscript{5} have led to the conclusion that einsteinium is the first divalent metal of the actinide series.

\begin{itemize}
  \item 1. Work supported in part by Office of Basic Energy Sciences, Chemical Sciences Division, Department of Energy contract with Los Alamos National Laboratory.
  \item 2. Los Alamos National Laboratory.
\end{itemize}

Fig. 6.1. Vapor pressure of einsteinium metal over an (Es,Yb) alloy.
6.1.4 Magnetic Characterization of the Metals and/or Compounds of Americium to Einsteinium (S. E. Nave, R. G. Haire, P. G. Huray)

The magnetic properties of an element or compound are a sensitive reflection of its electronic state. Magnetic measurements of the actinides generate data which can be compared to established values for the lanthanides, to determine if the same magnetic systematics apply to both series of elements. The major differences between the transplutonium elements and their lanthanide counterparts are the larger spatial extension and the larger spin-orbit coupling energy of the 5f wavefunctions, both of which affect magnetic properties. Recent efforts have concentrated on three study areas: (1) magnetic properties of transplutonium compounds having the 5f<sup>6</sup> and 5f<sup>7</sup> electronic configuration; (2) the magnetic properties of einsteinium and (3) magnetism of californium metal.

**Elements Having the 5f<sup>6</sup> and 5f<sup>7</sup> Electronic Configuration**

A systematic study of magnetic ordering in actinide compounds leads to a better understanding of electronic structure and atom-atom interactions in these materials. The main object of this present effort was to try to understand the non-zero magnetic moments measured for tetravalent curium compounds, which were expected to have zero moments because of a 5f<sup>6</sup> electronic ground state. Several curium compounds (CmO<sub>2</sub>, CmF<sub>3</sub>, RaCmO<sub>3</sub>, (Cm, Th) oxides, CmO<sub>1.2</sub>, and two crystal forms of CmO<sub>3</sub>) were prepared, characterized by x-ray diffraction and absorption spectrophotometry, and then their magnetic behavior extensively examined. As part of this study, magnetic measurements were also made on BkF<sub>4</sub>, BkO<sub>2</sub> (both 5f<sup>7</sup>) and on AmF<sub>3</sub> (5f<sup>6</sup>). The results were that the moments measured for the tetravalent curium compounds and the trivalent americium compound (see Fig. 6.2) were not in accord with the zero moment expected for an ion having a localized 5f<sup>6</sup> wavefunction unmodified by ligands. In contrast, the moments derived for other compounds and the trivalent-curium compounds were in accord with theoretically derived moments.

Such non-zero moments for compounds containing tetravalent curium could arise from experimental problems (non-stoichiometry, impurities, etc.) or have a physical basis (interionic interaction, crystal-field splitting, low-energy excited states, etc.). Attempts to explain the non-zero moments on the basis of such experimental problems or on a physical basis as due to low-lying excited states or crystal-field splittings were unsatisfactory. At the present time, it is necessary to consider that simple free-ion theory is not adequate for these actinide compounds, due to interionic interactions. This conclusion is not surprising considering the perturbations that occur at this region of the periodic table. Specifically, in the vicinity of plutonium-americium, there is a change from non-localized to localized character of the electrons and there is a large change in the magnetic moment (classically, 0 to 8 μ<sub>B</sub>) in going from a 5f<sup>6</sup> to 5f<sup>7</sup> state.

**Magnetic Properties of Einsteinium**

The first quantitative magnetic measurements of trivalent einsteinium have been made on EsO<sub>3</sub> and EsF<sub>3</sub>. As a result of the infrequent availability and the short half-life (20 days) of the 253<sup>ES</sup> isotope, the scope of studies on einsteinium are limited. Data on the two einsteinium compounds were collected at temperatures between 4.2 and 180 K, while maintaining the samples in different magnetic fields. The experimentally determined magnetic moments for these compounds, after corrections for the ber-1<sup>14</sup>ium daughter contents (see Figure...
Fig. 6.2 Experimental effective moments of some transplutonium compounds as a function of their nominal electronic configuration. The solid curve traces the calculated values assuming simple L-S coupling and Hund's Rule.

Magnetism of Californium Metal

The magnetic properties of californium metal have been determined for the temperature range 4.2-300 K, and in an applied magnetic field up to 1600 gauss. The californium metal was found to exhibit three regions of different magnetic behavior with temperature. It was either ferro- or ferrimagnetic (presently unresolved) below 35 K, antiferromagnetic in the range 48-66 K, and exhibited paramagnetism above 160 K. This behavior is shown in Fig. 6.3 for an applied magnetic field of 52 gauss. The measured moment below 35 K sharply increases with decreasing temperature but reaches a plateau below 20 K.

An effective moment of 10.6 ± 0.2 μ₀ was derived from the data for californium metal. This experimental moment agrees well with a calculated (based on Hund's Rule and L-S coupling) moment for an isolated Cf⁴⁺ ion with a 5f⁹ electron configuration (see Fig. 6.2). The agreement of the experimental moment for the metal with that for a Cf⁴⁺ ion can be rationalized on the basis that in the metallic state, three electrons of californium were involved in some form of a conduction band that left an isolated 5f⁹ core.

The magnetic behavior of californium metal was found to be very comparable to the behavior of its lanthanide electronic homolog, dysprosium metal. This is in contrast to other properties of these two metals. For example, crystal form (dhcp for Cf vs hcp for Dy);
Fig. 6.3. Magnetic susceptibility versus temperature plot for a disc-shaped sample of californium metal (142 μg) in an applied field of 52G. The observed hysteresis was most likely due to that of the low temperature ferro- or ferri- magnetic transition (see text). + = data before traversing the transition. • = data after traversing the transition. The time sequence of the data is indicated by the arrows.

The immobilization of actinides by incorporation into synthetic monazite is an attractive concept for the long term storage of actinides. This stems from the known stability, over geological age, of natural monazites (which contain uranium and thorium) toward radiation and sea water. In seeking methods for the preparation of metal phosphates from insoluble metal compounds by simple reactions, we have identified both BPO4 and SiP2O7 as convenient reagents for such a task. The reactions, verified experimentally, can be represented by the following equations:

\[ 2\text{BPO}_4 + 2\text{MO}_2 - 2\text{MP}_0_4 + \text{B}_2\text{O}_3 + \frac{1}{2} \text{O}_2(g) \]  
\[ 2\text{BPO}_4 + \text{M}_2\text{O}_3 - 2\text{MP}_0_4 + \text{B}_2\text{O}_3 \]  
\[ 2\text{BPO}_4 + \text{MO}_2 - \text{MP}_0_4 + \text{B}_2\text{O}_3 \]  
\[ 2\text{BPO}_4 + 2\text{MF}_3 - 2\text{MP}_0_4 + 2\text{BF}_3(g) \]

and

\[ 2\text{SiP}_2\text{O}_7 + 2\text{MO}_2 - 2\text{MP}_0_4 + 5\text{SiO}_2 + \frac{1}{2} \text{O}_2(g) \]  
\[ 2\text{SiP}_2\text{O}_7 + \text{M}_2\text{O}_3 - 2\text{MP}_0_4 + \text{SiO}_2 \]  
\[ 2\text{SiP}_2\text{O}_7 + \text{MO}_2 - \text{MP}_0_4 + \text{SiO}_2 \]  
\[ 3\text{SiP}_2\text{O}_7 + 4\text{MF}_3 - 4\text{MP}_0_4 + \frac{3}{2} \text{SiF}_4(g) \]  
\[ + 2\text{POF}_3(g) + \frac{3}{2} \text{SiO}_2 \]  

and

\[ 3\text{SiP}_2\text{O}_7 + 4\text{MF}_3 - 4\text{MP}_0_4 + \frac{3}{2} \text{SiF}_4(g) \]  
\[ + 2\text{POF}_3(g) + \frac{3}{2} \text{SiO}_2 \]  

The solid products were identified by Raman spectroscopy and also by x-ray diffraction. In Eq. (4) gaseous B3' was not identified, but weight losses verified the stoichiometry. The gaseous products SiF4 and POF3 in Eq. (8) were identified by mass spectrometry, and the evolution of oxygen [Eqs. (1) and (5)] was measured with a Beckman O2-Analyzer 741.

The reactions [Eqs. (1)-(8)] all started in the temperature range of 500-600°C and reached completion at 1000-1200°C. Reactions in which a tetravalent metal was reduced to trivalent [Eqs. (1) and (5)] were studied using Ce, Pr, Tb and Pu. The solids obtained with plutonium
dioxide and $\text{BPO}_4$ consisted of $\text{B}_2\text{O}_3$ and a mixture of $\text{PuP}_2\text{O}_7$ with $\text{PuP}_4\text{O}_7$. Additional studies indicated that both plutonium phosphates may form simultaneously and that the conversion of $\text{PuP}_2\text{O}_7$ to $\text{PuP}_4\text{O}_7$ is a slow reaction (1-2 weeks) even at temperatures in excess of 1050° C. However, the reverse reaction

$$\text{PuP}_4\text{O}_7 + 1/2 \text{B}_2\text{O}_3 \rightarrow \text{PuP}_2\text{O}_7 + 1.2 \text{O}_2$$

proceeds to completion in a few hours at 950° C.

Metathesis reactions involving trivalent metal compounds, represented by Eqs. (2), (4) and (6), were studied using La, Nd, Ho, Yb, Lu and Pu. Metathesis reactions involving tetravalent metal compounds (Eqs. (3) and (7)) were studied with U and Np. Studies of the thermal behavior of U, Np and Pu pyrophosphates allowed us to prepare and identify the following compounds: $\text{U}_2\text{O}_3\text{P}_2\text{O}_7$, $\text{NpO}_2\text{P}_2\text{O}_7$ and $\text{PuO}_2\text{P}_2\text{O}_7$, by x-ray powder diffractometry, and, in some cases, by Raman and visible absorption spectrometry. In addition, anhydrous crystalline trimetaphosphates of all the rare earths (except Pm), Y, and Pu were synthesized by solid state reactions. The Raman spectra of the trimetaphosphates reflected clearly the change in crystal structure encountered in going across the series, from orthorhombic (La-Eu, including Pu) to monoclinic (Gd-Lu, including Y).

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6.1.6 Preparation and Characterization of the Phosphates of the First Five Transplutonium Elements


Recent interest in lanthanide phosphates as potential matrices for radioactive materials emphasized the fact that only a limited amount of data existed for the trivalent actinide phosphates. The intent of the work described here was two-fold: (1) to synthesize and characterize the orthophosphates of the first five transplutonium elements; and (2) to determine the stability of the transplutonium orthophosphates with respect to self-irradiation. This initial goal was achieved, while the effects of self-irradiation as a function of time are in progress and these results will be reported at a later date.

The phosphates were prepared on a microscale, which involved an aqueous precipitation technique together with a subsequent high-temperature (800-1000° C) treatment. The orthophosphates ($\text{AnPO}_4$, $\text{An}$ = trivalent actinide) were characterized by Raman spectrophotometry, solid state absorption spectrophotometry, and x-ray powder diffraction. Raman spectra for these transplutonium orthophosphates are shown in Fig. 6.4. In addition, Raman spectra were also obtained for the trimetaphosphates ($\text{An}(\text{PO}_4)_3$) of americium, curium and californium, and these spectra were found to be discernible from the spectra for orthophosphates. X-ray diffraction data for the orthophosphate of americium through californium showed that these compounds exhibited the monoclinic, monazite ($\text{CePO}_4$) structure-type. The intense radioactivity of einsteinium precluded the attainment of x-ray data for its orthophosphate, but from the Raman and absorption spectra it has been concluded that this compound also initially crystallized in the monoclinic form. This result is in accord with the trivalent radius of einsteinium and the crystallization behavior of the lanthanide orthophosphates as a function of their ionic radii. The solid state absorption spectrum obtained for each of these transplutonium orthophosphates is shown in Fig. 6.5.

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3. Analytical Chemistry Division, ORNL.

Fig. 6.4. Raman spectra obtained from the orthophosphates of the first five transplutonium elements.

Fig. 6.5. Solid state absorption spectra of the Am, Cm, Bk, Cf, and Es orthophosphates.
6.1.7 Synthesis and Characterization of Quaternary Orthophosphates Containing Alkali Metals and Actinides or Lanthanides
(C. E. Bamberger, R. G. Haire, G. M. Begun, L. C. Ellingboe)

Double phosphates of alkali metals and lanthanides [e.g., $\text{Na}_3\text{M}(\text{PO}_4)_2$, $\text{M}_{16}^\text{II}(\text{PO}_4)_3$] have been known for the last two decades, and it has been determined that their solubility in water is higher than that of morazite. Recently, during the development of a titanium-based ceramic form for acid waste streams containing sodium, gadolinium (added as a neutron poison), and phosphate ion from the decomposer of TEF, it was found that $\text{Na}_3\text{Sc}_2\text{C}_2 \cdot \text{H}_2\text{O}$ formed as an additional phase. Because nuclear wastes contain a variety of elements, we sought to explore the effect of alkali metals on the synthesis of morazite with regard to the formation of double phosphates. Double phosphates of sodium and a lanthanide (Ce, Pr, Tb, or plutonium) were prepared mainly by the reactions:

$$2\text{Na}_3\text{M}(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O} \rightarrow \text{Na}_3\text{M}(\text{PO}_4)_2 \cdot \text{H}_2\text{O} \cdot 2\text{Na}_3\text{M}(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$$

The products were examined by Raman spectroscopy and x-ray diffraction. Because several stoichiometries are possible for these double phosphates and because there are questions about the existence of some compounds, we attempted to synthesize several compositions. These attempts included all the rare earth elements and made use of numerous reactions reported in the literature which ranged from solid-solid reactions to synthesis in molten media. Our results indicated that, contrary to the claims in the literature, only compounds of the type $\text{Na}_3\text{M}(\text{PO}_4)_2$ formed with the elements from La to Dy. The stoichiometry and/or crystal structure of compounds containing Ho(Y) to Lu will require additional study, but it has been observed that their Raman spectra and x-ray diffraction patterns differ from those of the lighter rare earths.

1. Student participant from St. Olaf College, Northfield, Minnesota.

6.1.8 Chemical and Structural Consequences of Radioactive Decay Processes (R. G. Haire, J. P. Young, J. R. Peterson, D. O. Enson)

Studies of the chemical and structural consequences of radioactive decay in the solid state were continued. These studies involve the preparation of radioactive compounds which are monitored with time to ascertain the effects of the decay processes on the oxidation state and crystal form of the progeny. In this regard, they differ from studies which are concerned with only the effects of radiation on the original material. Our studies have relied mainly on absorption spectrophotometry and x-ray diffraction as the investigative tools.

These long-term studies have concentrated on using transplutonium elements in oxidation states of II, III and IV mainly in the form of anhydrous halides. The einsteinium-253 and berkelium-249 decay chains are particularly well suited for examining alpha and beta decay progeny. More recently studies of oxides and phosphates of these elements have been initiated to determine if the anion will alter the trends established with the anhydrous halides. We have also incorporated the transplutonium elements in lanthanide hosts (5-10 mole % actinide) to extend the number of crystal forms that can be prepared and studied. This procedure enables us to better define how the crystal environment effects the progeny's structure.

The results to date show that the oxidation state of the progeny is controlled by the oxidation state of its parent (a result of heredity). The structure of the progeny seems to be controlled by its environment, which can be the structure of either the parent or the host. Thus, thermalization of recoil species resulting from either alpha or beta decay can be considered a process of charge-compensated ion implantation, where the resulting product reflects the environment into which it is implanted by the radioactive decay process. In the systems studied to date, no severe chemical and/or physical instabilities are imposed by the maintenance of the oxidation state or the structure by the progeny, and the
results must be considered in this limited context. Future efforts will be aimed at monitoring existing samples and examining other decay chains.

1. Supported in part by DOE contract DE-AS05-7EER04447 with The University of Tennessee, Knoxville.

2. Analytical Chemistry Division.

3. Chemistry Department, University of Tennessee, Knoxville, TN.

4. Chemistry Department, Tennessee Technological University, Cookeville, TN.

6.1.9 Neutron Thermal Cross Sections and Resonance Integrals for Es Isotopes


The heaviest nuclide produced to date for experimental purposes in at least microgram quantities has been $^{254}\text{Es}$. This and other transplutonium isotopes have been made at the HFIR-TRU facility which was especially designed to produce the heaviest nuclides accessible via neutron capture reactions. In a continuing effort to provide accelerator targets to investigate the most favorable nuclear reactions for producing elements with $Z \geq 110$ (i.e., in the predicted region of superheavy element stability), we have been examining parameters which determine the yield of the 276 day $^{254}\text{Es}$.

The path to $^{254}\text{Es}$ from $^{252}\text{Cf}$ is shown in Eq. 1:

$$^{252}\text{Cf} \rightarrow (n,\gamma) \rightarrow 253\text{Cf} \rightarrow 253\text{Es} \rightarrow (n,\gamma) \rightarrow 254\text{Es}$$

Harbour and MacMurdo have reported values for the thermal cross section and resonance integral of $< 3 \text{b}$ and 4300 b, respectively, for neutron capture in $^{253}\text{Es}$ to form $^{254}\text{Es}$. However, Bigelow and coworkers have demonstrated that these cross section values of Hart and MacMurdo overpredict the yield of $^{254}\text{Es}$ by almost a factor of ten. Bigelow has since investigated this discrepancy and has pointed out that Harbour and MacMurdo were most likely unaware of a significant $^{254}\text{Es}$ content in the sample of $^{253}\text{Es}$ provided them for their cross section measurement. Such an oversight would, of course, invalidate the cross section values that they report.

The $^{253}\text{Es}$ available to us initially for this measurement was contaminated by too large an amount of $^{254}\text{Es}$ to allow evaluating $\sigma_c(253\text{Es} \rightarrow 254\text{Es})$; and, the availability of isotopically pure $^{253}\text{Es}$ was scheduled for a future production run. However, it was possible to consider studying several related reactions with this initial material ($^{254}\text{Es}$ content > 20%). Neutron capture in $^{253}\text{Es}$ also results in formation of the 39.3 hr $^{254}\text{Es}$, an isomeric nuclide decaying almost exclusively by $\alpha$-decay to the alpha emitting $^{254}\text{Fm}$. By examining the alpha spectrum of the sample following neutron irradiation, we measure the partial capture cross section of $^{253}\text{Es}$. Further, by examining the ratio of $^{254}\text{Es}$ to $^{253}\text{Es}$ in the alpha spectrum both before and after the irradiation we can measure the relative neutron absorption cross section of these two nuclides as in a burnout experiment. In addition, since $38.3\text{d}^{255}\text{Es}$ is formed in neutron capture of $^{254}\text{Es}$, and its $\alpha$-decay leads to the $\alpha$-emitting $^{255}\text{Fm}$, alpha spectrum measurements provide a measure of $\sigma_c(254\text{Es})$.

The $^{253}\text{Es}$ sample together with cobalt monitors was irradiated under controlled conditions at the HFIR. The irradiation capsule incorporated...
two samples covered by cadmium neutron filters
with a bare sample centered between them.
Measurements of the cadmium filtered samples,
being sensitive only to activation by the
epithermal component of the reactor flux
spectrum, provided the means to interpolate
that resonance response to the bare position
and to evaluate the thermal response in that
position from the total reaction rate. Thus,
both thermal cross sections and resonance
integrals were evaluated for these reactions.

In Table 6.1 are summarized the results for
capture in $^{253}$Es forming $^{254m}$Es. The
tabulated cross sections are estimated to be
uncertain to ± 10%. These values are somewhat
larger than the $I = 155 ± 20$ b and
$I = 3009 ± 168$ b reported by Harbour and
MacMurdo. 3

Table 6.1 Partial Capture Cross Sections* of $^{253}$Es to form $^{254m}$Es

<table>
<thead>
<tr>
<th>$^\text{1}$Irrad</th>
<th>$^\theta_{\text{th}}$</th>
<th>$^\theta_{\text{r}}$</th>
<th>$^\gamma_{\text{eff}}$</th>
<th>$^I$</th>
<th>$^\theta_{\text{th}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(min)</td>
<td>(n/cm$^2$-sec)</td>
<td>(n/cm$^2$-sec)</td>
<td>(barns)</td>
<td></td>
<td>(barns)</td>
</tr>
<tr>
<td>1.44 x 10$^3$</td>
<td>4.20 x 10$^{14}$</td>
<td>2.16 x 10$^{13}$</td>
<td>380</td>
<td></td>
<td>3740</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>190</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Cross section values are estimated uncertain to ± 10%.

We have only preliminary values from the Es
burnout experiment, but it appears that the
$^{254m}$Es absorption cross section is smaller
than the $I = 3009$ b expected under the present
irradiation conditions. Similarly, preliminary
values for the capture cross section of
$^{254m}$Es appear to be less than the 40 b
limit listed in the Cross Section compilation,
BNL-325. 5

1. Chemical Technology Division.
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6.2 Solution Chemistry

6.2.1 Complexes of Np(V) in Aqueous Solution
(J. Halperin, J. H. Oliver)

We have made use of an organic extraction
technique and tracer $^{239}$Np to investigate
the formation of the mono-sulfate complex of
$\text{NpO}_2^+$. Solutions of the liquid cation
exchanger sodium dinonyl-naphthalene sulfonate
in n-neptane were used to extract Np from
aqueous solutions containing sulfate ion. In
this system containing tracer Np(V), complex
ion formation leads to anionic species which
are not extracted by the cationic exchanger.
Thus, the distribution ratio, D(org/aq),
decreases as sulfate ion ligand is added to the
solution allowing the calculation of stability
constants (K'). These studies have been
carried out at ionic strengths of I = 0.5, 1.0
and 2.0 and at temperatures of 5, 25 and 45°C.

Although the true values of the thermodynamic
quantities, free energy, enthalpy and entropy,
cannot be evaluated from the concentration-
dependent stability constants, K', we have
estimated effective values ($\Delta G^\circ$, $\Delta H^\circ$, $\Delta S^\circ$)
for these quantities. The values of the
stability constants and related thermodynamic
quantities obtained are listed in Table 6.2.
The stability constant of the monosulfate complex has been found here to be relatively small, but showing an enhancement with increasing ionic strength and with temperature. There is no evidence for formation of sulfate complexes having greater than a 1:1 ratio of $\text{SO}_4^{2-}/\text{NpO}_2^{2+}$ up to the 0.3 M sulfate ion concentration studied. Enthalpy and entropy determinations for the process of complex formation yield relatively large positive values which parallel the more highly charged actinide species ($\text{AnO}_2^{2+}$, $\text{An}^{3+}$, $\text{An}^{4+}$) and are consistent with inner sphere complexing. The possible formation of sulfate complexes of Np(V) in natural waters arising from the storage of nuclear wastes cannot be important unless one postulates aqueous media containing sulfate in excess of 0.1 M.

### Table 6.2 Stability Constants and Values of $\Delta G^\ominus$, $\Delta H^\ominus$ and $\Delta S^\ominus$ for $\text{NpO}_2\text{SO}_4^-$

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>I</th>
<th>$K'$</th>
<th>$\Delta G^\ominus (kJ/mol)$</th>
<th>$\Delta S^\ominus (J/Kmol)$</th>
<th>$\Delta H^\ominus (kJ/mol)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.5</td>
<td>0.37 ± 0.15</td>
<td>2.30 ± 1.00</td>
<td>95 ± 15</td>
<td>28.9 ± 4.6</td>
</tr>
<tr>
<td>5</td>
<td>1.0</td>
<td>0.66 ± 0.07</td>
<td>0.96 ± 0.25</td>
<td>76 ± 8</td>
<td>22.2 ± 2.4</td>
</tr>
<tr>
<td>5</td>
<td>2.0</td>
<td>0.91 ± 0.12</td>
<td>0.22 ± 0.30</td>
<td>66 ± 9</td>
<td>18.6 ± 2.5</td>
</tr>
<tr>
<td>25</td>
<td>0.5</td>
<td>0.79 ± 0.07</td>
<td>0.58 ± 0.22</td>
<td>-1.07 ± 0.11</td>
<td>-2.07 ± 0.10</td>
</tr>
<tr>
<td>25</td>
<td>1.0</td>
<td>1.16 ± 0.06</td>
<td>-0.37 ± 0.13</td>
<td>76 ± 8</td>
<td>22.2 ± 2.4</td>
</tr>
<tr>
<td>25</td>
<td>2.0</td>
<td>1.54 ± 0.07</td>
<td>-1.07 ± 0.11</td>
<td>66 ± 9</td>
<td>18.6 ± 2.5</td>
</tr>
<tr>
<td>45</td>
<td>0.5</td>
<td>1.76 ± 0.07</td>
<td>-1.30 ± 0.11</td>
<td>-2.07 ± 0.10</td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>1.0</td>
<td>2.19 ± 0.08</td>
<td>-2.07 ± 0.10</td>
<td>-2.42 ± 0.16</td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>2.0</td>
<td>2.50 ± 0.15</td>
<td>-2.42 ± 0.16</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The assumption was made that valid estimates could be derived in view of the similarities between Ag$^+$ and NpO$_2^{2+}$ such as charge, hydrolytic behavior and M-O distances. The conditional constants obtained at 25°C in 1.0 M NaClO$_4$ as background electrolyte are $\log \beta_{\text{AgCO}_3^-} = 1.5$ and $\log \beta_{\text{AgC}_2\text{O}_4^-} = 0.9$. These values reflect the fact that both complexes are rather weak. Comparison of $\log \beta_{\text{AgC}_2\text{O}_4^-}$ with $\log \beta_{\text{NpO}_2\text{C}_2\text{O}_4^-}$ = 3.3, which had been reported in the literature, shows considerable differences in complexation behavior between Ag$^+$ and NpO$_2^{2+}$ for oxalate. On the other hand, if the ratio of the complexation constants of the two ions with oxalate is the same as that for carbonate, an estimate of $\log \beta_{\text{NpO}_2\text{CO}_3^-}$ of 3.97 is obtained. These estimates were important in defining the best experimental approach to obtain the complexation constant of the Np(V) carbonate complex. The actual value for the complexation constant $\log \beta_{\text{NpO}_2\text{CO}_3^-}$ was found to be 4.49, in fair agreement with the Ag$^+$-based estimate.

#### 6.2.2 Carbonate and Oxalate Complexation of Silver(I) Ion
(L. Maya)

Complexation constants for silver ion with carbonate and oxalate were derived from potentiometric titrations using a silver ion sensitive electrode. These values were required in order to derive estimates of the carbonate complexation constant of NpO$_2^{2+}$.

#### 6.2.3 Hydrolysis and Carbonate Complexation of Dioxioneptunium(V)
(L. Maya)

The estimates of complexation constants for Np(V)-CO$_3^{2-}$ derived from the work with
Ag⁺ ion suggested that potentiometric titrations of Np(V) solutions would be sensitive enough to detect and obtain the complexation constants for this system. An experimental constraint was that of the low solubility of Np species for which existing reports in the literature placed rather stringent limitations. Attempts were made to effect supersaturation so that titrations could be completed at a high enough neptunium concentration to obtain meaningful results. These attempts failed; consequently, the measurements of the Np(V) carbonate complexation were made from the solubility profile of NaNpO₂CO₃·3.5H₂O as a function of carbonate concentration. The solid phase used in these experiments was characterized by x-ray diffraction and Raman spectroscopy. Tests conducted to ascertain that this solid was stable through the carbonate concentrations covered in the study confirmed its stability. Additional tests were conducted to assess whether bicarbonate complexation was significant in this system. The results showed no significant bicarbonate complexation on Np(V).

The values obtained for the carbonate complexation constants were \( \log K_{11} = 4.49 \pm 0.06 \), \( \log K_{12} = 7.11 \pm 0.07 \), and \( \log K_{13} = 8.53 \pm 0.09 \) while the hydrolysis constant was \( \log K_H = -9.12 \pm 0.15 \). These complexation constants were used to calculate speciation schemes under conditions similar to those in ground waters. The results lead to the prediction that neptunium will be present in ground waters as the mono and dicarbonato complexes.

6.2.4 Raman Spectrometric Studies of Actinide (V) and (VI) Complexes in Aqueous Sodium Carbonate Solution and of Sodium Actinide(V) Carbonate Compounds
(C. Madić, D. E. Hobart, G. M. Begun)

A better understanding of the chemistry of the actinide elements in aqueous carbonate solutions is important in the areas of reprocessing of irradiated nuclear fuels, actinide separations, environmental concerns, and for basic scientific studies to provide correlations to the other members of the transition elements. The existence of the higher oxidation states of the actinides as the oxycations, M₄O²⁺ and M₄O₂⁺, for the pentavalent and hexavalent oxidation states, respectively, makes Raman scattering experiments a rather useful technique for studying these ions in solution as well as in the solid state. Raman spectral literature involving actinide ions is relatively scarce. Uranium has been the subject of many studies, but only a few reports on Raman studies of the transuranium elements have been published.

The purpose of the present work was to obtain Raman spectra of actinide(V) and (VI) ions of U, Np, Pu, and Am in concentrated aqueous sodium carbonate solutions in order to obtain structural information on the various species and to compare this data with that available in the literature. Depleted uranium was used and ²³⁷Np, ²⁴²Pu, and ²⁴³Am were obtained from ORNL. These materials were converted from the oxides to concentrated actinide chloride solutions or hydroxide precipitates and introduced into the carbonate medium.

For the sparingly soluble actinide(V) complexes in carbonate solution, an appreciable concentration of solute was required for Raman studies. This necessitated preparation of supersaturated solutions and immediate recording of the Raman scattering data. Within a short time, less than 2 hours, the actinyl(V) "double-carbonate" precipitates formed and the Raman spectra of these solids were also recorded. No double-carbonate precipitates formed for the U(V) solutions.

The colors and positions of the symmetric stretching frequency of the actinyl carbonate complexes are summarized in Table 6.3.

Raman spectra of all the actinide(V) (except Pa) complexes in 2 M Na₂CO₃ solutions have
Table 6.3 Colors and Frequencies of the Symmetric Stretching Vibrations of Actinyl Carbonate Complexes

<table>
<thead>
<tr>
<th>Actinide</th>
<th>Color in Solution</th>
<th>Color of double carbonate solid</th>
<th>Actinyl solution ν1 frequency (cm⁻¹)</th>
<th>Actinyl Solid ν1 frequency (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U(V)</td>
<td>Colorless</td>
<td>--</td>
<td>759</td>
<td>--</td>
</tr>
<tr>
<td>Np(V)</td>
<td>Light blue</td>
<td>Light grey</td>
<td>755</td>
<td>772</td>
</tr>
<tr>
<td>Pu(V)</td>
<td>Yellow-brown</td>
<td>Light green</td>
<td>755</td>
<td>760</td>
</tr>
<tr>
<td>Am(V)</td>
<td>Light yellow</td>
<td>Grey</td>
<td>755</td>
<td>747</td>
</tr>
<tr>
<td>U(VI)</td>
<td>Yellow</td>
<td>--</td>
<td>812</td>
<td>--</td>
</tr>
<tr>
<td>Np(VI)</td>
<td>Dark green</td>
<td>--</td>
<td>802</td>
<td>--</td>
</tr>
<tr>
<td>Pu(VI)</td>
<td>Red or green*</td>
<td>--</td>
<td>788</td>
<td>--</td>
</tr>
<tr>
<td>Am(VI)</td>
<td>Dark red-brown</td>
<td>--</td>
<td>755</td>
<td>--</td>
</tr>
</tbody>
</table>

*The color is a function of the thickness of the solution!

been obtained and are shown in Fig. 6.6. A resonance Raman effect was observed for Np(VI), Pu(VI), and Am(VI) and found to be related to the position of the charge-transfer bands observed in the corresponding electronic spectra and to the formal potential of actinide(VI)/(V) couples in carbonate solution. No resonance effect was observed in the Raman spectrum of U(VI). The symmetric stretching frequency (ν1) of the MO2⁺ group was shifted in carbonate solutions as compared to acidic non-complexing solutions and decreased regularly with an increase in the atomic number of the actinide considered (see Fig. 6.7). In contrast, the ν1 frequencies of the MO2⁺ group for actinide(V) species in carbonate solutions did not vary as the atomic number of the actinide increased. Compared to their ν1 frequencies in acidic solutions, in carbonate solution a small negative shift was observed for ν of Np(V) and a positive shift was obtained for ν1 of Am(V). The Raman spectra of Na₃MO2(CO₃)₂ solid compounds were obtained for M = Np, Pu, and Am. The ν1 frequencies of the MO2⁺ ions decreased linearly with increasing atomic number of the actinide and were higher than the corresponding values for aqueous MO2⁺ ions. The differences in behavior observed between actinide(V) and (VI) species in non-complexing media and in carbonate media may be related to

Fig. 6.6. Raman spectra of actinide(V) species in 2 M Na₂CO₃ solution (514.5 nm excitation).
possible hydrogen bonding between the oxygen of the actinide(V) oxycation and water molecules. A more detailed report of this work will be published. 10

1. Research sponsored by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under contracts W-7405-eng-26 with the Union Carbide Corporation and DE-AS05-76ER04447 with the University of Tennessee (Knoxville) and by the Centre d'Etudes Nucleaires, Fontenay-aux-Roses, France.

2. Guest Scientist on assignment from Centre d'Etudes Nucleaires, Fontenay-aux-Roses, France.
stretching frequency, \( v_1 \), of the PuO\(_2\)\(^{2+} \) ion is found in this region. In the pH range studied the spectra were found to consist of four bands at 833, 817, 826, and 805 cm\(^{-1} \), respectively. Computer peak resolution, least-squares analysis, and relative intensity measurements led us to assign the observed bands to vibrational transitions of the following ions: PuO\(_2\)\(^{2+} \) (833 cm\(^{-1} \)), (PuO\(_2\)\(_2\))(OH)\(_2\)\(^{2+} \) (817 cm\(^{-1} \)), and (PuO\(_2\)\(_2\))(OH)\(^{7+} \) (826, 805 cm\(^{-1} \)). In addition, for high pH values (13-14), a new Pu(VI) band was found at 794 cm\(^{-1} \) which exhibited a resonance Raman effect. Fig. 6.9 shows the normalized relative intensities of the resolved Raman peaks as a function of pH, and illustrates the hydrolysis equilibrium which occurs. Our data are in agreement with the hydrolysis reactions proposed by Baes and Nesmer\(^{4} \) and later modified by Schedin.\(^{5} \)

The Raman spectra of a 4 x 10\(^{-2} \) M Pu(VI) solution at pH = 3.7 ([ClO\(_4\)\(^{-} \]) = 0.105 M, \( \mu = 1.0 \) adjusted with NaCl) and those of solutions obtained at different times during electrochemical reduction, Pu(VI) + e\(^- \) \rightarrow Pu(V), were obtained. During the electrolysis the 833 cm\(^{-1} \) PuO\(_2\)\(^{2+} \) band disappears and a new band (due to PuO\(_2\)\(^{2+} \)) centered at 748 \( \pm 1 \) cm\(^{-1} \) grows in intensity. These are the first reported Raman spectra of the PuO\(_2\)\(^{2+} \) \([\text{plutonium(V)}]\) ion. The Raman spectrum of a freshly prepared 4 x 10\(^{-2} \) M PuO\(_2\)\(^{2+} \) solution was recorded as a function of time, and the spectra are shown in Fig. 6.10. After six days had elapsed, the spectrum was found to be essentially identical to that obtained the first day. The spectrum obtained after 10 days was quite different, however, in that a large decrease of the intensity of the 748 cm\(^{-1} \) band and the appearance of new bands at 833 and 817 cm\(^{-1} \) were observed. These two new bands belong to PuO\(_2\)\(^{2+} \) and its first hydroxo complex (see above). This result constitutes the first evidence by Raman spectrometry of the disproportionation of PuO\(_2\)\(^{2+} \). Evidence for an increase of pH caused by the disproportionation reaction was also obtained by the appearance of the 817 cm\(^{-1} \) band belonging to the Pu(VI) first hydroxo-complex which was not present in the initial spectrum taken at pH = 3.7. The disproportionation of PuO\(_2\)\(^{2+} \) ion at pH 3.7 as studied here should result in the production of insoluble Pu(OH)\(_4\)\(^{-} \). A precipitate was indeed observed in our samples.

The symmetrical stretching frequencies of the aqueous actinide(V) ions are NpO\(_2\)\(^{2+} \), 767 cm\(^{-1} \); PuO\(_2\)\(^{2+} \), 748 cm\(^{-1} \); AmO\(_2\)\(^{2+} \), 732 cm\(^{-1} \). The full width at half maximum
HYDROLYSIS OF $\text{PuO}_2^+$

$[\text{Pu(VI)}]_7 = 0.1 M$

Fig. 6.9 Variations of the relative intensities of the $\nu_1$ plutonyl(VI) bands as a function of pH. 514.5 nm excitation.

The peak decreases from 24 cm$^{-1}$ for NpO$_2^+$ to 20 cm$^{-1}$ for PuO$_2^+$ to 17 cm$^{-1}$ for AmO$_2^+$. The high sensitivity of the PuO$_2^+$ ion for Raman spectral activation compared to the other possible methods for PuO$_2^+$ measurement suggests that Raman spectroscopy should be the preferred technique for further studies of this ion.

Hydrolysis studies of neptunyl(VI) ions were also done by observing the Raman spectra of NpO$_2^+$ solutions as a function of pH. Due to the precipitation of sodium neptunate at higher pH values (> 3.65) only one hydrolysis product, (NpO$_2$)$_2$(OH)$_2$,$^2+$, was characterized. A more detailed account of this research is being prepared for publication.

1. Guest scientist on assignment from Centre d'Etudes Nucléaires, Fontenay-aux-Roses, France.
2. Department of Chemistry, University of Tennessee, Knoxville, TN 37996.
6.2.6 Cation-Cation Complexes: New Complexes of a d-Electron Element, Vanadium (VO$_2^+$), and Comparison with the Complexes of Neptunium (NpO$_2^+$)


Dimerization of VO$_2^+$. Vanadium is the first element aside from the actinides, in the form of its vanadyl ion, VO$_2^+$, that has been found to form cation-cation complexes. We have used a variety of experimental methods to characterize these complexes of vanadyl, and to compare them with actinyl ion, AnO$_2^+$, cation-cation complexes.

Our experiments utilizing Raman and u.v.-visible spectrometry have demonstrated that a previously unknown soluble species, a dimer of vanadyl ion, is formed in very concentrated (≥ 7 M) HClO$_4$ or H$_2$SO$_4$ solutions. This result is especially striking since in dilute acid, the maximum concentration of VO$_2^+$ ion in solution is ~ 0.15 M; the corresponding maximum concentration in concentrated (~ 11 M) H$_2$SO$_4$ solution is ~ 3 M vanadium. The dimer is characterized spectroscopically by a strong absorption at 340 nm, with a tail extending to ~ 600 nm.

Raman spectra of solutions with different vanadyl concentrations in 12 M H$_2$SO$_4$ are shown in Fig. 6.11. At 0.12 M, the peaks observed are characteristic of the VO$_2^+$ ion (940 and 917 cm$^{-1}$) and the HSO$_4^-$ and SO$_4^{2-}$ ions (1036, 983 and 902 cm$^{-1}$). As the vanadium(V) concentration is increased, new bands are observed at 988, 750, 500 and 242 cm$^{-1}$. The relative intensities of these bands were found to be linearly related to the absorbances measured with the same solutions at $\lambda$ > 500 nm; this result demonstrates that the same species, i.e., the dimer, which is responsible for the absorbance increase at large wavelength, is also responsible for the appearance of the new Raman bands. By comparison of the Raman data with published vibrational spectra for known bridged M-O-M dimers such as V$_2$O$_3^{4+}$ and Cr$_2$O$_7^{2-}$, we conclude that the vanadium(V) dimer has a bent, oxygen bridged structure containing the V-O-V group. Specifically, the new bands are assigned to the following transitions: for the V-O-V bridge, the asymmetric stretch is at 750 cm$^{-1}$, the symmetric stretch at 500 cm$^{-1}$, and the bending mode at 242 cm$^{-1}$; for the terminal V=O, the symmetric stretch is at 988 cm$^{-1}$.

Other experimental techniques, specifically wide angle x-ray scattering, NMR spectroscopy, and cyclic voltammetry, were also used to study the dimer. All of these results are consistent with the conclusion that the dimer is an ion of form V$_2$O$_3^{4+}$, with a bent V-O-V bridge. Comparison of these data with those for the previously discovered dimer of NpO$_2^+$ lead us to conclude that even though the VO$_2^+$ and NpO$_2^+$ ions both form dimers, their structures are different. Unlike the
vanadium dimer, the Np dimer does not contain a M-O-M bridge.

A Complex of NpO$_2^+$ with VO$_2^+$. Since VO$_2^+$ was known to form a cation-cation complex with VO$_2^+$, and both VO$_2^+$ and NpO$_2^+$ behaved similarly in their ability to form dimers, it seemed likely that NpO$_2^+$ might form a complex with VO$_2^+$. We verified this possibility, as shown in Fig. 6.12, where it is seen that the absorption peak for NpO$_2^+$ at 980 nm decreases upon the addition of VO$_2^+$, and a new peak is developed at 990 nm. The isosbestic point in the spectra demonstrates that only one form of the Np-V complex exists.

As seen in the Raman spectra, Fig. 6.13, for mixtures of 1.42 M NpO$_2^+$ with differing concentrations of VO$_2^+$, there is competition between the formation of different cation-cation complexes in the solutions. The spectrum for the solution that is free of vanadium(IV) shows the peaks at 767 and 738 cm$^{-1}$ that are characteristic of the NpO$_2^+$ ion and the Np dimer. As VO$_2^+$ is added to the solution, the intensity of the 738 cm$^{-1}$ band decreases, the peak at 767 is shifted to 775 cm$^{-1}$ and its intensity increases. These results are consistent with the formation of a Np-V complex, effectively
competing with that of the Np-Np dimer. The
coeexistence of these different complexes
suggests that such species may be important
constituents in reactions involving highly
concentrated solutions.

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Transition, Paris, France.
4. P. Blanc, C. Madic, and J. P. Launay,
5. H. Stamreich, D. Bassi, O. Sala, and H.
6. B. Guillaume, G. M. Begun and R. L. Hahn,

6.2.7 Detection of Hydroxo and Carbonato
Species of Dioxouranium(VI) by Differential
Pulse Polarography
(L. Maya)

One of the difficulties with speciation
schemes for a complex system as derived by
computer-aided fits of potentiometric titra-
tions is the likelihood of introducing non-
existant species or using a set of species when
only one species can account for the data in a
given range; therefore, additional physico-
chemical means that identify a given set of
species serve the useful purpose of adding
confidence to a given speciation scheme.

It was found possible to identify the species

\[(\text{UO}_2)_2(\text{OH})_2^{2+}, (\text{UO}_2)_3(\text{OH})_5^+, (\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-\]

\[(\text{UO}_2)_3\text{CO}_3^{6-}, \text{UO}_2(\text{CO}_3)_3^{4-}\text{ and } \text{UO}_2(\text{OH})_4^{2-}\] by

means of differential pulse polarography. This
technique is quite sensitive, allowing observa-
tions to be made down to the \(10^{-6}\) M range
and even \(10^{-8}\) M under suitable conditions.

The range of existence in terms of pH and
\(\text{PCO}_2\) for each species as observed from
their typical reduction potentials was in

agreement with predictions made on the basis of
the speciation schemes previously derived from
potentiometric titrations. The electrochemical
results were also in agreement with Raman
spectroscopy observations of the characteristic
\(\gamma_1\)-\text{UO}_2 stretching frequencies of each
species.

This study demonstrated the utility of
differential pulse polarography in detecting
species at relatively low concentrations and
added considerable confidence to the assign-
ment of a speciation scheme for the uranyl ion as a
function of pH and \(\text{PCO}_2\).

6.2.8 Development of Radiopolarographic
Techniques for Use in the Neutral pH Range:
Complexation of Mn(II) by Carbonate
(G. D. O'Kelley, K. Samhoun\textsuperscript{1} and K. M.
Simpson\textsuperscript{2})

Radioelectrochemical methods can be very
useful in studies of the chemical behavior of
actinides in media which emulate solutions of
environmental interest, because experiments
with radiocoulometry and radiopolarography can
often be carried out at very low concentrations
and at potentials considerably more negative
than the hydrogen wave at -1.5 V vs SCE. As
reported previously\textsuperscript{3}, the relatively large
cathode areas used in radiocoulometry lead to
consumption of hydrogen ions such that control
of the pH becomes difficult. Because many of
the actinide systems of interest are expected
to require determination of electrochemical
waves at negative potentials, it was decided to
evaluate the use of radiopolarography, since it
was assumed that, although the hydrogen ion
countentration might be altered on a microscopic
scale near a dropping mercury electrode, the pH
of the bulk solution would not change very
rapidly.

The radiopolarograph shown in Fig. 6.14
resembles the design of a microcell used to
study the electrochemistry of mendelevium\textsuperscript{4},
except that the new cell has a larger, more
convenient volume of about 3.8 mL, which makes
it more practical for routine use. The cell is
arranged to function with a commercial
Fig. 6.14. Apparatus for radiopolarography. Potentiostat in a three-electrode configuration. A liquid jacket has been provided for precise temperature control. An unusual feature of the design is that the mercury drops are allowed to fall through the aqueous interface into air. The aqueous solution is suspended in the cell by slightly lowering the pressure over the solution. The reduction in pressure is achieved by allowing water to drain from the reservoir shown at the right of Fig. 6.14 and then adjusting the pressure in the polarographic cell with the vernier stopcocks. The thin aqueous film carried away with the mercury drops was removed by causing the drops to spiral down a filter paper cone into collection tubes.

Radiopolarograms equivalent to current-voltage curves are obtained by plotting the radioactivity collected in the mercury per unit time of electrolysis against the applied potential. Preliminary tests of the equipment used tracer concentrations of $^{154}$Eu and $^{54}$Mn in noncomplexing media to study the reduction to the amalgam state of Eu(II) ($E_{1/2} = 1.95$ V vs SCE) and Mn(II) ($E_{1/2} = -1.48$ V vs SCE). Values of the half-wave potential obtained were in agreement with previous work. The use of the filter-paper cone for removing the aqueous phase from the drops was found to be very effective, as the counting rates for potentials more positive than the onset of the wave were typically only about 1-2% of the counting rates at the diffusion-controlled part of the wave.

As a test of the method with solutions of environmental interest, we have begun a study of complexation of Mn(II) by carbonate ion at near-neutral values of pH. The polarographic wave for reduction of Mn(II) is quasireversible and has been widely studied in noncomplexing media. However, little is known of the carbonate complexation of Mn(II). We determined shifts in the Mn(II) half-wave potential at $25^\circ$ C for a series of solutions of NaHCO$_3$ and NaClO$_4$ at a pH of 7.9 and an ionic strength of 1.0. Concentrations of species and the ionic strength were calculated with the aid of the computer program CARBEX. Reversible half-wave potentials were determined by the method of Gellings. The shifts in half-wave potential were analyzed by the technique of DeFord and Hume, as modified by Irving.

Overall formation constants were derived for two complexes, believed to be the mono and bis carbonate complexes of Mn(II). The overall formation constant of the dominant complex, bis carbonate manganese(II), $\text{Mn(CO}_3\text{)}^2^-$, is given by $\log \beta = 4.9 \pm 0.04$, while that of the mono carbonate complex, $\text{MnCO}_3^+$, is given by $\log \beta = 2.2 \pm 0.4$. Additional studies in progress will focus on measurements of half-wave potentials as a function of pH and over a greater range of ligand concentration.

1. Lebanese University, Beirut, Lebanon.
2. Student research Participant, Murray State University, Murray, Kentucky.
5. EG&G Princeton Applied Research, Model 1730.
6.2.9 Electrochemical and Spectroscopic Studies of Less Stable Oxidation States of Transuranium Elements in Aqueous Carbonate-Bicarbonate Media


Actinide ions exhibit interesting properties in aqueous carbonate solutions which are quite different from those exhibited in acidic solutions. Oxidation states which are unstable in acid solutions may be quite stable in carbonate solutions. Complexation by carbonate ligands can cause significant shifts in the formal potentials of actinide redox couples and can effect dramatic changes in the solution absorption spectra of these ions. The spectra and redox properties of the lighter actinides (U-Pu) have been largely investigated but are by no means complete. Although carbonate solutions have been used extensively for americium-curium separations, it has only been recently that more complete studies of the various oxidation states of Am in this medium have been made.5-7 Reports on Bk in carbonate solution are scarce and virtually no data are available for Cm, Cf, and Es in this medium. The behavior of these heavier members of the actinide series cannot be predicted with certainty from that of the lighter members of the series and, therefore, direct studies of the transamerucium elements in carbonate media are required to provide a more complete description of these ions in aqueous solution.

Multimilligram quantities of $^{237}$Np, $^{248}$Cm and $^{249}$Cf were received as air dried chloride salts and were converted to the hydroxides. The actinide hydroxide precipitates were washed and dissolved in 1-2 M Na$_2$CO$_3$ or 2-5.5 M K$_2$CO$_3$ for spectroscopic and electrochemical studies.

Investigation of the higher oxidation state redox couples of neptunium has continued.8 The Np(VI)/Np(V) couple in 2 M Na$_2$CO$_3$ was studied at higher pH values (12 to 14). As the pH increased, the formal potential of the couple shifted more than 200 mV to near 0 V/SCE at pH 14. Changes in the absorption spectrum of Np(V) in 2 M Na$_2$CO$_3$ with pH were also observed. The peak at 990 nm was noted to increase with increasing pH (12-14). A similar phenomenon was noted by Wester and Sullivan9 in bicarbonate solutions as the pH was lowered. The reduction of Np(V) at a mercury pool cathode in 2 M Na$_2$CO$_3$ at pH 13 results in an Np(IV) solid of unknown composition (probably Np(OH)$_4$). Attempts to study Np(III) in sodium carbonate media have been partially successful by observing unidentified spectral bands which disappear with time to give a pure Np(IV) spectrum when Np(III) in HCl was introduced into carbonate solution which had been purged of oxygen. This work is continuing as are attempts to obtain the Raman spectrum of pure Np(VII) in carbonate solution.

The solution absorption spectrum of trivalent curium in carbonate solution has been recorded and is quite similar to that in noncomplexing perchlorate medium.10 The spectrum of trivalent californium in carbonate solution, shown in Fig. 6.15, is somewhat different from that of Cf(III) in DCIO$_4$.11 The absorption bands are in the same wavelength regions, but their relative intensities and bandwidths are different, suggesting that Cf(III) is complexed by carbonate ligands.

Attempts to oxidize Cm(III) and Cf(III) in carbonate-bicarbonate solutions have been to
date unsuccessful. The pH and concentration of the carbonate-bicarbonate solutions were varied in hopes of finding the proper conditions for stabilization of these higher oxidation states.

It is, of course, the "difference" in the carbonate ion complexation of the An(III) and An(IV) ions which could produce a significant decrease in the potential of the couple. If the difference in carbonate ion complexation is not as great as that found for Am(IV) and Am(III), for example, then the potential shift may not be sufficient to allow for stability of Cf(IV) or Cm(IV) in aqueous carbonate media. It is also possible that we have failed to employ an oxidizing agent powerful enough to generate Cf(IV) or Cm(IV) in the carbonate solution, even if the An(IV) species have a limited lifetime in this medium.

Studies involving the exploitation of complexing aqueous media to alter the oxidation-reduction potentials of higher oxidation state actinide couples will be continued. Additional work on Cm(III) and Cf(III) oxidation in both carbonate and hydroxide media may provide information on the optimum conditions for stabilization of higher oxidation states of these elements.

Fig. 6.15. Solution absorption spectrum of californium(III) in 2 M sodium carbonate solution.

6.2.10 Spectroscopy and Electrochemistry of Selected Lanthanides in Molten Dimethyl Sulfone

(P. G. Varlashkin, J. R. Peterson)

Electrochemical and spectroscopic studies of some lanthanide salts in molten dimethyl sulfone (DMSO$_2$) at 400 K have been carried out as precursor investigations for anticipated actinide studies in DMSO$_2$. DMSO$_2$ is highly polar, but is a poorly co-ordinating solvent. Due to the wider electrochemical range of this solvent than that of water, DMSO$_2$ was chosen as a nonaqueous solvent for studies of both lower and higher oxidation states of the actinides.

Absorption spectra of EuCl$_3$·6H$_2$O, YbCl$_3$·6H$_2$O, and SmCl$_3$·6H$_2$O dissolved in DMSO$_2$ were recorded using a Cary 14
spectrophotometer equipped with a resistively heated sample cell as supplied by Cary for obtaining spectra of solutions at elevated temperatures. The striking differences between the DMSO$_2$ and aqueous spectra of Eu(III), Yb(III), and Sm(III) lie in the UV region. In aqueous solutions, Eu(III) and Sm(III) show only weak f-f bands in the UV, and Yb(III) shows a weak broad-band absorbance in the UV. In DMSO$_2$, Eu(III) shows two large UV absorption bands centered at 250 and 288 nm. Both Sm(III) and Yb(III) exhibit steeply rising absorption bands with UV cutoffs around 240 and 210 nm for Yb(III) and Sm(III), respectively.

Europium(II) was prepared by electrochemical reduction of Eu(III), as described below. Noticeable differences in the aqueous and DMSO$_2$ spectra exist for Eu(II). Europium(II) in aqueous solution has two broad-band absorption peaks centered at 240 and 320 nm, which do not appear in the Eu(II) in DMSO$_2$ spectrum. In water, Eu(III) is colorless and Eu(II) is pale yellow, but in DMSO$_2$, the reverse is true. The reasons behind these dramatic differences are unknown, but one factor may be the poor co-ordinating properties of DMSO$_2$ allowing for increased interaction between the lanthanide cations and the chloride ligands. Additional spectroscopic work with anhydrous divalent halides of Yb and Sm are in progress to help understand the differences seen in Eu(II).

Cyclic voltammograms of the Ln(III)/Ln(II) couple in DMSO$_2$ for Eu, Yb, and Sm were determined in an electrochemical cell wrapped with nichrome wire for resistive heating. The reference electrode consisted of a Pt wire in a fitted glass tube filled with the supporting electrolyte, tetrabutylammonium perchlorate. The formal potentials of the Ln(III)/Ln(II) couples in DMSO$_2$ as determined by cyclic voltammetry are -0.36 ± 0.05 V, -1.07 ± 0.01 V, and -1.61 ± 0.05 V for Eu, Yb, and Sm, respectively. The larger errors for Eu and Sm are due to the poorly defined anodic peaks of these couples. To date, only Eu(II) has been electrochemically generated in DMSO$_2$ at a Hg pool electrode. Bulk reduction at potentials more negative than -1.1 V vs a Pt reference has not been achieved. The inability to do bulk electrolysis in DMSO$_2$ at large negative potentials seems to be unrelated to the species in solution and may be due to some complex solvent-electrode interaction.

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6.2.11 Electrodeposition of Np(V) on Noble Metal Electrodes
(L. Maya)

Deposition of neptunium on electrodes was detected in the course of electrochemical conversions of the Np(V)/Np(VI) couple in perchlorate media in the presence of carbonate ions. A study was undertaken to characterize the electrodeposited films by chemical and spectroscopic means. Particularly attractive was the possibility of observing surface enhanced Raman scattering of the sorbed neptunium species. This is a phenomenon observed with organic species, e.g., pyridine on silver whereby the scattering factors of the sorbed species are enhanced by factors of up to $10^6$. The spectroscopic observations failed to detect enhanced scattering but gave indications of chemical interactions between the substrate and the sorbed species. It was found that the species sorbed into the noble metal electrodes was NaNpO$_2$CO$_3$. The oxidation state of the sorbed species was established on the basis of electrochemical measurements, while the presence of carbonate was detected by Raman spectroscopy.

The deposition of neptunium films, generated while reducing Np(VI), was dependent on the composition of the initial solutions. Sorption occurred when the resulting Np(V) and carbonate concentrations exceeded the solubility of NaNpO$_2$CO$_3$; while this behavior could be anticipated, the strength of adhesion could not. This allowed for rinsing and soaking of the electrodes in neutral electrolyte without loss of the films. Similarly, the films are
preserved through electrochemical cycling from -1.1 to +0.8 volts. This last characteristic suggests that it would be possible to enclose the neptunium films by an additional coat of an electrodeposited noble metal film.

6.2.12 Sorted Uranium(VI) Species on Hydrous Titania, Zirconia and Silica Gel

(L. Maya)

This study was undertaken in order to resolve inconsistencies in the literature regarding the sorption mechanism of uranyl tricarbonate onto hydrous titania, which is, additionally, of relevance to the recovery of uranium from seawater. The inconsistencies in the literature relate to the number of carbonate ligands assumed to be associated with the sorbed uranium species. The use of uranyl dicarbonate and uranyl hemi-carbonate in addition to the bicarbonate provided additional insight into the sorption mechanism. In addition to titania, zirconia and silica gel were also examined. The experimental approach involved characterization of the sorbed species by direct analytical methods, Raman spectroscopy and x-ray diffraction. It was found that, in the case of titania, a common sorbed species lacking carbonate ligands was formed irrespective of the starting uranyl carbonate complex. Similar results were obtained in the case of zirconia and silica gel. The sorption mechanism appears to involve displacement of the carbonate ligands to yield a uranyl species directly attached to the substrate through oxygen bridges. The $\nu_{\text{UO}_2}$ stretching frequency of the sorbed species suggested considerable electron density transfer from the substrate into the metal thus weakening the axial $\text{UO}_2^-$ bonds.

The results of this study are also very relevant to the fate of actinides in the environment because they indicate that complex anionic species which could not be retained by cation exchange mechanisms on clays can nevertheless be retained through reactions with hydrous oxides which are also pervasive components in nature.

6.2.13 Sorption Isotherms for Np and Eu on Various Geological Materials

(R. E. Meyer, W. O. Arnold, F. L. Case)

Studies of adsorption behavior on geological materials of nuclides of interest to nuclear waste are necessary to aid in estimation of the rates of transport of these nuclides through geological formations. Most release scenarios postulate penetration of the repository by the natural groundwater which then is assumed to follow a path through the host geological formation to the accessible environment. Sorption isotherms of the nuclides are incorporated into the mathematical codes used to estimate these rates of transport. Clay minerals and hydrous oxides are ubiquitous components of the formations of interest to nuclear waste, and they can be obtained or prepared in relatively pure forms. Also, they have fairly high sorption capacities and are, therefore, likely to dominate the properties of the geological formations in which they are present. For these reasons, we have concentrated our experiments on these two classes of sorbents. The task of determination of sorption isotherms for the many different conditions found in natural formations would be considerably simplified if it could be shown that fairly consistent patterns of sorption are observed. This might then allow the development of sorption models which could be used for the prediction of behavior for those conditions not explicitly tested in the laboratory. We have, therefore, systematically investigated the adsorption behavior of ions of Cs(I), Sr(II), Eu(III), Np(V), U(VI), and Tc(VII) with clay minerals and hydrous oxides. In these investigations, experiments were completed for a wide range of pH, solution compositions, and concentrations of the nuclide. In this report, we present new results for sorption of Eu(III) and Np(V).

Adsorption of Eu(III). Adsorption on layer-type clay minerals such as montmorillonite can be described fairly well by ordinary ion exchange equilibria for sorption of monovalent and divalent ions. However, adsorption
behavior for Eu(III), a typical trivalent ion, generally cannot be described by simple ion exchange equilibria. The main features of sorption of Eu(III) on montmorillonite are shown in Fig. 6.16, where distribution coefficients (D) are given as a function of pH and concentration of NaCl. [The distribution coefficient is defined as the concentration of the nuclide on the sorbent (moles/kg) divided by the concentration of the nuclide in the solution (moles/L).] At low pH, there is a fairly significant effect of the concentration of NaCl, and at constant pH, the distribution coefficient decreases as the salt concentration increases, behavior which is typical of ideal ion exchange. However, as the pH is increased, the distribution coefficient increases sharply, and there is considerably less sensitivity to the concentration of NaCl. We have observed this type of behavior also for sorption of Eu(III) on natural oxides.

This type of behavior can be explained if isotherms derived from ideal ion exchange behavior are combined with those observed for sorption on hydrous oxides. Using such combined isotherms, and assuming reasonable values for the various parameters necessary to describe the isotherms, we derived the combined overall isotherms shown in Fig. 6.17. The shapes of the isotherms shown in Figs. 6.17 and 6.16 are quite similar. Because montmorillonite has a fairly large number of sorbing groups that behave as hydrous oxides, it can be considered to be a mixture of a small amount of oxides and a clay mineral. The sharp rise of distribution coefficient with pH shown in Fig. 6.17 suggests that these oxide groups are dominating the sorption of Eu(III) at pH>5.

Adsorption of Np(V). In the absence of complexing agents, Np(V) normally exists as the neptunyl ion, NpO_2^+. In the pH range 4-8 of many natural groundwaters. Because this ion is
a large, singly charged ion, we might expect it to be adsorbed only weakly on most adsorbents. Also, we would expect from theory, and from the behavior of Cs(I), that with a pure hydrous oxide, a plot of log $D$ vs pH would have a slope of about 0.5 in this pH range. In Fig. 6.18, data are shown for adsorption of Np(V) on alumina from 0.1 M NaCl. In the pH range 4.5 to about 6.5 it is difficult to estimate the slope of log $D$ vs pH, but roughly it is on the order of 0.5 to 0.75. However, as the pH is increased above pH 6.5, the distribution coefficient increases at a greater rate, with a slope of log $D$ vs pH somewhat greater than one. Distribution coefficients are quite high at these intermediate pH levels, and it is evident that alumina is a very effective adsorbent for Np(V). In these experiments, electrochemical techniques were used to insure that Np(V) was not reduced to a lower, more adsorbing valence state. These techniques are described in Section 12.2.3 of this report.

Fig. 6.18. Adsorption of NP(V) on alumina. Recirculating column method, 0.1 M NaCl. 1x10^{-12}$ M Np-235. Circles, pH increasing; diamonds, decreasing; triangles, pH increasing; squares, decreasing.

7. SEPARATIONS CHEMISTRY

The purpose of the research described in this section is to obtain basic information about separation methods and processes that may lead to improved recovery, handling, and disposition of energy-related materials. Studies of solvent extraction continue to emphasize organophosphorous extractants used for the recovery of uranium. Structures have been determined by x-ray diffraction of two additional crystalline complexes formed by such reagents (Sects. 7.1 and 7.2) and for a crown-ether complex of uranium (VI) (Sect. 7.3). The information thus obtained has been useful in the design of new extractants (Sect. 7.4) for testing. The Chemistry of a commercial process developed at ORNL for the recovery of uranium from phosphoric acid has been studied in further detail as a means of improving its efficiency (Sect. 7.5). Studies of activated carbon filled with hydrous oxides have indicated the potential value of such a material for the chromatographic separation of aqueous ions (Sect. 7.6). Finally, various high-temperature two-liquid phase systems have been investigated for separating radioactive ruthenium from spent nuclear-fuels, for the purpose of recovering the non-radioactive palladium and rhodium daughter products (Sect. 7.7).

7.1 Crystal and Molecular Structure of Uranyl Bis(di-n-butylphosphate)

(J. H. Burns)

A structure determination by x-ray diffraction has been completed for crystals of \( \text{UO}_2(\text{DBP})_2 \), in which DBP = di-n-butylphosphate. This was done to increase our understanding of the mechanism by which the acid extractant HDBP, alone and in synergistic combination with neutral tri-n-butylphosphine oxide (TBPO), extracts the uranyl ion from an aqueous nitrate solution into an organic phase. Crystals of the complex are triclinic, \( \text{P}_{\text{1}} \), with \( a = 8.402(6) \text{Å}, b = 15.648(9) \text{Å}, c = 5.385(3) \text{Å}, \alpha = 99.46(4)^\circ, \beta = 98.51(4)^\circ \) and \( \gamma = 10.44(3)^\circ \); there is one formula weight in the unit cell.

Because of the high viscosity of solutions of \( \text{UO}_2(\text{DBP})_2 \) in benzene, it was previously surmised\(^1\) that this complex is a polymer and a structure was proposed for it. In this model the uranyl ions are linked by shared phosphate \( \text{O} \) atoms to form chains. The structural analysis of \( \text{UO}_2(\text{DBP})_2 \) has shown the proposal to be essentially correct and able to account for the viscosity, yet the actual polymer differs in significant details from the proposed one. In the solid, pictured in Figure 7.1, the uranyl ions are indeed doubly bridged by DBP molecules to form chains; but no single \( \text{O} \) atom is shared by two \( \text{U} \) atoms as proposed. In fact the equatorial coordination number of each uranyl ion is only four. Through this arrangement electroneutrality is achieved, each metal atom is surrounded by a hydrophobic coating of hydrocarbon groups, and the chains are held only weakly to each other. A structure of the type found here was proposed earlier\(^2\) to explain the high viscosity of the...
analogous complex with di-(2-ethylhexyl)phosphoric acid.

By comparison of the present structure with that obtained\textsuperscript{3} when a mixture of HDBP and TBPO are used to extract uranyl nitrate, some insight can be gained into the role played by structure in synergistic extraction in this case. The complex formed with the mixture is a dimer having the formula \([\text{UO}_2(\text{DBP})(\text{TBPO})\text{NO}_3]_2\). In this molecule the uranyl ions are doubly bridged exactly as in \(\text{UO}_2(\text{DBP})_2\), but instead of the chain continuing, it is terminated by a TBPO molecule and a nitrate ion. This suggests that the TBPO molecule helps fill the coordination needs of the U atom, interferes with polymer formation, and thereby produces a more extractable species.


7.2 X-ray and Neutron Diffraction Analysis of the Structure of Uranyl Bis(tri-n-butylphosphate) Nitrate

(J. H. Burns, George M. Brown)

In examining the effect of structure on the solvent extraction of uranium it is desirable to include complexes of tri-n-butylphosphate (TBP), one of the most frequently used extractants. Although TBP readily extracts the uranyl ion from nitrate solutions, the complex formed has a m.p. of -6°C.\textsuperscript{1} The analogous compound with tri-i-butylphosphate (TIBP) is solid at room temperature and grows easily into crystals several mm in diameter. With these large specimens it was possible to study \(\text{UO}_2(\text{TBP})_2(\text{NO}_3)_2\) by neutron as well as by x-ray diffraction.

Crystals of this complex are triclinic, \(\overline{1}\), and contain one centrosymmetric molecule in the unit cell: \(a = 11.690(2)\text{\AA}, b = 9.960(1)\text{\AA}, c = 9.241(2)\text{\AA}, \alpha = 101.44(2)^\circ, \beta = 98.67(1)^\circ,\) and \(\gamma = 100.02(1)^\circ\). Determination of the structure verified the stoichiometry which had been deduced from solution measurements\textsuperscript{1,2} and provided the details of molecular geometry (Figure 7.2). The configuration found is ubiquitous among complexes having the formula \(\text{UO}_2(\text{NO}_3)_2\), in which L represents a variety of neutral organophosphorus ligands.\textsuperscript{3-5} Two bidentate nitrate ions plus two phosphoryl O atoms occupy six coordination sites around the equator of the linear O=U=O ion. The P=O---U distance (2.39Å) is shorter and the bond presumably stronger than the H_2O---U distance (2.45Å) in the hydrates of uranyl nitrate, which have the same molecular geometry. This agrees with the fact that the more basic phosphoryl O atom displaces water in the uranyl coordination.

There is considerable thermal motion of the atoms of the butyl groups; it is especially large at the ends of the groups away from their attachments to the phosphate group.
Because of this thermal motion and possible disorder in this part of the structure the structural refinement is not yet complete.


7.3 Crystal Structure of Uranyl(12-crown-4) Nitrate Dihydrate

(P. L. Ritger,^1 J. H. Burns)

Macro cyclic polyethers (crown ethers) form inclusion complexes with many ions ranging from Na^+ to UO_2^{2+}; hence they have been investigated as possible extraction reagents. Of particular interest initially was the possible complexation of the UO_2^{2+} ion by crown ethers; but as a number of structures involving this combination were analyzed, it was found that none of them had the UO_2^{2+} ion inserted into the crown - with one exception, the complex with 12-crown-4. Because of the small size of this ring and for several other reasons, this reported structure appeared to be erroneous; and since the answer to whether complexation occurs is rather important, we carried out a redetermination of this structure. Crystals were prepared in the same way as published; the monoclinic unit-cell dimensions found are nearly identical to the reported values, thus verifying the identity of the substances. Our values are a = 9.064(2) Å, b = 14.366(4) Å, c = 6.765(1) Å, β = 99.64(1)°; space group P2_1/c, Z = 2.

Our structure analysis by x-ray diffraction showed that the uranyl ion in UO_2(NO_3)_2-12-crown-4-4H_2O is not in the crown or in any way directly bonded to it. Instead, the linear UO_2^{2+} ion is equatorially coordinated by two bidentate NO_3^- ions and by two H_2O molecules, Figure 7.3. Each of the H_2O molecules forms hydrogen bonds to O atoms of adjacent crown ether molecules, forming a hydrogen-bonded network perpendicular to the b axis of the crystal. Thus it is seen that the existence of this compound is not due to complexation by the crown ether, but, as in the cases of 18-crown-6 and benzo-15-crown-5, merely results from hydrogen bonding by coordinated water.

1. GLCA/LCM student from Lawrence University, Appleton, WI.

Fig. 7.3. A portion of the crystal structure of UO_2(NO_3)_2-12-Crown-4-4H_2O showing one UO_2(NO_3)_2(H_2O)_2 molecule and its H-bonded neighbors.
7.4 The Design of Improved Solvent Extraction Reagents
(C. F. Baes, Jr., W. R. Busing, L. O. Gilpatrick)

The extraction of a metal ion from an aqueous solution into an organic solvent generally requires that three conditions be met: The charge on the ion must be neutralized, its coordination number must be satisfied by appropriate donor ligands, and the resulting extraction complex must be surrounded by hydrocarbons so that it will dissolve in the organic solvent.

These three conditions are generally provided by more than one extractant molecule, sometimes in synergistic combinations and sometimes accompanied by the extraction of inorganic anions to neutralize the cation charge. Since the extractant is usually a polar molecule, it can be polymeric in the organic diluent and/or it can interact with other reagents that are present. The extraction product formed can also be polymeric. In short, the three conditions needed for extraction often produce considerable chemical complexity. As a consequence, to understand in detail the chemistry of even a simple solvent-extraction process can require a considerable effort, and detailed characterization of more involved systems is often beyond the power of present experimental methods.

To minimize the complications in solvent extraction chemistry, we are presently endeavoring to design and synthesize extractants that provide charge neutralization, the coordinating ligands, and the organic covering for the cation all in a single molecule. For our first such reagent we have selected a cyclic alkylphosphoric acid:

\[
\begin{array}{cccccccc}
H & H & H & H \\
0 & 0 & 0 & 0 \\
P \rightarrow O \rightarrow O \rightarrow P \rightarrow O \rightarrow O \rightarrow O \\
0 & 0 & 0 & 0
\end{array}
\]

By use of a computer-graphics program written by one of us (WRB), we concluded that if the alkyl groups are n-propyl, the four phosphate groups could be arranged about a U\(^{4+}\) ion in such a way that eight oxygen atoms surround it at appropriate distances in a dodecahedral arrangement (Fig. 7.4). Through the loss of the four hydrogen ions, this central UO\(_4\) group would have a net charge of zero. The resulting structure could be a stable extraction product.

Fig. 7.4. Proposed structure for a complex salt that might be formed between U\(^{4+}\) and a cyclic tetra-propyl-tetraphosphate anion \([-R-O-P(0)-O-]_4^{4+}\). The central UO\(_4\) group is dodecahedral.
formed by such a reagent, a reagent that would be specific for tetravalent actinide cations (i.e. Th⁴⁺, Pa⁴⁺, U⁴⁺, Np⁴⁺, Pu⁴⁺).

We are now attempting to prepare this reagent, with the use of Th⁴⁺ or U⁴⁺ ion to act as a template in the synthesis. If we can form a uranium or thorium salt of the tetraprotic acid, we will attempt to verify its structure by x-ray diffraction and study the properties of the acid as an extraction reagent. It may be necessary to add side chains to the propyl groups to enhance the solubility of the salt in organic solvents. After appropriate modification we will test this reagent type for its selectivity as an extractant for tetravalent actinide ions.

7.5 Equilibrium and Kinetic Studies of the Reductive Strip of Uranium from DEPA-TOPO Reagent into Aqueous Phosphoric Acid

F. J. Kost

At the present time five uranium recovery plants in the U.S. are recovering an estimated 1500 tons of U₃O₈ per year using the DEPA-TOPO process developed at ORNL. Three operating plants, two of which used other recovery processes, have closed because of technical problems coupled with poor market conditions. Feedback from all of the plants have indicated a number of unexpected operating problems, and indicated a definite need for a better understanding of the basic chemistry and mechanisms involved in the process.

We discovered last year that one of these problems was due to a very high solubility of oxygen in the solvent. This year we have addressed another problem area which involves the reductive strip step. Our major goal is to make this process more efficient and more economical in order to increase the attractiveness of recovery in smaller plants where another 3000 tons of U₃O₈ per year passes through unrecovered. At current market conditions, the value of this uranium is about 130 million dollars.

7.5.1 Interphase Transfer Kinetics of Uranium Rate constants for the interphase transfer of U(VI) between typical DEPA-TOPO extractant (0.5 M DEPA-0.125 M TOPO-H₂SO₄) and 5 to 10 M phosphoric acid solutions have been measured in a baffled mixer with a fixed interface (Lewis cell) over the temperature range of 25-50°C. Most of the data were obtained for the transfer of U(VI) from the solvent to the acid since our primary aim in this study is stripping, and such information is necessary for understanding and predicting behavior during the reductive strip. The rates of uranium extraction and stripping are rapid and first order with respect to uranium concentration and, as expected, the forward rate constant, k₁, divided by the reverse rate constant, k₂, is equal to the equilibrium constant, D. In a plot of log k₁ (organic-to-aqueous transfer) vs H₃PO₄ concentration at 50°C, k₁ increased linearly from 7.8 x 10⁻³ cm/min in 5 M H₃PO₄ to 2.6 x 10⁻² cm/min in 10 M H₃PO₄. The data may be represented by

$$\log k₁ = 0.1034[H₃PO₄] - 2.625. \quad (50°C)$$

An Arrhenius plot of log k₁ vs reciprocal temperature is also linear and indicates that k₁ doubles for each 10° rise in temperature. For example, in 6 M H₃PO₄ k₁ increased from 2.7 x 10⁻³ cm/min at 30°C to 1.0 x 10⁻² cm/min at 50°C. The data may be represented by

$$\log k₁ = -2796 \frac{1}{T} + 6.66.$$  

The activation energy, δEₐ, calculated by means of the Arrhenius' equation was 13.9 kcal/mole, which indicates that the rate-controlling step is an exchange reaction rather than diffusion.

The values of k₂ (aqueous to organic transfer) measured in this study are in excellent agreement with those measured by Ryon, et al. in the Dapex (DEPA-TBP-H₂SO₄) system, and are about a factor of two lower.
than those measured by Horner, et al. in a fuel reprocessing system (3.5 M HNO₃ - 30% TBP).³

7.5.2 Equilibrium and Rate Measurements of Uranium(VI) Reduction by Iron(III)

Equilibrium Studies. The key step in the DEPA-TOPO process is the reductive strip, which is based on the reaction:

\[ 2\text{Fe(II)} + \text{U(VI)} = 2\text{Fe(III)} + \text{U(IV)} \]  

In 1956, Baes⁵ reported that the equilibrium quotient \( K \), where

\[ K = \frac{[\text{Fe(III)}]^2[\text{U(IV)}]}{[\text{Fe(II)}][\text{U(VI)}]} \]

varied directly in proportion to about the eighth power of the \( H₃P₀₄ \) concentration in the range of 1.8 to 4.8 molar. His value of \( K \) for 4.8 M \( H₃P₀₄ \) was 173. We have extended Baes' data to 7 M \( H₃P₀₄ \), in order to cover the 5 to 7 molar range of commercial interest and have found that the eight power dependence obtains through this range, with \( K \) reaching over 150,000 in 7 molar \( H₃P₀₄ \).

Baes also showed that both the value of \( K \) and the rate of the reduction are strongly influenced by the presence of fluoride (which is normally present in wet-process \( H₃P₀₄ \)). In 3.7 M \( H₃P₀₄ \), Baes' value of \( K \) increased from 13 to 300,000 as the fluoride concentration was increased from 0 to 0.8 M. In the new tests, which were made in 5 M \( H₃P₀₄ \), the value of \( K \) increased from about 500 to 10,000 as the fluoride concentration was increased from 0 to 0.16 M. In both cases, the slope of the linear plots of \( \log K \) vs fluoride concentration is about eight. All of these tests were made in pure \( H₃P₀₄ \), under conditions where the free \( F^- \) concentration (uncomplexed with iron and uranium) was much higher than might be expected in wet-process acid which contains much higher amounts of elements such as aluminum and silica which can tie up the fluoride ion very strongly. Kinetic studies described below show that the free fluoride ion rather than total fluoride is the active ingredient that increases the reduction rate.

In tests with fluoride present, it was observed that the height of the major \( U(IV) \) absorption peaks, which occur at 621 and 660 nm, changed significantly so that peak height could no longer be used as a measure of uranium(IV) concentration. This change in absorption spectra is a strong indication that fluoride reacts with the \( U(IV) \) as it is formed, and helps explain, not only the catalytic effect of \( F^- \), but also the increase in the equilibrium quotient. Because of the importance of this variable, and its complexity, a more detailed investigation into the mechanism of its interaction is warranted.

Rate Studies. The rate of uranium reduction was determined by mixing solutions of uranyl phosphate and ferrous phosphate in a cell in a spectrophotometer (Hitachi 100-80AH or a Durram stop-flow model with an oscilloscope readout), and recording the rate of change in absorbance at 660 nm with time. The molar absorptivity for \( U(IV) \) at this wavelength is 38.2. Plots of \( \log (A_A - A_T) \) vs time were linear indicating that the reaction (Eq. 1) is first-order with respect to uranium. Rate constants were calculated from data extending over at least three half-lives.

Rate data were obtained in 5 to 10 M \( H₃P₀₄ \) solutions containing 0.001 to 0.25 M \( \text{Fe(II)} \) (added as \( \text{FeS}_2O₄ \)) and 0.001 to 0.01 M \( U(VI) \) over a temperature range of 25 to 60°C. In some of the tests, \( HF, H₂S₂O₄, \text{Fe(III)}, \text{Al}, \) and active \( Si \) were added to study the effect of complexing on the rate.

The rate constant, \( k_2 \), was strongly dependent on the concentration of \( \text{Fe(II)}, H₃P₀₄, \) free \( F^- \), and temperature. For example, in the 5 to 10 molar \( H₃P₀₄ \) solutions tested, \( k_2 \) increased by a factor of 2 as the \( \text{Fe(II)} \) concentration was doubled (Fig. 7.5). In tests where the \( \text{Fe(II)} \) concentration was held constant at 0.05 M (10 times the uranium concentration so that the reverse reaction would be negligible), \( k_2 \) increased by a factor of about 100 as the \( H₃P₀₄ \) concentration was increased from 5 to 10
Fig. 7.5. The effect of Fe(II) concentration on the rate of reduction of U(VI) to U(IV) in 5 to 10 molar H₃PO₄ at ~27°C.

Thus, at room temperature $k_2$ increased from 0.086 to 8.4 min⁻¹, and at 50°C, from about 0.8 to 84 min⁻¹. Equations obtained by linear regression analysis of the data are

$$\log k_2 = 0.3935[H_3PO_4] - 3.021 \quad \text{~25°C}$$
$$\log k_2 = 0.4022[H_3PO_4] - 2.114 \quad \text{~50°C}$$

An Arrhenius plot of the data obtained in 5 to 10 molar H₃PO₄ containing 0.05 molar Fe(II) shows that $k_2$ increased by a factor of about 2.5 for each ten degree rise in temperature (Fig. 7.6). The activation energy is about 13.7 kcal/mole.

7.5.3 Uranium(IV) Extraction

We have measured U(IV) extraction coefficients for typical 0.5 M DEPA-0.125 M TBP extractant with 5, 6, and 7 M H₃PO₄ solutions at temperatures of 30, 40, and 50°C. All of the solutions were sparged with argon and the system was purged with argon to completely remove oxygen. The data show that the coefficients decrease by a factor of about 2.5 as the H₃PO₄ concentration was increased from 5 to 7 molar for all temperatures tested (Fig. 7.7) and by a factor of about 1.4 for each 10° rise in temperature. Under the most stringent conditions tested, i.e. 7 M H₃PO₄ at 50°C, the U(IV) extraction coefficient was 0.009. In this process, where the extraction coefficient for U(VI) is marginal (e.g., ~3 to 5), and the concentration of U(IV) is allowed to build-up to the range of 10 to 20 g/L in
the aqueous strip solution, it is desirable to operate under conditions where the extraction of U(IV) is minimal (e.g. $E_{a}^{*} < 0.005$). Otherwise, extracted U(IV) will be recycled to the extractor and reduce extraction efficiency. According to these measurements we would need to increase the strip acid to 8.2 M or greater for maximum efficiency. In a plant, this could be done by using evaporated or merchant grade acid rather than raffinate.

7.5.4 A Model of the Reductive Strip System

Typically, the strip system consists of three countercurrent mixer-setter stages operated at about 50°C. The DEPA-TOPO extract containing about 0.3 g U(VI)/L (≈0.0015 molar), is contacted in the first mixer with a very small volume (1/35 to 1/50 of the solvent flow) of advancing 5 to 6 molar phosphoric acid strip solution containing Fe(II) in order to reductively strip the uranium and concentrate it to 10 to 15 g/L. This large disparity in flow rates necessitates a rather large internal recycle of the aqueous phase from each settler to each mixer in order to achieve efficient mixing of the solutions and stripping of the uranium. In a 3-stage system, removal of 75% of the uranium per stage is sufficient to remove over 99% of the uranium from the solvent.

There has been a considerable amount of controversy over how much phosphoric acid should be recycled. In our original papers, we suggested a recycle ratio of $2^{10}$ using at least 6 molar H$_3$PO$_4$, but most plants have opted to use ratios of only $1^{15}$ or $1^{30}$, because they felt they could get by with smaller, less expensive equipment. We feel that insufficient aqueous recycle, coupled with the lower concentration of H$_3$PO$_4$ (5 to 5.5 molar) produced by the phosphate industry during the past few years has contributed to some of the problems they have experienced.

The primary purpose of our model is to optimize the recycle ratio with retention time in the mixer in order to maximize stripping efficiency while minimizing equipment size and solvent inventory.

By incorporating the rate constants and stripping coefficients into a material balance around a single mixer, we have derived the following equation to describe the system:

$$\frac{c_1}{c_2} = 1 + S[F + kt(F+R) - R]$$

(2)

$c_1$ and $c_2$ are the concentrations of uranium entering and exiting the mixer, respectively, $S$ is the stripping coefficient [reciprocal of the extraction coefficient for U(VI)], $F$ is the volume flow ratio of acid to solvent, $R$ is the recycle ratio of acid to solvent, $t$ is the retention time in the mixer, and $k$ is the controlling rate constant.

Actually, two rate steps are involved: (1) the transfer of U(VI) from the solvent to the acid $\text{A} \rightarrow \text{B}$, and (2) the reduction of U(VI) to U(IV) with Fe(II) in the acid phase $\text{B} \rightarrow \text{C}$. Under the right conditions this
system conforms to an essentially irreversible consecutive reaction scheme: A $\rightarrow$ B $\rightarrow$ C.

For maximum stripping efficiency, conditions in the mixer should be set so that $k_1$ is rate controlling. Since $k_1$ is a transfer rate between two phases, it is expressed as a product of the interfacial area (calculated from the data of Ryon and Vermeulen) and the transfer rate obtained in the Lewis cell to give an effective rate constant $k_a$. Values for $k_a$ and $k_2$ have been calculated from the data presented above for 50°C and 0.05 molar Fe(II) over a 5 to 10 molar range of H$_3$PO$_4$ (Table 7.1).

Retention times, calculated from Eq. 2, for aqueous/solvent recycle ratios of 2, 1, 0.5 and 0.33 and assuming 75% stripping per stage, show that a H$_3$PO$_4$ concentration of about 8 molar is needed before $k_a$ is rate controlling and maximum efficiency is achieved (Fig. 7.8). We may also recall from Sect. 7.5.3 that 8 molar H$_3$PO$_3$ is needed to reduce the U(IV) extraction coefficient to about 0.005, a condition also necessary for maximum efficiency.

Of course, stripping efficiency can be increased at lower acid concentrations by increasing the concentration of Fe(II), but this adds to contamination problems. The
presence of fluoride ion, already present in wet-process acid, can also enhance stripping efficiency. However, we should not rely on this approach, because the concentration of free fluoride ion in the commercial acids is usually low and variable. In fact, some plant acids are treated with active silica to complex any free fluoride ion that may be present in order to minimize its corrosive properties.

Fortunately, concentrated H$_3$PO$_4$ is readily available in the plants and the use of such acids offer a very easy way to increase stripping efficiency.

To test our model, we calculated $k$ for some continuous stripping data presented in our initial DEPA-TOPO paper$^7$ and compared it with $k$ values determined in this study. The comparison was very good, e.g., $k$ was 4.3 in the old data compared to 4.2 for the new.


7.6 Chromatographic Separations with Activated Carbon Filled with Hydrous Oxide Ion Exchangers

J. S. Johnson, Jr., S. Y. Shiao, C. G. Westmoreland, W. M. Doerr,$^1$ G. Mohiuddin,$^2$ W. Y. Hata,$^2$ J. S. Tolan$^2$)

A main interest of the now discontinued Basic Energy Sciences program "Flow Through Porous Bodies" has been equilibria and kinetics of adsorption on inorganic materials. Besides the intrinsic fundamental interest of the subject, the research had implications for isolation of nuclear wastes and for the preparation of ion exchangers usable in high radiation fields and under other aggressive conditions. In the previous report of this series, increases of an order of magnitude in the uptake of cations on activated carbon were shown to be attainable by treatment of the carbon with nitric acid. Procedures were developed which effected filling of the pores of such carbons with substantial amounts of hydrous Zr(IV) oxide. It was further shown that treatment of carbon containing Zr(IV) with phosphoric acid resulted in a material filled with a mixed Zr(IV)/P(V) oxide. We have been attempting to prepare such materials for a long time, in order to combine high selectivities$^3$ of hydrous Zr(IV) oxide and of zirconium phosphate with the excellent chromatographic properties of activated carbons. The oxides themselves are difficult to prepare in forms suitable for use in large-scale columns, and they tend to peptize when exposed to some solution compositions.

In the period of this report, we have shown that the cation-exchange properties of the filled Zr(IV)/P(V) carbon are similar to those of the hydrous oxide alone and that the filled material operates well in columns.

7.6.1 Alkali-Metal Ion Separation

In comparison with organic ion exchangers, the selectivities of various mixed oxides, such as Zr(IV)/W(VI), Zr(IV)/Mo(VI), and Zr(IV)/P(V), between alkali-metal and
alkaline-earth ions is striking. We elected to use a separation of Cs⁺ and Na⁺ tracers to evaluate activated carbon filled with Zr(IV)/P(V). The as-received carbon is a high-surface-area Barneby-Cheney sample (about 1000 m²/gm), ground to ~200 mesh. Oxidation treatment was exposure to 70% HNO₃ for two hours at 60°C. Zirconium (IV) was incorporated from a 0.05 M zirconyl chloride in 1 M HNO₃ solution. Conversion to the hydrous Zr(IV) form was by exposure to NH₃ (successive Zr(IV) and NH₃ treatments were alternated), and to the mixed phosphate oxide, by passing 1 M H₃PO₄ through a column of carbon previously equilibrated with the Zr(IV) chloride solution. By x-ray fluorescence, the mixed oxide was amorphous, and the mole ratio of P to Zr was 2.3, in comparison with 2.1 for a commercial (Biorad) sample.

Figure 7.9 compares the distribution coefficients D (counts per gram of adsorbent/counts per ml of solution) of trace Cs on activated carbon as-received, nitric acid treated, and filled with Zr(IV)/P(V); measurements were at pH 5.5. Oxidation increases the values of D, as was also the case for divalent cations in the previous report, and on carbon filled with the mixed oxide, distribution coefficients are even higher. Values decrease with concentration of the supporting electrolyte, NH₄Cl. The slope is approximately that expected (-1 for log D$_{Cs⁺}$ vs log M$_{NH₄⁺}$) for ideal exchange of monovalent ions in the case of the oxidized material, and somewhat less for the filled material.

Selectivities for alkali-metal ions of Zr(IV)/P(V) are highly dependent on pH, and the filled carbon reflects this (Figure 7.10). There is a reversal between Cs⁺ and Na⁺, Cs⁺ being more strongly adsorbed from acidic solutions and Na⁺ from basic.

If the kinetics of exchange are fast relative to contact time, as they are with columns of hydrous oxide powders, these variations in adsorptivity with solution composition have obvious potential for design of separations.
Figure 7.11 demonstrates that the filled carbon meets the rate criterion. Cs⁺ and Na⁺ tracers were introduced in 0.1 M HCl, and the sodium, as expected, was eluted in a few column volumes. When the effluent activity reached background levels, the eluent was changed to 1 M NH₄OH/NH₄Cl, and cesium was removed in a few column volumes.

Further details may be found in a report.⁴

7.6.2 Anion Exchange

Hydrous Zr(IV) oxide adsorbs with high capacity and distribution coefficients from acidic media many polyvalent anions, such as those of Cr(VI), W(VI), and Mo(VI), and the adsorbed species can be eluted with base. This property could be valuable for example in ore processing or recovery of metal from industrial waste streams. We attempted to evaluate activated carbon filled with hydrous Zr(IV) oxide for this purpose. Chromium was indeed removed from acidic solutions by passage through a column, but we found that removal was roughly the same by carbon which had not been filled with the oxide. Apparently, chromium was being reduced to a lower valence state by contact with the carbon. A few spectrophotometric measurements on the eluents indicated this. There was not time left on the program to establish conclusively what was occurring, but we mention the observations here, because of the interesting possibility of a redox cycle for separation of such ions on activated carbon. Another application which might be explored is backfill for high-level nuclear waste disposal in geological formation. Many nuclides which pose problems are much more likely to be retarded in their migration if in reduced valence state — technetium and several actinides are examples. Both the adsorption and reducing properties of activated carbon might therefore be useful.

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**Fig. 7.11.** Separation of Na⁺ and Cs⁺ by activated carbon filled with hydrous Zr(IV)/P(V) oxide (column length, 3.2 cm; flow rate, 0.5 cm/min).
7.7 Recovery of Nonradioactive Palladium and Rhodium from Spent Nuclear Fuel Elements

(F. J. Smith)

We have continued to develop the basic chemistry for processes that could be used to recover nonradioactive palladium and rhodium from spent nuclear fuel elements. The processes are based on essentially complete removal of radioactive ruthenium (the precursor of nonradioactive palladium and rhodium) from the radioactive palladium and rhodium and other fission products. Decay of 368-d \(^{106}\text{Ru}\) produces nonradioactive \(^{106}\text{Pd}\), while decay of 40-d \(^{103}\text{Ru}\) yields nonradioactive \(^{103}\text{Rh}\). After an appropriate waiting period for decay, separation of this nonradioactive palladium and rhodium from the remaining \(^{106}\text{Ru}\) and \(^{103}\text{Ru}\) gives a product suitable for unrestricted commercial use. Previously a process was developed which provided the required ruthenium, palladium, and rhodium separations (separation factors greater than \(10^6\)) by utilizing liquid-liquid partitioning between liquid magnesium and molten uranium-iron eutectic at 750°C. This viable process provides good separations, but has the disadvantages of high temperature and limited suitable container materials. Therefore, we are continuing to search for and evaluate alloy and salt systems which could produce the largest separation of ruthenium from the other noble metals under less stringent conditions of temperature and which would utilize conventional materials of construction.

One system chosen for study was the \(\text{AlBr}_3-\text{KBr}\) system. A dominant common feature of the alkali metal halide-aluminum halide systems is a two-liquid phase region which exists at relatively low temperatures. The two-liquid region occurs at high overall aluminum halide concentrations, with the composition of one phase being essentially pure aluminum halide (>99 mole %) and the other phase a more ionic mixture containing about 20 mole % alkali halide. The distribution behavior of palladium, rhodium, and ruthenium bromides between the two immiscible liquid phases in the \(\text{AlBr}_3-\text{KBr}\) system was determined at 110°C. The results are shown in Fig. 7.12.

![Fig. 7.12. Concentrations of palladium, rhodium and ruthenium in the \(\text{AlBr}_3-\text{KBr}\) (99.6 - 0.4 mole %) phase as a function of their concentrations in the immiscible \(\text{AlBr}_3-\text{KBr}\) (77.8 - 22.2 mole %) phase at 110°C.](image)

Distribution coefficients of 1.3, 1.6 and 3.1 were determined for \(\text{PdBr}_2\), \(\text{RhBr}_3\), and \(\text{RuBr}_3\), respectively. The ratio of the distribution coefficients indicates that the maximum separation factor that could be achieved between palladium and ruthenium is 2.3. This small separation factor demonstrates that the \(\text{AlBr}_3-\text{KBr}\) system has a very small capability for practical palladium-rhodium-ruthenium separations.

Comparison of the spectra of palladium(II) dissolved in the two phases with spectra previously reported indicates palladium to be present as a square-planar \(\text{PdBr}_4^{2-}\) complex in both phases and also provides evidence that Al(III) is entering into the second coordination sphere of the palladium. Similar comparisons of spectral data for ruthenium distributing between the two phases indicate that octahedral \(\text{RuBr}_6^{3-}\) is the dominant species in both phases.
Also chosen for study was the liquid Al—
molten AlCl₃-LiCl system. This system was
chosen since, in the conventional fuel reproc-
essing scheme, the residue from the nitric acid
dissolution step contains a large fraction of
the fission product noble metals in the elemen-
tal state. These metals are soluble in liquid
aluminum. No distribution data could be found
in the literature for palladium, rhodium, or
ruthenium between liquid aluminum and molten
chloroaluminate salts. However, the system
Al-LiAlCl₄ has been studied for separation and
extraction of actinides from aluminum alloys.
Palladium and ruthenium are known to form
stable solid and gaseous chloroaluminate
complexes (i.e., PdCl₂-AlCl₃ and RuCl₃-AlCl₃).
This information, along with empirical com-
parisons of the relative stability of the
complexes and the Pu-Al, Ru-Al, and Rh-Al phase
diagrams, led us to suspect that the
Al-LiAlCl₄ system might be useful in achieving
the critical Pd-Ru and Rh-Ru separations
necessary for recovery of non-radioactive
palladium and rhodium. However, it was found
that PdCl₂, RhCl₃ and RuCl₃, initially
dissolved in molten LiAlCl₄, were all rapidly
and quantitatively reduced by both liquid and
solid aluminum.
These studies are concerned with the kinetics of interfacial and mass-transport processes that take place during localized corrosion of metals (such as crevice corrosion, pitting, and stress corrosion cracking), and with the effects of hydrolytic, complexing, and precipitation reactions that influence corrosion rates. Materials of interest include pure metals (Ti, V, Mo, Cr, Fe, etc.), their alloys prepared by conventional metallurgical methods, and novel near-surface alloys of these metals prepared by ion implantation and characterized by Rutherford backscattering. The kinetic behavior of coupled active-passive electrode systems composed of these metals and alloys is of special interest because of its direct relevance to the development of localized corrosion under geometric constraints and because of its potentiality for design of corrosion-resistant alloys on the basis of electrochemical kinetic considerations. The application of photoacoustic spectroscopy coupled with electrochemical measurements to the detection of film formation and changes in surface concentrations and identity of reactive intermediates of corrosion processes is being investigated as a new tool for in-situ mechanistic studies. In addition, electrochemical methods have led to the development of new chemical processes for efficient, economical removal and recovery of silver from photographic and photoreproduction effluents.

8.1 Electrochemical Behavior of Molybdenum and Mo-Implanted Titanium "Near-Surface" Alloys
(E. J. Kelly, J. Williams, and G. Beardsley)

As our earlier work with Pt-implanted titanium demonstrated, electrochemical studies of well-defined (i.e., known concentration/depth profiles of constituents) near-surface alloys, prepared by ion implantation and profiled by Rutherford backscattering, can be very useful in determining the roles played by alloying elements in corrosion processes. For metals other than the noble metals, relatively large (>10^15 atoms cm^-2) implantation fluences are required if significant effects on corrosion rates of titanium are to be obtained. Molybdenum, vanadium, and chromium are typical of the alloying elements in this category. The proximity of the atomic weights of Cr, V, and Ti preclude accurate determination of concentration profiles of Cr or V in Ti by backscattering and, consequently, the Mo-implanted titanium system was chosen for this study.

As a necessary prerequisite to the evaluation of electrochemical data obtained with Mo-Ti alloys, the electrochemical characteristics of zone-refined Mo were determined. Anodic (metal dissolution) and cathodic (hydrogen evolution) polarization curves in H_2-sat’d. 1 M H_2SO_4 (T=30°C) were measured, and are shown in Fig. 8.1 together with analogous curves for zone-refined titanium. Curves i_H(Ti) and i_H(Ti) correspond to the dissolution of Ti to form Ti(III) ions, and to the hydrogen evolution reaction on Ti, respectively. The intersection of these curves fixes the active-state corrosion potential (E_{corr}) and corrosion rates (i_{corr}) of pure titanium. It is evident from Fig. 8.1 that in the active (<-530mV vs SCE) and active-passive transition (-300 to -530 mV vs SCE) potential regions of titanium, molybdenum is electrochemically inert, i.e., i_H(Mo) is vanishingly significant. However, it is also evident that molybdenum should catalyze the hydrogen evolution reaction in these potential regions since i_H(Mo) >> i_H(Ti). Consequently, for a Mo-implanted titanium alloy, i_H should be given by a curve lying between i_H(Mo) and i_H(Ti), for example, by i_H(Mo-Ti), a curve which intersects i_H to give a corrosion potential more noble (positive) than E_{corr}. The greater the Mo surface area per unit area of alloy surface, the more positive the open-circuit potential.

In Fig. 8.2, open-circuit activation curves (1 - 5) are shown for Ti and a series of Mo-implanted titanium alloys (near-Gaussian
distribution of Mo in Ti with the peak concentration at 40 nm, and with a zero surface concentration. Upon immersion in acid, the initial potential is quite positive due to the presence of an air-formed oxide layer on the electrodes. Dissolution of the oxide film is accompanied by a rapid shift in the potential in the negative direction (activation). In the case of pure Ti, the potential moves monotonically to the expected value of $E_{\text{corr}} = -750$ mV vs SCE (cf. Fig. 8.1). For the Mo-implanted alloys, active-state dissolution of titanium results in a buildup of the electrochemically inert Mo on the alloy surface, and a resultant catalysis of the hydrogen evolution reaction. As explained above, this results in a displacement of the potential to values more positive than -750 mV vs SCE. In all cases, the Mo is eventually lost and the potential becomes identical with that of pure Ti (post-corrosion backscattering confirmed the complete loss of Mo when the potential stabilizes at -750 mV vs SCE). Potential/time data shown in Fig. 8.2 may be converted into $I_d(t)/$time data by use

![Fig. 8.1. Electrochemical polarization curves for zone-refined molybdenum (Mo) and titanium (Ti) in H$_2$-saturated 1 M H$_2$SO$_4$ (30°C).](image)

![Fig. 8.2. Activation of Ti (curve 1) and Mo-implanted titanium (curves 2-5) electrodes in H$_2$-saturated 1 M H$_2$SO$_4$ (30°C). Also shown is instantaneous atom % Mo on surface of electrode 3 if Mo accumulation occurs.](image)
of curve $t_g(T(t))$ shown in Fig. 9.1. This enables one to calculate the instantaneous corrosion depth, i.e., the thickness of the layer of alloy removed by titanium dissolution. By comparing the corrosion depth with the original Mo concentration profile, one can calculate the instantaneous surface concentration of Mo, assuming no accumulation of Mo, i.e., assuming Mo is lost as it is brought to the surface by alloy dissolution. The results are shown in Fig. 8.2 for electrode 3, although the results are very similar for all implanted alloys. Even though the entire implant region has been removed in a few hours, the effect of Mo persists. This proves conclusively that Mo preferentially accumulates on the surface via ad-atom diffusion and aggregation to form three-dimensional surface clusters in a manner analogous to that observed with Pt-implanted titanium alloys.

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8.2 Electrochemical Behavior of Vanadium
(H. R. Bronstein, E. J. Kelly)

Earlier studies by Kelly$^1$ have shown the importance of the role of soluble corrosion products of titanium in its localized corrosion behavior, and have led to investigation of the effect of other soluble redox systems, especially those derived from alloying constituents, on titanium corrosion.$^2$ Recently a study was carried out using both titanium and vanadium electrodes in 0.5 M H$_2$SO$_4$ at 30°C in which the role of the soluble corrosion product of vanadium on passivation of titanium was demonstrated. Vanadium is an important alloying constituent of titanium, and the V(IV)/V(III) redox couple exhibits a standard reversible electrode potential in a region that suggests the possibility of passivation of actively corroding titanium by V(IV).

In one series of experiments a vanadium electrode was polarized anodically at a constant electrode potential of -250 mV vs SCE and anodic current was monitored with time. Simultaneously the open-circuit corrosion potential of an actively-corroding titanium electrode was observed with time. The titanium electrode passivated after 8,200 minutes under the prevailing experimental conditions, as shown in Fig. 8.3. From the current-time transient of the vanadium electrode, under the assumption that the anodic dissolution reaction of vanadium proceeds according to the stoichiometry $\text{V} + \text{V(IV)} + 4\text{e}^-$, it was determined that the critical concentration of V(IV) required for passivation was $1.6 \times 10^{-2}$ M. In addition, from a knowledge of the potential-time transient of Fig. 8.3 and of the anodic polarization curve of titanium in this medium, it was estimated that $8.1 \times 10^{-4}$ M V(III) was produced by reduction of V(IV) during the time required for passivation of the titanium electrode. Spectrophotometric analysis of the solution showed that $[\text{V(IV)}] = 1.6 \times 10^{-2}$ M and $[\text{V(III)}] = 9 \times 10^{-4}$ M at the time of passivation, in excellent agreement with the estimated values.

Furthermore, the current density for reduction of V(IV) to V(III) at the maximum in the anodic polarization curve of actively-corroding titanium ($E_{\text{max}} = -530$ mV vs SCE) was estimated to be $7.0 \times 10^{-5}$ A/cm$^2$, in good agreement with the value $7.1 \times 10^{-5}$ A/cm$^2$ obtained by Brown$^3$ under the same conditions by direct addition of V(IV) to solution. These experiments show that passivation of titanium can be achieved by the soluble corrosion product, V(IV), of the alloying constituent vanadium, and that the anodic dissolution reaction of vanadium under these conditions is described well by the stoichiometry $\text{V} + \text{V(IV)} + 4\text{e}^-$.  

8.3 Hydrogen Evolution Reaction on Titanium in Acidic Media

(H. R. Bronstein, E. J. Kelly)

Although the mechanism of titanium dissolution in acidic media has been thoroughly investigated and may be considered to be reasonably well understood, that of the hydrogen evolution reaction (HER) which accompanies corrosion of the metal remains uncertain. The reactions normally considered in a discussion of the HER are (1) \( \text{H}^+ + \text{e}^- \rightarrow \text{H}_2 \) [hydrogen ion discharge], (2) \( \text{H}_2 + \text{H}_2 \text{O} \) \( \rightarrow \text{H}_2 \text{O} + \text{H}_2 \) [electrochemical desorption], and (3) \( 2\text{H}_2 \text{O} \rightarrow \text{H}_2 \text{O} + \text{H}_2 \) [recombination].

The primary diagnostic criteria for determination of the rate-determining step in the HER are the magnitude of the Tafel slope, \( \frac{d\text{E}}{d \log i} \), and the reaction order with respect to the hydrogen ion activity, \( \frac{-d \log i}{d \log \text{pH}} \), where \( i \) is the current density corresponding to the net rate of hydrogen ion discharge, and \( E \) is the electrode potential. Normally one expects to observe a Tafel slope equal to \( (-2.303RT/F)y \), where \( y \) is equal to 2, 2/3, or 1/2; i.e., slopes of -120, -40, or -30 mV/decade, respectively, at 30°C. Similarly, one expects to find simple reaction orders, such as 1 or 2. However, for the HER on titanium in acidic sulfate solutions, the following values of the Tafel slope have been reported by various workers: -70, -119, -127, -135, -135, -150, -172, and -172 mV/decade. Similarly, in acidic chloride solutions, values of -120, -150, -153, and -180 mV/decade have appeared in the literature. In acidic sulfate media, the reported values of the hydrogen ion reaction order range from 0.6 to 1.0, and in acidic chloride media from 0.8 to 1.0. Investigators reporting values of the Tafel slope > -120 mV/decade invariably attribute the anomalous values to the presence of an oxide film on the metal. Such a conclusion is in conflict with what is known about the mechanism of titanium dissolution. In order to resolve the controversies surrounding the HER on titanium, we have initiated a careful re-examination of the subject.

In 0.5 M SO_4^{2-} solutions at pH values of 3.0, 2.5, and 2.0, Tafel behavior has been observed as shown in Fig. 8.4. Although the Tafel regions encompass less than a decade of current density, the Tafel slopes are clearly -120 mV/decade. This result is consistent with slow
In addition to the normal hydrogen ion discharge reaction of Eq. (1), discharge also occurs through the proton-ated surface species $S_{OH}^+$, as indicated in Eqs. (2) and (3). The titanium surface is known to be totally occupied by adsorbed species $S_{OH}^+$ such as $\text{(TiOH)}_n^{2+}$, $\text{(TiOH)}_n^{3+}$ and $\text{(TiOH)}_n^{4+}$. The current density corresponding to the reaction scheme of Eqs. (1) .. (3) is given by Eq. (4):

$$i = \frac{F K_1}{1 + \frac{k_3}{1 + (k_2/i_{H^+})}} \exp\left(-\frac{E}{RT}\right) \tag{4}$$

This expression accounts accurately for the effects of both pH and electrode potential.


8.4 Effect of Redox Couples on the Kinetics of Titanium Dissolution

(Gilbert M. Brown)

An investigation of the effect of redox couples on the corrosion behavior of titanium is continuing. As a part of this effort, studies are being carried out on the reactions of the $\text{V(IV)}/\text{V(III)}$ and $\text{V(III)}/\text{V(II)}$ couples on titanium in the active and active-passive transition potential regions. The partial cathodic current for reduction of $\text{V(IV)}$, measured as a function of $\text{V(IV)}$ concentration, gives a reaction order, $(\partial \log |i|/\partial \log [\text{V(IV)}])_E$, over the range of 0.81 to 0.84 in the potential range of -350 to -530 mV vs SCE in 1 M $\text{H}_2\text{SO}_4$ at 30°C. The relationship between partial cathodic current and electrode potential does not obey the classical Tafel equation for any $\text{V(IV)}$ concentration in the range examined (1 to 10 M). Nonetheless, the logarithm of the initial rate constant (obtained by extrapolation of $[\text{V(IV)}]$ to zero) varies reasonably linearly with electrode
potential with a slope of $a E/2 \log k \sim -165$ mV/decade. This result and the observed potential dependence of the reduction of Ti(IV)$^2$ suggest that the reductions of these tetravalent species on titanium cannot be regarded as simple charge-transfer reactions.

To get a better understanding of the nature of the surface of titanium electrodes in the active-passive transition potential regions, the reductions of the chemically well-defined complex ions $\text{Co(NH}_3)_5\text{SO}_4^-$, $\text{Co(NH}_3)_6\text{Cl}^{2+}$, and $\text{Cu(NH}_3)_4^+$ were studied in the appropriate potential region in $1 \text{ M H}_2\text{SO}_4$ at 30°C. The reactions of these species were found to be first order in the concentration of the Co(III) complexes, and the potential dependences of the reduction reactions were observed to be in the range -110 to -135 mV/decade. These results and those for the reduction of V(III)$^1$ are consistent with simple one-electron charge-transfer reactions at an electrode surface free of any film which might affect the potential distribution at the metal-solution interface. In the same potential region, the reduction reactions of V(IV) and Ti(IV) have unusual potential and/or concentration dependences. The unusual results with these aquo ions are attributable to chemical rather than electrochemical effects.

2. E. J. Kelly, personal communication.

8.5 Application of Photoacoustic Spectroscopy to In-Situ Corrosion Studies
(C. E. Vallet, Gilbert M. Brown)

Photoacoustic spectroscopy coupled with electrochemical measurements is being investigated as a new tool for the detection of film formation, for identification of reactive intermediates, and for determination of changes in surface concentrations of species important in corrosion processes. Several studies using this promising non-destructive method have been reported recently.$^1$ Among the advantages of this in-situ method are the possibility of depth-profiling, the ability to study comparatively rough surfaces (commonly encountered in corrosion), and the capability of detection of monolayer amounts of substances with suitable signal processing.$^5$

A single-beam photoacoustic spectrometer has been assembled. The photoacoustic cell, comprising a conventional three-electrode arrangement with test, reference, and counter electrodes together with an optically transparent window, is equipped with a Radio Shack No. 270-092A microphone as detector. The photoacoustic signal is recorded through a lock-in amplifier tuned to the chopping frequency of the monochromatic light.

The photoacoustic spectrum of vacuum deposited carbon on a thin (0.1 mm thickness) copper disc, shown in Fig. 8.5, reproduces the power spectrum of the lamp and monochromator, as expected from the Rosencwaig-Gersho theory.$^6$ Easily detectable signals (~10 μV) were obtained with 1 mW power and a bandwidth of

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Fig. 8.5. Comparison of lamp-monochromator power spectrum and photoacoustic spectrum of carbon. Upper curve: power spectrum of 1000 W Xe lamp and monochromator obtained with surface-absorbing disc calorimeter. Lower curve: photoacoustic spectrum of carbon vacuum deposited on thin copper disc.
2 nm. The assembly was tested with a titanium disc electrode (Alfa products, 0.025 mm thickness with an area of 0.3 cm$^2$) in 1 M H$_2$SO$_4$ for which the potential relative to a standard calomel electrode was maintained constant by a PARC potentiostat. Photoacoustic spectra were recorded for the electrode in an "active" state (-530 mV vs SCE and 14 $\mu$A) and in a "passive" state (0 mV vs SCE and 0.05 $\mu$A). Values of the steady current densities at these potentials agreed with those reported by Kelly.\(^7\) Figure 8.6 shows the photoacoustic spectra, corrected for the spectral response of the lamp + monochromator, and the difference spectrum between the spectra on a "passive" and an "active" electrode. While the photoacoustic signals are very similar for the two electrode potentials over the 450-700 nm wavelength range, the photoacoustic signal for the "passive" electrode at 350 nm is double that for the "active" electrode. The difference spectrum shows the absorption starting at 400 nm which agrees with absorption measurements on C.V.D. TiO$_2$ layers.\(^8\) The band edge as measured by the position of the knee in the photoacoustic spectrum\(^9\) is at 340 nm. This leads to a value of 3.6 eV for the valence band—conduction band gap energy in agreement with that recently reported\(^{10}\) for TiO$_2$ films grown by vapor decomposition of ethyl titanate. The difference spectrum clearly indicates the formation of a TiO$_2$ passivation layer. Further investigations with varying chopping frequencies of the monochromatic light should give the thickness of the passivation layer.

These preliminary experiments showed that detectable acoustic signals can be obtained with an illumination intensity of the electrode which does not produce a significant photoelectrochemical effect. We therefore are confident that in-situ photoacoustic spectroscopy coupled with electrochemical measurements will bring new insights into the mechanism of formation and breakdown of passive oxide films, with consequent implications for localized corrosion.

8.6 Influence of Anions on Titanium Corrosion

(Gilbert N. Brown)

The electrochemical behavior of titanium in aqueous solution was reviewed recently by Kelly.\textsuperscript{1} Titanium is characterized by a passive state in which the metal is covered by a protective TiO\textsubscript{2} layer, an active-passive transition region, and an active state in which the metal is oxidized to Ti(III) ions in solution. The steady-state anodic polarization curve of titanium shows a current axis as the potential becomes more noble, and a decrease in current is observed as the electrode is passivated. A mechanism for the anodic dissolution of titanium in the active and active-passive transition regions was proposed by Kelly.\textsuperscript{1}

This mechanism, indicated by Eqs. (1) - (8),

\[
\text{Ti(aq)} = \text{Ti(I)} + e^- \quad (1) \\
\text{Ti(I)} + \text{Ti(II)} + e^- \quad (2) \\
\text{Ti(II)} + \text{Ti(III)} + e^- \quad (3) \\
\text{Ti(II)} + \text{Ti(III)} + e^- \quad (4) \\
\text{Ti(III)} + \text{Ti(III)} \quad (5) \\
\text{Ti(III)} + \text{Ti(IV)} + e^- \quad (6) \\
\text{Ti(III)} + \text{Ti(IV)} + e^- \quad (7) \\
\text{Ti(IV)} + \text{Ti(IV)} \quad (8)
\]

postulates a monolayer coverage of the surface by low valent species. For convenience, the hydrolytic reactions of the species are omitted; subscript \text{a} refers to an adsorbed species and subscript \text{s} refers to a solution species. Expressions for the dissolution current, the potential maximum, and the current maximum are given in Eqs. (9), (10), and (11), respectively. In these equations, \(k_i\) is the rate constant of the \(i\)th reaction. The proposed mechanism did not specify the role of the acid anion other than noting that the reaction sequence was the same in sulfate or chloride media. It is of considerable interest to define the role of these anions more precisely.

A titanium electrode, initially covered by an air-formed oxide film, will spontaneously activate in 1 M HCl or 1 M \(\text{H}_2\text{SO}_4\) at 30°C. A plot of open-circuit potential vs time shows a characteristic potential arrest (Flade potential) at about -300 mV vs SCE, in which the potential suddenly decreases to a value near the active-state corrosion potential of the particular medium. However, titanium with an air-formed film will not spontaneously activate in 1 M aqueous perchloric or p-toluenesulfonic acids at 30°C over a period of several days. But with the addition of \(10^{-2}\) M oxalic acid or sulfuric acid, spontaneous activation is observed within several hours. Chloride ion in perchlorate or p-toluenesulfonate media is also effective in activating titanium, but a higher concentration is required. Thus, electrodes will activate in 0.2 M HCl, with a total acid concentration of 1 M, although the corrosion potential is relatively noble.

The dissolution of anodically grown TiO\textsubscript{2} films on titanium was studied by Allard and Heusler.\textsuperscript{2} The rate-determining step in acidic solution is the conversion

\[
[\text{Ti(OH)}_2^- + \text{Ti(OH)}_2^+ \quad (12)
\]

The present work shows that the complexing ability of the anions in solution is important in reaction (12). The first step in activating the electrode is dissolution of the passive film. The present work also shows that 1 M HClO\textsubscript{4} at 30°C is not a sufficiently effective oxidizing agent to passivate titanium.

\[
E_{\text{max}} = \frac{3F(k_3 + k_4) \ln[(k_5k_7)/((2k_4k_7))]}{(3/2)(2k_3)^{1/3}} \\
I_{\text{max}} = \frac{3F(k_3 + k_4)}{(3/2)(2k_3)^{1/3}} \quad K = \frac{k_4k_7}{k_5k_7}
\]
In the active region, these anions function by an adsorption mechanism in addition to acting as complexing agents. The steady-state polarization curve for Ti in chloride solution at pH = 0.92 and at an ionic strength of 1.0 M, maintained with NaCl, is shown in Fig. 8.7. The influence of $10^{-2}$ M oxalate and $10^{-2}$ M sulfate on the polarization curves at the same pH and ionic strength is also shown. The effect of oxalate or sulfate is to increase the anodic dissolution current with a smaller change in the hydrogen evolution current. With the potential held constant at $E_{\text{max}}$, the value of $i_{\text{max}}$ is not linear in the concentration of the added anion (constant pH and ionic strength). Rather, plots of $i_{\text{max}}$ vs sulfate or oxalate concentration show progressively smaller increases in current with an increase in the anion concentration. This saturation behavior is characteristic of an adsorption process. In addition to stabilizing the solution species by complexation, these anions are postulated to react with the monolayer coverage of species on the surface. Oxalate and sulfate have a large influence on $i_{\text{max}}$ but leave $E_{\text{max}}$ relatively unchanged. Inspection of Eqs. (10) and (11) suggests that the reactions of the Ti(II) surface species [cf. Eqs. (3) and (4)] are those influenced most strongly. The mechanism for the action of sulfate or oxalate in perchlorate or p-toluenesulfonate media is similar to that noted above.

The influence of chloride on the polarization curves of titanium in perchlorate or p-toluenesulfonate at 1 M total acid is much smaller than that of sulfate or oxalate. Detailed polarization measurements in mixtures of HCl and HCO$_3$ at constant [H$^+$] = 1.0 M indicate that $E_{\text{max}}$ is independent of [Cl$^-$]. The dependence of the dissolution current at $E_{\text{max}}$ on [Cl$^-$] shows the same saturation behavior noted for sulfate and oxalate. Frayret and Caprani$^3$ studied the polarization of titanium as a function of chloride ion activity at constant hydrogen ion activity. These workers used solutions of NaCl and HCl at a total chloride concentration of 2 - 4 M. The oxidation of titanium to Ti(III) was reported to be first order in the activity of chloride ions. The present work suggests that the rate of oxidation of Ti(II)$_a$ is dependent on chloride concentration, but that the dependence is less than first order and is indicative of an adsorption process.

8.7 Inhibition of Titanium Corrosion by Chromium Species
(A. L. Bacarella)

A study combining electrochemical and ESCA measurements on the effect of the Cr(III)/Cr(II) redox couple on the dissolution kinetics of titanium in deoxygenated acidic sulfate solutions has continued. Previously, it was shown that Cr(III) was not reducible in the active and active-passive potential regions, and therefore had no effect on the dissolution kinetics of titanium. However, oxidation of Cr(II) in solution at the titanium electrode surface caused a remarkable inhibition of the rate of the anodic dissolution process. The effect becomes increasingly significant as the potential approaches the passive region. This is true whether Cr(II) is present because of addition of the appropriate reagent, because of corrosion of pure metal in the same solution, or (presumably) because of dissolution of an alloy phase in the case of localized corrosion. Depending on the concentration of Cr(II) and the pH, a chromium oxide film forms at potentials that are somewhat more negative than that at which a three-dimensional TiO$_2$ film forms on pure titanium. X-ray photoelectron spectroscopy showed the presence of three different valence states of sulfur in the film formed in the presence of Cr(II); these were identified as sulfate and two reduced species. In the absence of Cr(II), and at potentials where titanium is in the passive state, and presumably where a three-dimensional TiO$_2$ film is present, no sulfur can be detected in the film.

In the earlier studies solutions containing Cr(II) were prepared by dissolution of pure chromium metal at the open-circuit corrosion potential. The concentration of Cr(II) was obtained by analysis of total chromium content using atomic absorption spectroscopy, on the assumption that homogeneous oxidation of Cr(II) to Cr(III) was slow, so that analysis of total chromium content provided a satisfactory estimate of the Cr(II) concentration. This assumption was shown to be valid by later measurements. In the more recent work spectrophotometric procedures developed by Brown were used to determine both Cr(II) and Cr(III) concentrations. In one procedure [Cr(II)] was determined by addition of NH$_4$Fe(SO$_4$)$_2$·12H$_2$O to solution followed by spectrophotometric analysis of the complex formed by Fe(II) and 1,10-phenanthroline.

Total chromium content was determined spectrophotometrically by conversion to Cr(VI) using alkaline H$_2$O$_2$; [Cr(III)] could then be obtained by difference. In an alternative method both [Cr(II)] and [Cr(III)] could be determined in the 0.5 M sulfate solutions by measurement of absorbance at 580 and 740 nm; ratios of molar absorption coefficients of the two ions are sufficiently different at these wavelengths to allow reasonably accurate estimation of [Cr(II)] and [Cr(III)].

Some experimental results on the effect of Cr(II) on polarization of titanium in 0.5 M sulfate solutions (initial pH = 0.8) at 30°C are shown in Fig. 8.8. As the concentration of Cr(II) is increased the anodic current density is decreased and the maximum in the anodic polarization curve (E$_{max}$) is shifted to more negative values of electrode potential. It is necessary for accurate determination of the anodic polarization curves to correct the measured anodic current densities for the current densities due to the hydrogen evolution reaction (cf. dashed curves in Fig. 8.8). This correction becomes more important with increasing [Cr(II)].

Currently the results are being analyzed in terms of a model involving oxidation of Cr(II) to an adsorbed Cr(III) species at the interface. The surface coverage of the adsorbed species strongly inhibits the anodic dissolution reaction of titanium. The model correctly predicts that a plot of log[1/(I/I$_0$ - 1)] vs electrode potential should be linear [I and I$_0$ are anodic current densities with and without Cr(II) present]. Further work on this interesting system is in progress; the results
Fig. 8.8. Polarization of titanium in acidic sulfate solutions as a function of Cr(II) concentration; [SO\textsubscript{4}\textsuperscript{2-}] = 0.5 M, T = 30°C.

are expected to bear directly on the question of the susceptibility of chromium-containing alloys of titanium to localized corrosion.

2. Gilbert M. Brown, unpublished results.

8.8 Removal and Recovery of Silver from ORNL
Photographic and Photoreproduction Effluents
(F. A. Posey, A. A. Palko)

During the past several years, storage of silver-containing photographic and photoreproduction wastes generated at ORNL became necessary, as a temporary measure, to avoid exceeding discharge limitations set by regulatory agencies.\(^1\) No entirely satisfactory processes were known which could remove silver to the desired level without simultaneous creation of other problems, such as sludge separation and disposal. Because of our experience in earlier studies on metals recovery and the design of extended-surface-area electrolytic cells,\(^2\) we were asked to work on development of a solution to this problem. Our first successful chemical process for removal and recovery of silver from spent photographic fixer was developed following frustrating attempts to use direct electrolytic methods,\(^3\) all of which possess some basic limitations for silver removal to environmentally acceptable levels.

As a consequence of research on the electrochemical reactivity of the components of spent fixer (which contains typically 5 - 6.5 g/l of dissolved silver along with high concentrations of thiosulfate, sulfite, halide, acetate, ammonium, aluminum, and other ions) a chemical process was developed which allows reduction of the silver content from >5 g/l to <0.5 mg/l, so that the resulting effluent may be discharged directly to sanitary sewage treatment facilities after pH adjustment. Silver is recovered as the pure metal, no sludges are produced, and both biological oxygen demand and chemical oxygen demand are reduced significantly. In this method, called the hypochlorite-hydrazine process, the principal complexing agents for silver ion in the spent photographic fixer, thiosulfate (hypo) and sulfite ions, are destroyed by addition of fixer to alkaline hypochlorite, while monitoring the oxidation-reduction potential of the solution to avoid formation of Ag\textsubscript{2}S. During this reaction some of the silver is precipitated as AgCl.

Subsequently, a small amount of hydrazine monohydrate is added to the reaction vessel, whereupon with time all the dissolved silver and precipitated silver chloride are converted to pure metallic silver, which is easily separated from the liquid phase by filtration.

Subsequent research showed that, under the proper conditions, silver may also be removed efficiently from spent fixer by controlled addition of fixer to an ammoniacal solution of sodium dithionite. This second process, the
ammoniacal dithionite process, is more economical than the hypochlorite-hydrazine process, but does not reduce biological oxygen demand or chemical oxygen demand of the resulting effluent since thiosulfate and sulfite are not destroyed. Silver removal efficiency is also >99.9% with the ammoniacal dithionite process, so that the silver content of the resulting effluent is <0.5 mg/l. In later work, a process was developed for recovery of silver from spent camera plate developer (a monobath containing both developer and fixer) and developer rinse. Both soluble and precipitated colloidal silver (total concentration ~1 g/l) are present in the effluent from this wash-off process, which is exceedingly difficult to filter and contains high concentrations of hydroquinone, thiosulfate, sulfite, and many other chemicals. It was found that addition of sodium dithionite to mixed spent developer and developer rinse, with heating of the solution, reduces the soluble silver concentration to the desired level (<1 mg/l) and affects the particle size distribution of precipitated metallic silver so that conventional means of filtration may be used. Precipitated and filtered silver from each of these processes may be washed and melted in a reducing atmosphere or with an appropriate flux to form solid metallic silver of high purity if desired.

Both of the dithionite processes were tested successfully in a full-scale (200 gal.) pilot plant operation, and the Laboratory's backlog of stored photoreproduction wastes (>125 drums) has now been eliminated and the silver recovered using our process. Numerous inquiries from this country and abroad about the processes have been received. Present plans include preparation of a comprehensive technical memorandum on the work and a paper using material that is suitable for publication in one of the photographic research journals.

9. CATALYSIS

Section 9.1 contains descriptions of recent results in an ongoing study of the reactions of aromatic hydrocarbons in molten SbCl₃. Molten SbCl₃ is a molecular liquid and a good solvent for hydrocarbons. By adding various amounts of redox resistant C⁺⁻⁺⁺⁺⁺ donors (KCl, [CH₃]₂NCl, etc.) and acceptors (AlCl₃), both the Lewis acidity and the potential of the Sb⁺⁺⁺⁺⁺⁺/Sb⁺⁺⁺⁺⁺⁺ couple can be tuned over substantial ranges. By making use of this tunability we have been able to cause dissolved arenes to undergo various reactions in a controlled way. These reactions include both catalytic reactions and stoichiometric reactions with the melt. Many of these reactions are different from those in more familiar solvents and some are very different.

Much of our earlier work was done with arenes that have ArH⁺⁺⁺⁺⁺⁺/ArH standard potentials within or slightly above the tuning range of the Sb⁺⁺⁺⁺⁺⁺/Sb⁺⁺⁺⁺⁺⁺ couple. For these arenes both the acidic and redox functionalities of the melt played important roles. Currently we are investigating the behavior of arenes with oxidation potentials far above the tuning range and the results of one such investigation are reported here. Recently we started investigating SbCl₃-rich mixtures that melt below ambient temperature and a first study is reported here. In an effort to learn more about the role that the melt plays in controlling the reactions of hydrocarbon solutes, we have carried out a series of investigations of the structural properties of the melts and report here the results of two recent investigations.

Section 9.2 concerns recent studies of the development of low-energy ion-scattering as a surface-specific structural tool. Emphasis has been focused on the structure of adsorbates on a clean single-crystal surface of molybdenum. Such studies of surface structure are continuing and will be complemented in the future by more catalytically-oriented studies of similar systems.

9.1 Reactions and Catalysis in SbCl₃-Rich Molten Salts

9.1.1 Selective Bond Cleavage Reactions of α,ω-Diphenylalkanes
(A. C. Buchanan, III, A. S. Dworkin, G. P. Smith)

This research produced the first evidence of a mechanism for the transaralkylation reaction (and the much studied transalkylation reaction) that does not involve protons as key catalytic agents. In addition to the impact on physical organic chemistry, this research is also significant to the general area of coal model compound chemistry. The selective cleavage of only the benzyl bond in the α,ω-diphenylalkanes at temperatures below those required for thermolysis is now explained for the first time by the formation of a benzyl cation as the important organic reactive intermediate.

The chemistry of the α,ω-diphenylalkanes, C₆H₅(CH₂)ₙC₆H₅ [n = 1-4], in highly purified anhydrous SbCl₃ and SbCl₃-10 mol % AlCl₃ melts has been investigated from 100-130°C by in situ H NMR and by quench and separation techniques. These substrates, which are often used to model the aliphatic chains that link aromatic and hydroaromatic clusters in coal, are found to undergo selective cleavage of the sp²-sp³ bond. For n = 1 and 2, products are formed via the transaralkylation reaction, the transfer of an aryl-substituted alkyl group as shown in Eq. 1 for n = 1) while for n = 3 and 4, the cleavage results in the selective production of only benzene and either indane (n = 3) or tetralin (n = 4).

\[
\begin{align*}
\text{C}_6\text{H}_5\text{CH}_2\text{C}_6\text{H}_5 & \text{ (n = 1-4), in highly purified anhydrous SbCl}_3 \text{ and SbCl}_3-10 \text{ mol } \% \text{ AlCl}_3 \text{ melts has} \\
\text{been investigated from 100-130°C by in situ } & \text{H NMR and by quench and separation techniques. These substrates, which are often} \\
\text{used to model the aliphatic chains that link} & \text{aromatic and hydroaromatic clusters in coal,} \\
\text{are found to undergo selective cleavage of the} & \text{sp²-sp³ bond. For n = 1 and 2, products are} \\
\text{formed via the transaralkylation reaction, the} & \text{transfer of an aryl-substituted alkyl group as} \\
\text{shown in Eq. 1 for n = 1) while for n = 3 and} & \text{4, the cleavage results in the selective} \\
\text{production of only benzene and either indane (n =} & \text{3) or tetralin (n = 4).} \\
\end{align*}
\]

Toluene is also reactive in SbCl₃-AlCl₃, and typical transalkylation chemistry is observed.
The relative rates for reactions in the aprotic SbCl₃ melts are in the order PhCH₂Ph > Ph(CH₂)₂Ph > Ph(CH₂)₃Ph > PhCH₃. For n = 1, the reaction rate is 1st order with respect to diphenylmethane over the concentration range studied, 0.028-1.2 M. For n = 2, the reaction rate in SbCl₃-10 mol % AlCl₃ at 100°C is greater than that in SbCl₃ at 130°C by about $1 \times 10^6$. These relative reactivities, the discovery that AlCl₃ is a much more active catalytic medium than SbCl₃ alone, and the product distributions can be explained by a mechanism in which the rate determining step involves the generation of a benzylic cation as the key reactive intermediate by hydride abstraction by SbCl₂⁺ in the melt.

This research provides new insights into the mechanism by which an aprotic molten salt medium catalyzes bond cleavage reactions for the α,ω-diphenylalkanes at temperatures substantially below those required for thermolysis.

This research, in which the substrates are not oxidizable to radical cations by Sb³⁺, represents our first observation of a reaction in which the Lewis acid function of the melt rather than the redox function plays the crucial catalytic role.

9.1.2 Reactivity of Anthracene in a Novel Room-Temperature Melt
(S. P. Zingg, A. S. Dworkin, Morten Sørlie, D. M. Chapman, A. C. Buchanan, G. P. Smith)

Studies of polycyclic aromatic hydrocarbons and hydroaromatics in anhydrous SbCl₃-based melts have shown these melts to be extremely active catalysts for a variety of hydrogen redistribution reactions at surprisingly low temperatures, 80-130°C. This research has revealed that SbCl₃ melts possess a previously unrecognized redox functionality and reactions have been observed which involve SbCl₃ as an oxidant in both a catalytic and stoichiometric fashion. The melts investigated previously have either been pure SbCl₃ or SbCl₃ with 1-10 mol % of added chloride ion donor such as KCl (basic) or chloride ion acceptor such as AlCl₃ (acidic). The added chloride donor or acceptor serves to reduce or increase, respectively, both the oxidizing power and the Lewis acidity of the melt. These melts are liquid above approximately 75°C.

The development by Osteryoung, et al. of binary room-temperature melts consisting of n-butyldipyrromidinium chloride (BPC) and AlCl₃ led us to prepare a ternary SbCl₃-rich melt (consisting of a fixed amount of SbCl₃ and varying amounts of BPC and AlCl₃) which is also molten at room temperature (25°C). These new room temperature melts consist predominantly of SbCl₃ (60 mol %), in order to retain its redox function, and varying amounts of AlCl₃ and BPC. The acidity of the melt can be varied by varying the AlCl₃:BPC ratio. SbCl₃, AlCl₃, and BPC were purified as previously described and stored in a controlled atmosphere dry box. The melts were also prepared in the dry box.

The ternary melts were found to be liquid at 25°C over a range of compositions (from a basic melt composed of 75:25 SbCl₃:BPC to an acidic 60:22:17 SbCl₃:AlCl₃:BPC melt). These melts were characterized by NMR, viscometry and density measurements. The electrochemical window was also determined for both acidic and basic melts and was found to be significantly wider than that of the SbCl₃-rich high temperature melts. This may be due to high overvoltage effects.

Because of the extensive investigation of the reactivity of anthracene in the SbCl₃-rich high temperature melts, anthracene was chosen as a model compound for investigation in the new room temperature melts. Reactions were followed in situ by UV spectroscopy, particularly the formation of protonated anthracene. After quench and separation, the organic products were analyzed by GC, GC-MS, UV and HPLC. Antimony metal was determined by AA.
spectroscopy. The effects of temperature, melt acidity, concentration and impurities such as \( \text{H}_2\text{O} \) on the reactivity of anthracene in the melt were also investigated.

In the room temperature ternary melts (\( \text{SbCl}_3\):\( \text{AlCl}_3\):\( \text{BPC} \)) the following results were obtained. For \( \approx 30 \text{ mM} \) anthracene at \( 25^\circ\text{C} \) in a \( 60:22:18 \) melt approximately 50-60% of the anthracene reacts in 23 hrs. The following products are formed: 15-20% protonated anthracene, 3-5% dihydroanthracene, 10-12% bianthryls, 2-5% anthra[2,1-a]aceanthrylene, 3-4% dihydroanthraaceanthrylene and a small amount of higher condensed materials. At higher concentrations (\( \approx 150 \text{ mM} \)), a larger portion (75-80%) of the anthracene reacts under the same conditions. The same products were observed but with an increase in the percentage of the dihydro and highly condensed products.

Previous studies have shown that the dissolution of anthracene in the aprotic liquid \( \text{SbCl}_3\cdot10 \text{ mol}\% \text{AlCl}_3 \) (\( \text{AlCl}_3\):anthracene >2) at 100-130°C results in the formation of stable solutions of protonated anthracene (anthracenium ion). The proton source is the condensation-dehydrogenation of a stoichiometric portion of the anthracene to give anthra[2,1-a]aceanthrylene. The reaction is driven by the reduction of \( \text{SbCl}_3 \). In neat, molten \( \text{SbCl}_3 \) anthracene undergoes a spontaneous catalytic disproportionation in which some of the anthracene molecules are condensed to larger aromatics liberating hydrogen which is quantitatively captured by unreacted anthracene molecules to form dihydro- and tetrahydro-anthracene.

In the room temperature melts, then, anthracene undergoes a combination of the stoichiometric and catalytic reactions. We have recently been able to observe this dual reaction behavior in low acidity high temperature melts (\( \text{SbCl}_3\):1-3 mol \% \( \text{AlCl}_3 \); \( \text{AlCl}_3\):anthracene \( <1 \)). The reactions are, however, much slower in the ternary melts at \( 25^\circ\text{C} \).

This investigation has demonstrated that the addition of BPC lowers the melting point and increases the electrochemical limits of the \( \text{SbCl}_3 \)-based melts; however, the redox and catalytic activity of the melt are maintained. Thus room temperature melts may prove to be effective media for studying the redox chemistry of arenes in \( \text{SbCl}_3 \)-rich molten salt catalysts especially via electrochemical and spectroelectrochemical techniques.

1. Guest scientist from the University of Tennessee, Knoxville, Tennessee.

9.1.3 Electrical Conductivity of Molten Mixtures of \( \text{SbCl}_3\)-\( \text{AlCl}_3 \) and \( \text{SbCl}_3\)-\( \text{AlCl}_3\)-\( \text{NaCl} \)


Previously we showed that the addition of \( \text{AlCl}_3 \) to \( \text{SbCl}_3 \) has a pronounced effect on its properties as a reaction medium. This behavior was rationalized in terms of the reaction

\[
\text{SbCl}_3 + \text{AlCl}_3 \rightarrow \text{SbCl}_2^+ + \text{AlCl}_4^- \quad (1)
\]

However, we know that \( \text{SbCl}_2^- \) is strongly solvated to \( \text{SbCl}_3 \) and under some circumstances may be solvated to \( \text{AlCl}_4^- \) so that an equilibrium between ionized and unionized forms might occur, thus

\[
\text{SbCl}_2(\text{AlCl}_4) + \text{SbCl}_3 \leftrightarrow \text{SbCl}_2^+ \cdot \text{SbCl}_3^- + \text{AlCl}_4^- \quad (2)
\]

Also we showed that at 220°C Raman shifts due to \( \text{AlCl}_4^- \) could not be detected in these melts. This suggested that reaction 2 might be strongly shifted toward the left, at least at this relatively high temperature. Since \( \text{SbCl}_3 \) and \( \text{AlCl}_3 \) melt to form nonconducting molecular liquids, and since ions are products of reactions 1 and 2, we investigated the electrical conductivity of \( \text{SbCl}_3\)-\( \text{AlCl}_3 \) mixtures to obtain more information on the entities formed when \( \text{AlCl}_3 \) is added to \( \text{SbCl}_3 \).
The experimental results, particularly the temperature dependence of conductivity, proved more complex than expected and suggested the possibility of conduction by Cl⁻ exchange. To obtain further information on this possibility we investigated the conductivities of SbCl₃-AlCl₃-NaCl mixtures.

The temperature dependence of the conductivities of 11 SbCl₃-AlCl₃ mixtures were measured. These melts contained 2.5-60.0 mol % AlCl₃. In general the dependence deviated from Arrhenius behavior and was represented quite accurately by the equation \( \ln \kappa = A_1 - A_2 T^{-1} - A_3 T^{1/10} \), where \( \kappa \) is the specific conductivity and \( A_1, A_2 \) and \( A_3 \) are adjustable parameters. For melts containing 2.5-30.0 mol % AlCl₃, deviations from Arrhenius behavior were large, and in the range 2.5-10.0 mol % AlCl₃ the conductivity passed through a maximum \( T_m \) as a function of temperature. At 2.5 mol % AlCl₃ the maximum occurred at 180°C with a specific conductivity of 0.00107 S cm⁻¹. Isothermal conductivity-composition curves passed through maxima that shifted from 0.042 S cm⁻¹ and 25 mol % AlCl₃ at 100°C to 0.092 S cm⁻¹ and 35 mol % AlCl₃ at 200°C. Conductivity as a function of temperature up to about 225°C was measured for SbCl₃-AlCl₃-NaCl melts containing 5.0-5.0, 10.0-5.0 and 10.0-10.0 mol % AlCl₃ and NaCl, respectively. It was found that at low temperatures the addition of NaCl to a SbCl₃-rich SbCl₃-AlCl₃ mixture results in a substantial conductivity decrease. These SbCl₃-AlCl₃-NaCl data argue strongly for a non-Stokesian chloride-exchange transport process in parallel with Stokesian conductivity.

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9.1.4 Depolarized Raman Scattering in Normal and Supercooled SbCl₃

(F. Aliotta,¹ G. Maisano,¹ H. Micali,¹ P. Migliardo,¹ C. Vasi,¹ F. Wanderlingh,¹ R. Triolo², G. P. Smith)

In a previous study we used Raman spectroscopy to investigate the temperature dependence of the intramolecular vibrations of SbCl₃ in the liquid state. These vibrations give rise to Raman shifts in the 250-450 cm⁻¹ region for the stretching modes and in the 100-200 cm⁻¹ region for the bending modes. In the present study we investigated the low-frequency region of 2-100 cm⁻¹ in an endeavor to learn more about intermolecular dynamics. Our measurements covered the temperature range from 20.2-180°C. At the low end of this range we were working with a supercooled liquid 53.2° below its normal melting point of 73.4°C. The exciting source was the 5145 Å line of an argon ion laser. The resolution was 0.4 cm⁻¹ in the 2-20 cm⁻¹ range and 2.5 cm⁻¹ in the 15-100 cm⁻¹ range. The data were normalized to the intensity of the incident beam, which was continuously monitored.

From an analysis of the anisotropic component of the spectrum we showed that in the 10-100 cm⁻¹ region there is a solid-like contribution to the intensity that furnishes an effective density of states. We interpret these collective excitations as arising from the chlorine bridge bonds that interconnect SbCl₃ molecules. Similar collective excitations have previously been observed in structured liquids including molten ZnCl₂, that we studied previously.

In the 2-20 cm⁻¹ range we found an anisotropic quasielastic contribution that is Lorentzian in shape. We attributed this contributor to fluctuations in the number of chlorine bridge bonds and used a simple thermodynamic model to interpret the temperature dependence. The results show that chlorine bond breaking is thermally activated. The binding energy was calculated to be 2.4 kcal mol⁻¹ while the reverse barrier height was found to be 0.7 kcal mol⁻¹.

1. Institute of Physics, University of Messina, Italy.
2. Institute of Chemical Physics, University of Palermo, Italy.
9.2 Low-Energy Alkali and Inert Gas Ion Scattering from Clean and Adsorbate-Covered Single Crystal Surfaces
(S. H. Overbury)

Important properties of any adsorbate/substrate system are the local bonding geometry of the adsorbate and the effect of the adsorbate upon the underlying solid substrate structure. A complete understanding of chemisorption and reactions on a model or technical catalytic surface requires a knowledge of the dynamic structure of the surface. Surface structure can be probed by analysis of energy and angular distributions of scattered ions. An apparatus has been built for preparing clean and adsorbate-covered surfaces in ultra-high vacuum and characterizing them by low energy electron diffraction (LEED) and Auger electron spectroscopy (AES) in addition to angle and energy resolved low energy alkali and inert gas ion scattering. Recent work has concentrated on the Mo(001) surface which was chosen not only because Mo and its oxides are extremely important catalytically, but because this surface is very reactive and exhibits many interesting chemisorption properties.

The ability to interpret ion scattering results obtained from a surface with molecular or atomic overlayers requires a firm understanding of the scattering from the clean surface. Ion scattering results were obtained under various conditions of incident energy and of incident and scattered angle for clean Mo(001) using Li⁺, K⁺ and He⁺. The Li⁺ results were most extensive and exhibited many interesting properties which have not been observed previously. Strong focusing effects, leading to enhanced scattered intensity along particular azimuthal directions, were observed and were found to be dependent upon incident energy. It was also found that the depth analyzed depends upon incident energy and azimuth, so that under some conditions only scattering from first layer atoms is obtained while at other conditions scattering from second or third layer atoms may contribute or even dominate the spectrum. These conclusions were obtained from detailed analysis of computer simulation results and from comparison of the calculated energy distributions with those observed experimentally as shown in Fig. 9.1. The computer simulation was performed by assuming an unreconstructed perfect termination of the bulk structure. This comparison allowed

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![Figure 9.1](image-url)

Fig. 9.1. Experimental (point) and computed (histogram) energy distributions of Li⁺ backscattered from clean Mo. The three different figures correspond to three different azimuthal angles of incidence.
various model parameters in the simulation program to be set, and qualitative agreement was obtained between experimental and simulated distribution. In addition, the most prominent aspects of the azimuthal angle dependence were reproduced by the simulation. In \( \text{K}^+ \) scattering from clean Mo(001), similar focusing effects were observed and reproduced by computer simulation, but there was still some disagreement between computed and experimental distribution. Although the cause of this discrepancy is not yet fully determined, it seems likely to be due to either incomplete consideration of the surface response to the energetic incident ion, or to the presence of defects on the surface. \( \text{He}^+ \) scattering from clean Mo(001) was also investigated and, as found in previous studies of inert gas ion scattering,\(^4\) neutralization occurs with high probability which results in distorted energy distributions and makes comparison with computer simulation results difficult or impossible.

Because of the importance of understanding the effects of adsorbed oxygen on the co-adsorption of other molecules on the Mo(001) surface, the adsorption of \( \text{O}_2 \) was studied using \( \text{K}^+, \text{Li}^+, \text{He}^+ \) scattering. The adsorption was studied as a function of oxygen coverage and substrate temperature of adsorption. The adlayer was characterized by AES and LEED to allow correlation between the ion scattering results and other published results. Very strong oxygen induced changes in the ion scattering spectrum were observed during the adsorption of the first monolayer (ML). Analysis of the backscattered ion energy distribution indicates that at 1100 K the first ML of oxygen adsors on top of the surface at the four-fold hollow of the Mo(001) surface. Principle evidence for this is the oxygen induced decrease in intensity when the scattering plane contains the [100] azimuth. A second key evidence shown in Fig. 9.2, is that oxygen adsorption causes the high energy double scattering peak present in the clean surface spectrum to be strongly attenuated relative to the lower energy single scattering peak. Also, this single scattering peak is shifted toward higher energy. These facts are expected on the basis of qualitative arguments and can be reproduced by computer simulation if the oxygen adatoms are located at the four-fold sites. The computer simulation also determined that the oxygen adatoms have a vertical height above the surface of between 0 and 0.9 Å. Analysis of computed and experimentally observed dependence of \( \text{Li}^+ \) scattering intensity upon polar angle of incidence more precisely indicated that the oxygen is about 0.3 Å above the surface. The energy distributions observed for adsorption at 400 K are broader and have larger background intensity at low energies and between peaks. The cause for this effect is still not clearly understood, although it seems to correlate with
more poorly defined LEED patterns observed under these conditions. At higher exposures, greater than 1.0 ML of oxygen can be adsorbed at 1100 K. For coverages above 1.0 ML the K⁺ energy distributions are roughly unaffected by further oxygen exposures except for gradual and continuous decrease in the intensity of the sharp scattering peaks relative to the broad background. This indicates that the oxygen is penetrating below the surface as is consistent with the surface faceting observed by LEED and with oxide formation.

Other adsorbates have also been studied using the same basic ion scattering techniques. Similar to the case for oxygen, the adsorption of CO and of C₂H₄ is dissociative, so adsorption of these molecules results in overlayers of oxygen and carbon atoms. These overlayers gave scattered K⁺ energy distributions which were very similar to those obtained from pure oxygen overlayers as shown in Fig. 9.2. Energy distributions are shown for about .73 ML of carbon obtained by a 20 Langmuir (L) exposure to C₂H₄ (the hydrogen desorbs), for .70 ML of oxygen and for a mixture of 0.5 ML carbon and 0.5 ML oxygen obtained by 20 L exposure to CO. The small differences between the resulting energy distributions are principally due to differences in coverage. These results indicate that both carbon and oxygen atoms adsorb or co-adsorb at four-fold sites. From the shape of the incident angle dependence of Li⁺ scattering, it was found that adatoms obey a simple site filling model. Therefore, the different LEED patterns obtained for these overlayers are due only to differences in long range ordering in the overlayer. The height of the carbon and oxygen atoms above the surface are roughly equal as determined from analysis of the incident angle dependence.

Measurement of the dependence upon oxygen exposure of the intensity of various scattering features led to interesting conclusions about neutralization of ions scattered from adsorbate covered surfaces. Neutralization of the probe ions is a serious and poorly understood complication in the analysis of inert gas ion scattering results. The intensity of the spectral feature corresponding to He⁺ single scattered from Mo surface atoms was found to always decrease sharply with increasing oxygen exposure and to slowly level off at higher exposures. This behavior has been reported elsewhere in the literature with other surface and adsorbate combinations and has been attributed to geometric blocking of the scattering by the adsorbate. However, quite different behavior is observed for Li⁺ and K⁺ scattering from the Mo(001) surface as a function of oxygen exposure even though the surface geometry is identical. These results show for the first time that the intensity decrease observed in He⁺ scattering is due to adsorbate induced changes in the neutralization probability of the He⁺ ions. In this way, direct comparison of the alkali and inert gas ion scattering has improved current understanding of the ion scattering process and the use of scattered ions as a probe of chemisorption.

10. CHEMICAL PHYSICS

This Section describes recent research in the areas of structural chemistry, photoelectron spectroscopy, and electron spin resonance spectroscopy.

In order to develop any meaningful model for understanding and predicting the chemical or physical properties of a substance, it is necessary to have a detailed knowledge of its structure at the atomic or molecular level. The structural chemistry program includes the experimental determination of this information by using the techniques of x-ray and neutron diffraction and the development of computational methods for interpreting the results. The work described below involves the crystallographic determination of the molecular structures of two new inorganic compounds, the modeling of the structures of fundamental rock-forming minerals, and an experimental study of ionic hydration in aqueous solutions.

The range of fundamental information concerning atoms and molecules which can be derived from photoelectron spectroscopy has been greatly broadened by the use of a range of excitation-energies available from a synchrotron source. A very prolific collaboration in this area has developed among ORNL and the Universities of Wisconsin and Tennessee. A selection of recent results is discussed below with particular emphasis on the Cooper minima in molecules, shape resonances, and free atoms. The experimental results provide a stringent test of current theory.

Work has continued on the application of high-temperature electron spin resonance to the study of pyrolytic organic reactions. Section 10.3.1 typifies the degree of quantitative kinetic information which can be obtained in free-radical processes. The studies of jet fuel stability described in Section 10.3.2 apply the same methodology to a problem supported by NASA.

10.1 Structural Chemistry

10.1.1 Novel Structural Features in Two New Binuclear Molybdenum Carbonyl Complexes Stabilized by Strong π-Acceptor Ligands: An Unexpected Mo-Cl-Mo Bridge and a New Tridentate Ligand, PF₂-N(C₆H₅)-PF-N(C₆H₅)-PF₂

(Leonard M. Brown)

The work described here is a continuation of research reported previously relating to the coordination properties of strong π-acceptor ligands, which are of interest relative to the design of homogeneous catalysts. Two molybdenum coordination compounds of unknown structure prepared in the laboratory of Professor R. B. King at the University of Georgia were subjected to single-crystal x-ray structure analysis, and their structures were found to exhibit the novel and unexpected features mentioned in the title above. Table 10.1 shows the formula, the unit-cell data, and the final discrepancy index R(F) for each compound.

Table 10.1. The molybdenum complexes studied and their crystal data

<table>
<thead>
<tr>
<th>Compound</th>
<th>Space Group</th>
<th>Mo-C₁</th>
<th>Mo-C₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>P₂₁/C</td>
<td>17.453 (7)</td>
<td>11.498 (3)</td>
</tr>
<tr>
<td>2</td>
<td>P₂₁/C</td>
<td>9.718 (2)</td>
<td>19.521 (5)</td>
</tr>
<tr>
<td>3</td>
<td>P₂₁/C</td>
<td>14.568 (5)</td>
<td>21.713 (5)</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>107.21 (2)</td>
<td>101.08 (1)</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>R(F)</td>
<td>0.028</td>
<td>0.036</td>
<td></td>
</tr>
</tbody>
</table>

*The symbol X denotes an unidentified atom (see text).

Compound 1. This dark brown-red compound was found to have the binuclear structure shown in Fig. 10.1. The structure is unusual in that the two Mo atoms are bridged by two CH₃PF₂ groups, by a PF₂ group, and by a Cl⁻ ion.
Since compound 1 was prepared by reaction of \textit{fac-}(\textit{CH}_3\textit{CN})_3\textit{Mo(CO)}_3\textit{ with the bidentate strong }\pi\textit{-acceptor ligand }\textit{CH}_3\textit{N(PF}_2\textit{)}_2\textit{, the presence of the bridging }\textit{CH}_3\textit{N(PF}_2\textit{)}_2\textit{ groups was no surprise. Not surprising either, though not predicted, was the presence of the PF}_2\textit{ bridge and the atom group CH}_3\textit{NPF}_2\textit{ (eventually shown to be protonated at }\textit{N})\textit{ on one of the Mo atoms. The PF}_2\textit{ and CH}_3\textit{NPF}_2\textit{ groups evidently result from cleavage of a CH}_3\textit{N(PF}_2\textit{)}_2\textit{ molecule; they have been }\textit{known previously to appear under similar conditions and to function similarly as ligands in the compound }\textit{[u-CH}_3\textit{N(PF}_2\textit{)}_2\textit{]}_3\textit{(u-PF}_2\textit{)}\textit{-Fe}_2\textit{(CH}_3\textit{NPF}_2\textit{)}\textit{(CO)}\textit{.}^{3}

The presence of a chlorine atom in compound 1 is a totally unexpected result, since the reaction mixture that produced 1 was not known to contain chlorine atoms in either reactants or solvent. Chemical analysis confirmed the presence of the chlorine in 1, and the last stage of the x-ray analysis showed the presence of the necessary accompanying hydrogen atom on atom N(3) of the CH}_3\textit{NPF}_2\textit{ group. The latter finding explained what had been a puzzling feature of the infrared spectrum of the compound, namely, a sharp band at 3430 cm\textsuperscript{-1}\textit{ suggesting an N-H stretching frequency. The HCl in 1 had its origin as an impurity in the CH}_3\textit{N(PF}_2\textit{)}_2\textit{ used in the preparation.}

The elucidation described here of the stoichiometry and structure of compound 1 has led to a deliberate synthesis of the compound by a different method with about 50% yield.\textsuperscript{2}

The distance Mo(1)-Mo(2) in 1 is 2.975(1)Å, considerably longer than the distance of \textasciitilde2.6 Å characteristic of a single Mo-Mo bond. The
distances Mo(1)-Cl and Mo(2)-Cl in 1 are 2.529
and 2.531 Å, normal values for Mo-Cl-Mo bridge
bonds.

**Compound 2.** This yellow compound has the
structure shown in Fig. 10.2. The structure
determination leaves unidentified the atoms
labeled "X" in the formula in Table 10.1 and
in Fig. 10.2 but is satisfactory so far as the
remainder of the structure is concerned. The
ligand containing the X atoms appears to be a
disordered triatomic unidentate ligand coor­
dinated to atom Mo(2) through a phosphorus atom
[P(10) in Fig. 10.2].

**Compound 2** is, like 1, a quadruply bridged
binuclear complex. There are three bridging
\(\text{C}_6\text{H}_5\text{N(PF}_2\text{)}_2\) ligands. The fourth bridge is
produced by coordination of one terminal P
atom and the central P atom of a tridentate
ligand, \(\text{F}_2\text{P-N(}\text{C}_6\text{H}_5\text{)}_2\text{-PF-N(}\text{C}_6\text{H}_5\text{)}_2\text{-PF}_2\). The other
terminal P atom of this ligand also coordinates
to the Mo atom linked to the central P, so that
a four-membered chelate ring is present. The
tridentate ligand is easily discerned in Fig.
10.2; it contains atoms P(7), P(8), and P(9).

Atom Ho(1) is included in the chelate ring.

It is the presence of the tridentate ligand
in compound 2 that is the most interesting
structural result, because it is a ligand not
previously known. Compound 2 was prepared by
thermal decarbonylation of \(\text{[C}_6\text{H}_5\text{N(PF}_2\text{)}_2\text{-Mo-
(CO)}_3\text{]}\), a type of reaction used to produce a
variety of binuclear complexes of transition
metals having \(\text{Ru(PF}_2\text{)}_2\) bridges (R = Me, Ph).

Evidently two molecules of \(\text{C}_6\text{H}_5\text{N(PF}_2\text{)}_2\) condense
to \(\text{F}_2\text{P-N(}\text{C}_6\text{H}_5\text{)}_2\text{-PF-N(}\text{C}_6\text{H}_5\text{)}_2\text{-PF}_2\), losing a mole­
cule of \(\text{PF}_3\) in the process. The tridentate
ligand \(\text{P[N(}\text{C}_6\text{H}_5\text{)}_2\text{]}_3\) was already known to be
produced similarly from three molecules of
\(\text{C}_6\text{H}_5\text{N(PF}_2\text{)}_2\).

The Mo(1)-Mo(2) separation in compound 2 is
3.200(1) Å, indicating much less electronic
interaction between the two Mo atoms than be­
tween those in 1, consistent with the lighter
color of 2.

1. (a) G. M. Brown and J. E. Finholt, Chem.
10.1.2 Calculation of the Elastic Constants for the Olivine and Spinel Forms of Mg₂SiO₄ (M. Matsui, M. R. Busing)

Matsui and Matsumoto¹ (MM) have developed a computational model for the olivines including Mg₂SiO₄, forsterite, which reproduces the observed structure quite well. Their atom-atom potential includes an r⁻¹² repulsion and Coulomb terms with charges of +2, +2.28, and -1.57 e for Mg, Si, and O, respectively. Structural variables include 3 lattice parameters, 2 translations for Mg(2), and 2 translations and 1 rotation for the rigid SiO₄ group. Other parameters conform to the orthorhombic space group Pbnm. Table 10.2 compares the observed structure² and calculated structures for this model and another model mentioned below.

External normal forces or shearing forces can be simulated in a computational model by minimizing the total energy of the crystal and the force-producing device. For a normal tension σ₁ along a, the extra energy term is proportional to -σ₁a₁. The resulting structure has a larger a and smaller b and c. The elastic compliance constants s₁₁ can be computed from σ₁/a₁ = s₁₁a₁, σ₁b₁ = s₁₂b₁, etc.

For a shear σ₁ about b, the extra energy term is proportional to σ₁b₁. Minimizing the total energy, assuming monoclinic space group P2₁/a, produces a structure with c = 90°, and the compliance constant s₅₅ = d₅/σ₅ can be computed. In similar ways the 9 independent elastic constants for an orthorhombic crystal are obtained. In practice 2 to 4 values are used for each σ₁ so that s₁₁ at zero stress can be computed by interpolation.

Table 10.2. Observed and calculated structures of magnesium olivine (forsterite). Calc I is based on the model of MM; Calc II results from the present work. The net translation of Mg₂ or Si is given by t, and the rotation of SiO₄ by θ.

<table>
<thead>
<tr>
<th></th>
<th>Obs²</th>
<th>Calc I</th>
<th>Δ(t)</th>
<th>Calc II</th>
<th>Δ(t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a/A</td>
<td>4.75</td>
<td>4.75</td>
<td>0.0</td>
<td>4.54</td>
<td>-4.4</td>
</tr>
<tr>
<td>b</td>
<td>10.19</td>
<td>10.22</td>
<td>0.3</td>
<td>10.37</td>
<td>1.8</td>
</tr>
<tr>
<td>c</td>
<td>5.98</td>
<td>5.97</td>
<td>-0.2</td>
<td>6.16</td>
<td>3.0</td>
</tr>
<tr>
<td>V/A³</td>
<td>289.6</td>
<td>289.7</td>
<td>0.0</td>
<td>290.5</td>
<td>0.3</td>
</tr>
<tr>
<td>t(Mg2)/A</td>
<td>0</td>
<td>0.03</td>
<td>0.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>t(Si)</td>
<td>0</td>
<td>0.03</td>
<td>0.05</td>
<td></td>
<td></td>
</tr>
<tr>
<td>θ(SiO₄)/°</td>
<td>0</td>
<td>0.07</td>
<td>0.13</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 10.3. Observed and calculated compliance constants for magnesium olivine (forsterite). Calc I is for the model of MM; Calc II is based on the present work. Units are kbar⁻¹ x 10⁶.

<table>
<thead>
<tr>
<th></th>
<th>Obs²</th>
<th>Calc I</th>
<th>Calc II</th>
</tr>
</thead>
<tbody>
<tr>
<td>s₁₁</td>
<td>336</td>
<td>112</td>
<td>342</td>
</tr>
<tr>
<td>s₁₂</td>
<td>584</td>
<td>244</td>
<td>518</td>
</tr>
<tr>
<td>s₂₂</td>
<td>494</td>
<td>199</td>
<td>557</td>
</tr>
<tr>
<td>s₁₃</td>
<td>-82</td>
<td>-23</td>
<td>-79</td>
</tr>
<tr>
<td>s₂₃</td>
<td>-158</td>
<td>-70</td>
<td>-183</td>
</tr>
<tr>
<td>s₃₃</td>
<td>1503</td>
<td>748</td>
<td>1306</td>
</tr>
<tr>
<td>s₅₅</td>
<td>1230</td>
<td>430</td>
<td>1025</td>
</tr>
<tr>
<td>s₅₆</td>
<td>1234</td>
<td>568</td>
<td>1430</td>
</tr>
</tbody>
</table>
Those computed from the model of MM are too small by a factor of two or more, indicating that this model is too stiff. A new potential energy expression has now been derived (using an exponential repulsion) which reproduces the experimental elastic constants reasonably well. The new results are also given in Table 10.3. Table 10.2 shows that the structure predicted using the new potential is not quite so good as that obtained by MM.

Both potential energy models have now been used to calculate the structure and elastic constants of cubic Mg-spinel, and the results are given in Table 10.4. The MM model again

<table>
<thead>
<tr>
<th></th>
<th>Calc</th>
<th>Calc II</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal structure</td>
<td>Obs</td>
<td>a(5)</td>
</tr>
<tr>
<td>a/a</td>
<td>8.06</td>
<td>8.06</td>
</tr>
<tr>
<td>Mg-O/a</td>
<td>2.07</td>
<td>2.07</td>
</tr>
<tr>
<td>Compliance constants</td>
<td>371</td>
<td>102</td>
</tr>
<tr>
<td>$s_{12}$/Nbar$^{-1}$</td>
<td>-94</td>
<td>-24</td>
</tr>
<tr>
<td>$s_{44}$</td>
<td>794</td>
<td>283</td>
</tr>
</tbody>
</table>

produces a good structure but poor elastic constants. The revised potential produces reasonably good elastic constants if the model is constrained to be centrosymmetric. If this constraint is relaxed, however, the cubic structure appears to be unstable. It is hoped that an improved potential will eliminate this problem.


## 10.1.3 Direct Determination of Ionic Solvation from Neutron Diffraction

(A. H. Marten, R. L. Hahn)

In order to understand and predict the properties of electrolyte solutions it is necessary to know what the entity called an ion is — that is, whether it is the bare ion, or whether it carries with it water molecules sufficiently firmly bound to be regarded as part of the ion and, if so, how many such water molecules are involved. A traditional approach has been to infer these hydration numbers from measurements of bulk thermodynamic and transport properties that are predominantly determined by ion-water interactions. Other techniques, such as nuclear magnetic resonance and Raman infrared spectroscopy, have also been used in this way. In many instances the numbers thus obtained vary greatly with the experimental approach and with the method used to analyze and interpret the data.¹

It has now become clear that these difficulties in probing the ion-water interactions directly at the molecular level can be overcome by diffraction studies. Defining ion-water interactions as the positional and orientational correlations between ion-water pairs in solution, we have a measurable quantity, the diffraction pattern, from which these correlations can be determined. Ionic solutions were among the first liquids to which x-ray diffraction was applied, and a large number of studies have been reported over the years.² However, the interpretation of a single diffraction pattern is always difficult, often ambiguous, and never unique. This ambiguity of interpretation can be eliminated by measuring the neutron diffraction...
patterns from several ionic solutions that are identical in all respects except the isotopic state of one of the ions. The algebraic difference between any two sets of measurements then yields the ion-water correlations. In order to obtain sufficiently good statistics for the differences, very large numbers of neutrons have to be counted. Hence, the method is at present limited to the study of relatively concentrated solutions (> 1 molal), and the results may not be representative for the dilute regime.

We measured the neutron diffraction patterns of four neodymium trichloride solutions in D$_2$O (Table 10.5). The experiments were carried out at the High Flux Isotope Reactor. We discuss here only the main results of our study.

The neutron cross sections of the $^{144}$NdCl$_3$ solution (having the smallest scattering factor; see Table 10.5) were subtracted from those of the other three solutions to yield three difference curves, from which a structure function was extracted, namely

$$H^{\text{Nd}}(k) = 0.279H^{\text{NdO}}(k) + 0.079H^{\text{NDCl}}(k)$$

where $k = (4\pi/\lambda)\sin \theta$, $\lambda = 0.89$ Å being the neutron wavelength and $2\theta$ the scattering angle.

The numerical coefficients in Eq. 1 depend only on the neutron scattering factors and the concentrations of the nuclides in the solutions.

Table 10.5. Neutron-scattering factors ($f$) of the Nd-nuclei in the four 2.85 molar solutions studied by neutron diffraction.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Abundance (%)</th>
<th>$f$ (10$^{-12}$ cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{144}$Nd</td>
<td>57.51</td>
<td>0.31</td>
</tr>
<tr>
<td>nat Nd$^*$</td>
<td></td>
<td>0.72</td>
</tr>
<tr>
<td>$^{142}$Nd</td>
<td>97.55</td>
<td>0.78</td>
</tr>
<tr>
<td>$^{146}$Nd</td>
<td>97.63</td>
<td>0.87</td>
</tr>
</tbody>
</table>

*Natural abundance.

The functions $\hat{h}_{ij}(k)$ are the Fourier transforms of the atom-pair correlation functions $h_{ij}(r) = g_{ij}(r) - 1$, where the atom pair distribution functions $g_{ij}(r)$ measure the probability of finding a $j$ atom at a radial distance $r$ from an $i$ atom in the solution.

Fourier transformation of the function $H^{\text{Nd}}(k)$ derived from experiment yields an average radial distribution function, namely

$$G^{\text{Nd}}(r) = 0.279g^{\text{NdO}}(r) + 0.642g^{\text{NdD}}(r) + 0.079g^{\text{NDCl}}(r)$$

which contains the desired information on the ion-water interactions in the functions $g^{\text{NdO}}(r)$ and $g^{\text{NdD}}(r)$. The function $g^{\text{Nd}}(r)$ is shown in Fig. 10.3.

The maxima in the function $G^{\text{Nd}}(r)$ derived from experiment correspond to the most frequent Nd-O, Nd-O, and Nd-Cl distances in the solution. The first two pronounced maxima at 2.48 and 3.13 Å must be ascribed, respectively, to Nd-O and Nd-Cl interactions. This is because the areas under these peaks, which are related to the number of atoms at these relative positions, have a ratio of ~ 1:2. The area under the peak at 2.48 Å corresponds to 8.6 oxygen atoms, and the area under the peak at 3.13 Å to 16.7 deuterium atoms around a neodymium ion. Taking the average (8.6 ± 16.7/2)/2 as the best estimate of the number of water molecules around the ion, we obtain a coordination number of 8.5 ± 0.2. These numbers, together with the sharpness of the first two peaks in Fig. 10.3, show that the Nd$^{3+}$ ion has a very well-defined first hydration sphere with the deuterium atoms pointing away from the ion at a tilt angle $\approx 55^\circ$, as shown in Fig. 10.4.

This picture is, of course, an average one; at any instant an average Nd$^{3+}$ ion "sees" the water molecules in its primary hydration sphere as indicated in Fig. 10.4. The residence time of these molecules is finite, but may be as long as 10$^{-6}$ second.

We emphasize that these distances and coordination numbers should be regarded as direct measurements, no assumptions or models being
Fig. 10.3. Radial distribution of water molecules around the Nd\(^{3+}\) ion in a 2.85 molal solution of NdCl\(_3\) in D\(_2\)O. The peaks at 2.48 and 3.13 \(\AA\) correspond to 8.6 oxygen and 16.7 deuterium atoms from 8.5 \(\pm\) 0.2 water molecules in the first hydration sphere.

Fig. 10.4. Arrangement of a water molecule in the first hydration sphere of a cation, M\(^{n+}\), in solution. There are 8.5 such molecules around Nd\(^{3+}\), and the tilt angle is 55°.

used in the analysis of the neutron data. This method avoids the difficulties encountered in other experimental techniques; the primary hydration sphere is precisely defined in terms of the number of water molecules involved and their average distance from the cation. The 8.5 water molecules are sufficiently firmly bound to be regarded as part of the Nd\(^{3+}\) ion in statistical mechanical calculations of the properties of these solutions.6

3. A short summary of this work has been published in Science 217, 1033 (1982); the full report has been submitted to J. Phys. Chem.
5. In a recent x-ray diffraction study by A. Habenschuss and F. H. Spedding [J. Chem. Phys. 70, 3758 (1979)] a coordination number of 8.9 water molecules at a...
distance of 2.51 Å from the neodymium ion was obtained by fitting the total radial distribution function with five Gaussian distributions.


10.2 Photoelectron Spectroscopy with the Use of Synchrotron Radiation

10.2.1 Photoelectron Dynamics of Free Molecules and Atoms

(T. A. Carlson, M. O. Krause, A. Rahiman, J. W. Taylor, P. R. Keller, M. N. Piancastelli, F. A. Grimm, T. A. Whitley)

A comprehensive study of the photoelectron dynamics of atoms and molecules is in progress. This study is being carried out through measurements using angle resolved photoelectron spectroscopy together with synchrotron radiation, provided by the Synchrotron Radiation Center, Stoughton, Wisconsin. Data are obtained on the partial cross sections and angular distribution parameters, $s$, for the individual valence and core shell orbital, as a function of photon energy. For randomly orientated gas phase molecules the $s$ parameter is determined from

$$\frac{\partial \sigma}{\partial \Omega} = \sigma \left[ 1 + \frac{1}{4} [3P \cos 2 \theta + 1] \right]$$

where $P$ is the degree of polarization of the synchrotron light, and $\theta$ is the angle between the direction of ejected photoelectron and the polarization vector.

The scope of the program is illustrated in Table 10.6 which lists the studies that have been pursued on molecules and rare gases since the last report. In addition, work on metal vapors will be discussed in the following report. The work spans research from small molecules to more complex heterocyclic compounds. Phenomenologically, investigations have included shape resonances, core shell effects, Cooper minima, autoionization and satellite structure.

In order to cover the extensive research required for this program, a collaboration has been set up between scientists at ORNL and the Universities of Wisconsin and Tennessee. Research is currently being carried out on two electron spectrometers designed for synchrotron radiation studies, one built at ORNL and a second constructed at Wisconsin. In the near future a beam line designed especially for gas phase studies, which will accommodate both spectrometers, will be put into operation at the recently completed storage ring, Aladdin, also at Wisconsin. To assist in the interpretation of the experimental data, a theoretical program for calculating cross sections and $s$ values has been put into operation at the University of Tennessee, and a close interweaving of theory and experiment is being achieved.

It would be too lengthy to cover in detail all the material suggested in Table 10.6. Thus, only two topics of particular importance and current interest will be explored: Cooper minimum and shape resonances.

**Cooper minimum in molecular orbitals.** The Cooper minimum, which is a minimum in the photoelectron cross section as a function of photon energy, has been known for some time in atomic physics. An atomic orbital, which possesses a radial node, can show a Cooper minimum if in the calculation of the photoelectron cross section a radial matrix element describing a transition to one of the permissible continuum channels changes sign as a function of photoelectron energy. In addition to the cross section, the $s$ values are also strongly affected and experimentally undergo changes near the Cooper minimum, which are often more susceptible to experimental measurement than the partial cross sections.

Reasoning that the Cooper minimum should also take place within molecular orbitals, we have made for the first time a systematic study of this phenomenon for the valence shell of molecules. Cooper minima have been experimentally
Table 10.6. Summary of Studies on Angle-resolved Photoelectron Spectroscopy of Molecules and Rare Gas Atoms Using Synchrotron Radiation

<table>
<thead>
<tr>
<th>Molecules</th>
<th>ORNL Spectrometer</th>
<th>Special Features</th>
<th>MSXa Calculations</th>
<th>Photon Energies (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>X</td>
<td>X</td>
<td>Cooper Minimum</td>
<td>X</td>
</tr>
<tr>
<td>HBr</td>
<td>X</td>
<td>X</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>HI</td>
<td>X</td>
<td>X</td>
<td>Cooper Minimum, 4d, 5s core shells</td>
<td>X</td>
</tr>
<tr>
<td>CH₃I</td>
<td>X</td>
<td>X</td>
<td>Cooper Minimum, 4d, 5s core shells</td>
<td>X</td>
</tr>
<tr>
<td>Cl₂</td>
<td>X</td>
<td>X</td>
<td>Cooper Minimum</td>
<td>X</td>
</tr>
<tr>
<td>N₂O</td>
<td>X</td>
<td>X</td>
<td>Shape resonances, autoionization</td>
<td>X</td>
</tr>
<tr>
<td>C₂H₂Cl₂</td>
<td>X</td>
<td>X</td>
<td>Cooper Minimum</td>
<td>X</td>
</tr>
<tr>
<td>C₃H₆</td>
<td></td>
<td></td>
<td>Jahn-Teller Splitting</td>
<td>X</td>
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<tr>
<td>Cl₂C≡CCl₂</td>
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<td></td>
<td>θ dependence for π orbitals</td>
<td></td>
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<tr>
<td>F₂C≡CF₂</td>
<td>X</td>
<td></td>
<td>θ dependence for π orbitals</td>
<td></td>
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<tr>
<td>Cyclopentene</td>
<td></td>
<td></td>
<td>θ dependence for π orbitals</td>
<td></td>
</tr>
<tr>
<td>Butadiene</td>
<td>X</td>
<td></td>
<td>θ dependence for π orbitals</td>
<td></td>
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<tr>
<td>Methyl Acetylene</td>
<td>X</td>
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<td>θ dependence for π orbitals</td>
<td></td>
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<tr>
<td>Azabenzene (5)</td>
<td>X</td>
<td></td>
<td>θ dependence for π and nitrogen non-bonding orbitals</td>
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<tr>
<td>CF₄</td>
<td></td>
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<tr>
<td>SiCl₄</td>
<td></td>
<td></td>
<td>Shape resonance</td>
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<tr>
<td>GeCl₄</td>
<td></td>
<td></td>
<td>Shape resonance</td>
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</tr>
<tr>
<td>TiCl₄</td>
<td></td>
<td></td>
<td>Shape resonance, autoionization</td>
<td></td>
</tr>
<tr>
<td>HCHO</td>
<td>X</td>
<td></td>
<td>θ dependence on orbital types</td>
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<tr>
<td>CH₃OH</td>
<td>X</td>
<td></td>
<td>θ dependence on orbital types</td>
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</tr>
<tr>
<td>Kr</td>
<td>X</td>
<td>X</td>
<td>Cooper Minimum in 5s Shell</td>
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<tr>
<td>Xe</td>
<td>X</td>
<td>X</td>
<td>Cooper Minimum in 5s Shell</td>
<td></td>
</tr>
</tbody>
</table>

*Research carried out by ORNL members and their collaboration at the Synchrotron Radiation Center (Tantalum I) Stoughton, Wisconsin since August 1981.*
investigated for the following molecules: 
CS$_2$, COS, CCl$_4$, Cl$_2$, HCl.
CCl$_2$CH$_2$, CH$_3$Br, HI and CH$_3$I. Parallel calculations using the multiple scattering $X_a$

method have been carried out on CS$_2$, COS, CCl$_4$, Cl$_2$, HCl, HBr & HI.

Typical results are to be seen in Fig. 10.5 for HCl. The lone pair orbital (which in the

Fig. 10.5. Effects of the molecular Cooper minima on the $\beta$ values for HCl. The upper plot is for experimental data, the lower plot are calculations based on MSXa theory. (Ref. 5).
case of HCl is the 2s) behaves closely like its atomic counterpart. (See, for example, the results\(^9\) on the 3p orbital of Ar which is isoelectronic with HCl.) The \(\beta\) values obtained from the 5 orbital also show a dip at about the same energy. However it is considerably more shallow and broader. Comparison between theory and experiment shows that the MS\(X\) method does an excellent job in predicting the general properties of the Cooper minimum. Quantitatively, it predicts the Cooper minimum about 7 to 8 eV below experiment. However, this magnitude of error is also found in atomic calculations\(^10\) on argon using a Hartree-Slater potential, which is the same order of approximation employed in the MS\(X\) method.

Examination of the calculations in more detail, both the MS\(X\) calculations and published cross sections using a Hartree-Fock model, gives us a closer insight into the nature of the Cooper minimum in molecules. Specifically, the photoelectron dynamics of the 2s is more atomic-like than the 5s. At the Cooper minimum for the 2s orbital, a contribution of 99% comes from the \(k\) continuum channel, while in contrast, the photoionization of the 5s orbital derives a contribution from the \(k\) continuum channel, which even though it goes through a minimum is never less than 80% of the \(k\) continuum channel. It is hoped that in the future, experimental data on the Cooper minimum will provide a useful criterion for understanding more complex molecular systems, both as to the nature of the photoionization process and the makeup of the original molecular orbitals.

**Cooper minimum in the 5s shell of Xe and CH\(_3\)I.** Photoelectron studies of the outer s-subshell using synchrotron radiation excitation give a sensitive test of the importance of a proper treatment of relativistic and correlation effects in atomic theory. In the nonrelativistic approximation, the angular asymmetry parameter \(\alpha\) is required to take the value of \(+2\) independent of photon energy since there is only one channel open for the photoelectric process. However, when relativistic effects are involved, at least two channels exist for the photoelectric process, leading to a variation of the value of \(\alpha\), especially close to a Cooper minimum. Early experiments\(^11\) on the \(\beta\) values of Xe suggested that the relativistic random phase approximation (RRPA) gave a good account\(^12\) of this phenomenon. It was hoped that the effects of the Cooper minimum would also be seen in molecular systems containing iodine (Xe is isoelectronic with I\(^-\)).

Careful examination\(^13\) of the \(\beta\) values and cross sections for the 5s subshell of Xe, taking into account the interference of Auger processes and second order radiation, revealed that, in fact, experiment is not in good agreement with theory (see Fig. 10.6). Results on the 5s subshell in CH\(_3\)I mimic the behavior of Xe 5s. The Cooper minimum in the 5s subshell is a highly sensitive test of relativistic many-body theory, and it appears that still more sophisticated theoretical calculations are required.\(^14\)

**Shape resonance.** Shape resonances can create distinctive change in the cross section and \(\beta\) values measured as a function of photon energy. This behavior can be used as another test of our understanding of photoelectron dynamics and as a measure of the nature of the molecular potential for molecules undergoing such resonances. A shape resonance arises from an electron being excited into a quasibound electronic state supported by a potential barrier. In molecules this barrier can be a centrifugal molecular potential. Shape resonances can be predicted within the framework of a single electron model, such as the multiple scattering \(X\) method. Experimentally, shape resonances are seen as broad peaks when partial photoionization cross sections are plotted against photon energy. In addition, the angular distribution parameter is strongly affected by a shape resonance. The behavior of the vibrational structure is sensitive to the presence of shape resonances. This has been evident, for example, in nitrogen for both
the branching ratios and variations in $\beta$ values.\textsuperscript{15,16} The effect on the vibrational structure arises from the fact that the shape resonance itself is strongly dependent on the internuclear distance. The effect on vibrational structure can be felt at a considerable distance in photon energy from the point where the resonance occurs.

We previously have reported\textsuperscript{17} on the well-defined behavior of a shape resonance in the photoionization of the $4g_2$ orbital of CO$_2$. In the photoionization of N$_2$O, shape resonances were also discovered\textsuperscript{18} for the $7\sigma$ and $6\sigma$ orbitals. In Fig. 10.7, the distinct minimum is due to a shape resonance. The calculated position of the minima is sensitive to, among other things, the choice of potential.

The calculations show that the shape resonances arise from contributions to the $k\sigma$ continuum channel. In principle, shape resonances could also occur in the photoionization of the $v$ orbitals, but the strong contributions of other continuum channels and the apparent weak overlap between the resonance in the $k$ channel and the ground state $v$ orbital, renders the resonance too small to be seen.

It is finally interesting to note that whereas shape resonances such as described above for the valence shell of N$_2$O are very sensitive to the molecular structure, shape resonances arising from the 4d subshell of iodine in HI and CH$_3$I are atomic in character and insensitive to the chemical environment.

\begin{thebibliography}{99}
\item University of Linkoping, Sweden.
\item Chemistry Department, University of Wisconsin.
\item Chemistry Department, University of Tennessee.
\end{thebibliography}
Fig. 10.7. Angular distribution parameter, $\beta$, derived from the photoionization of the $7\sigma$ orbital of $\text{N}_2\text{O}$. The experimental points are connected by a solid line. Calculations based on MSX method are plotted as dot-dash curve (ground state potential) and dash curve (transition state potential). (Ref. 15).

10. S. T. Manson, J. Electron Spectrosc. 1, 413 (1972-73).
14. Most recent calculations do show now improved agreement with our results (W. R. Johnson, private communication).

10.2.2 Photoelectron Spectrometry of Metal Vapors with the Use of Synchrotron Radiation
(M. O. Krause, T. A. Carlson, F. Cerrina,1 Anders Fahlman2)

The study of metal vapors provides the unique opportunity to delineate the electron structure and dynamics of openshell atoms. These atoms constitute the larger part of the periodic system and are both scientifically and technologically important. For example, a satisfactory theory of the interaction of an electromagnetic field with an openshell system is yet to be developed. On the other hand, the theory for the spherically symmetric rare gases is well advanced and compares favorably with the experimental results in most cases.3

In our program, we are aiming at laying an experimental basis for understanding the electronic processes and, at the same time, provide the basic data that are needed to be able to separate the molecular and solid state effects from the atomic effects in compounds, metals and alloys. We use our specially designed and ORNL-built electron spectrometer to measure electron spectra, spectral intensities and photoelectron angular distributions over a range of photon energies available to us from a synchrotron radiation source. The measured properties are closely related to the wavefunctions, the photon-electron and electron-electron interactions, and the anisotropy inherent in an openshell system. Up to now, we have investigated the group 1-8 metals copper and silver, the 3d transition series element manganese and the III-A element gallium. To vaporize these metals, oven temperatures ranging from 1100K to 1500K were required. In addition an experimental technique that felicitously combines the properties of monochromatized synchrotron radiation with those of electron energy analysis was introduced into the photoelectron spectrometry of metal vapors. We briefly describe the highlights in the following:

The Constant-Ionic-State Method. This so-called CIS method has proven valuable in solid state studies where generally high count rates are encountered; it was applied to one lone molecular study, that of H2, but never before to metal vapor work in which the signal rates are often quite low. However, the method neatly matches the state-selectivity of electron spectrometry with the tuneability of synchrotron radiation and allows the efficient, automatic measurement of cross sections and electron angular distributions for each state or orbital of the atom as a continuous function of photon energy. In practice, the electron spectrometer and the photon monochromator are controlled in such a manner as to always lock onto the electron associated with a selected ionic state while the photon energy is advanced in steps. Because the spectrometer scans linearly with energy whereas the monochromator scans linearly with wavelength, which is inversely proportional to energy, we used computer control to insure perfect synchronization between the photon source and the electron spectrometer. The CIS method is particularly useful in recording features across thresholds, resonances and autoionization regions and, as our study of gallium has shown, will be a valuable asset to our further work on atomic and molecular systems.

Characterization of a Complex Autoionization Resonance, the Case of Gallium. One class of resonances, the autoionization resonance, occurs when an excitation state or channel is embedded in one or more continuum channels.
The resonance can be complex if, as in the case of III-A elements ($\ell^2\ell^p$), several continuum channels are available for an innershell excitation channel. These resonances are very important because they offer another pathway for ionization and molecular dissociation and because they afford a severe test for the theory of multi-channel interactions. In our work on gallium vapor, we used the CIS method to record the intensities of the various pathways by which the $3d + 4p$ resonance excitation states can decay into the three available ionic states $4p^1S, 4s^3P$, and $4s^1P$. Figure 10.8 shows that each of the 19 resonance states, which can be observed in absorption, decays into the ionic states in somewhat different proportions but always enhances the ionization probability from the outer $4p$ and $4s$ orbitals manifold over the direct ionization outside the resonance (that is at energies greater than 22 eV or less than 18 eV). The processes occurring in the resonance region are summarized in the interpretive Figure 10.9, and the results of this work on the vapor can be used as a basis for inferring which states will be affected most in molecular and solid state systems.

**Photoionization of the 3d Level of Manganese.** We measured the cross section and angular distribution parameter of the 3a level of this typical 3d transition series element from near threshold to 100 eV, using, in two sessions, two different monochromators, a Seya instrument from 15 to 25 eV, and a toroidal grating monochromator with two exchangeable gratings from 20 eV upward. As an example of our results, which also include information on the 4s multiplet lines and correlation satellites, we show in Figure 10.10 the behavior of the angular distribution parameter $\sigma$. Following the rapid decrease of the $\sigma$ value above threshold, a slow increase toward higher energy is observed, which however is interrupted at about 50 eV by a sharp up and down excursion. This excursion is due to the interfering $3p + 3d$ excitation which is activated at this energy. As for the $\sigma$ parameter, the 3d partial cross section as well as the 4s and the satellite cross sections undergo excursions, namely resonance enhancements, in this energy region. Our data, shown in Fig. 10.10 are in good agreement with the recent data of Kobrin et al. and, most notably, with the prediction made most recently by Garvin et al. with the use of a many-body perturbation theory calculation that includes the important excitation and ionization channels. However, as seen in the graph, a single particle calculation in the Hartree-Fock model while reproducing the overall trend is, by its nature, incapable of predicting the resonance phenomenon.
Study of Copper Vapor. We investigated copper vapor as a link between the 3d element manganese and the 1-8 element silver previously studied by us. The 3d cross section and parameter were found to exhibit similarities with the 3d data of manganese and the corresponding 4d data of silver, except that the resonance features so clearly seen in manganese, and absent in silver, do not appear in the single-electron emission from the 3d shell but only in the two-electron process involving a 3d and a 4s electron. This is due to the fact that in copper with a completely filled 3d shell, a 3p electron can be excited only to the 4s shell (or 4d, 5d, etc.) which excitation state is more strongly coupled with the correlation satellite channel than with the 3d channel of photoionization.

1. Synchrotron Radiation Center, University of Wisconsin at Madison.
2. Visiting scientist, Linkoping University, Sweden.
Fig. 10.10. The asymmetry parameter $\beta$ for the 3d subshell of Mn, showing the effects of an autoionization resonance near 50 eV. Our data (1), and those by Krobin et al (2) are compared with the HF (dash line) and the Many-Body-Perurbation theory (solid line) by Garvin et al (3).

4. P. H. Kobrin et al., (private communication).
5. L. J. Garvin et al., (private communication).

10.3 Study of Reactive Intermediates by Electron Spin Resonance

10.3.1 Photolysis and Pyrolysis of Benzyl Ether
(Ralph Livingston and Henry Zeldes)

A study has been completed on benzyl ether where both pyrolytic and photolytic methods have been used. Thermal decomposition has been carried out at 452, 474, and 497°C at high pressures, and the various results can be interpreted by a chain process:

\[ \text{C}_6\text{H}_5\text{CH}_2 \rightarrow \text{C}_6\text{H}_5\text{OCH}_2\text{C}_6\text{H}_5 + \text{C}_6\text{H}_5\text{CH}_3 + \text{C}_6\text{H}_5\text{CHO} \]  

(1)

\[ \text{C}_6\text{H}_5\text{CH}_2 + \text{C}_6\text{H}_5\text{CH}_2\text{OCH}_2\text{C}_6\text{H}_5 + \text{C}_6\text{H}_5\text{CH}_3 + \text{C}_6\text{H}_5\text{CHO} \]  

(2)

\[ \text{C}_6\text{H}_5\text{OCH}_2\text{C}_6\text{H}_5 \rightarrow \text{C}_6\text{H}_5\text{CHO} + \text{C}_6\text{H}_5\text{CH}_2 \]  

(3)

\[ \text{C}_6\text{H}_5\text{CHOCH}_2\text{C}_6\text{H}_5 \rightarrow \text{C}_6\text{H}_5\text{CH}_2 \]  

(4)

\[ \text{C}_6\text{H}_5\text{CHOCH}_2\text{C}_6\text{H}_5 \rightarrow \text{C}_6\text{H}_5\text{CHO} + \text{C}_6\text{H}_5\text{CH}_2 \]  

(5)

Thermal initiation is through Eq. 1 while Eq. 2 is a transfer reaction in which C6H5CH2O is converted to C6H5CHOCH2C6H5 (1).

Eqs. 3 and 4 constitute the chain while Eq. 5 is the predominant chain terminating process.

Benzyl (2) was observed by ESR at the high temperatures, and at 497°C the steady-state concentration was $3.0 \times 10^{-7} M$. Quantitative assays for all stable compounds appearing in the reaction scheme have been made at the three temperatures, and the chain length at 452°C from stochiometry is 140. At higher temperatures thermal decomposition of benzaldehyde greatly perturbs the accuracy of determining chain length, but the length appears to decrease with increasing temperature.

Whereas 2 is observed during pyrolysis 1 is not seen. This suggests that the reaction of Eq. 4
is rapid compared to that of Eq. 3. This aspect has been placed on a quantitative basis by separately evaluating kinetic parameters for Eq. 4 using photolytically methods. To this end, \( \text{I} \) was prepared and studied with a solution of benzyl ether in benzene containing a small amount of di-t-butyl peroxide as a photolytic initiator. The conversion of \( \text{I} \) to \( \text{Z} \) (Eq. 4) was followed by ESR over the temperature range of 105 to 155°C at 6.9 MPa (68 atm). The activation energy was found to be 15.5 kcal/mol = 15% and the Arrhenius A factor estimated to be \( 1 \times 10^{-2} \text{s}^{-1} \).

Various lifetimes relating to the reaction scheme may be calculated. The kinetic parameters for Eq. 4 extrapolated to 497°C give a mean lifetime of \( \text{I} \) of 2.5 \( \times 10^{-6} \text{s} \). The observed linewidth for \( \text{Z} \) at 497°C allows calculation of a limit for the mean lifetime of \( \text{Z} \) in Eq. 3. It must be longer than 9.4 \( \times 10^{-7} \text{s} \). This shows that Eq. 3 is the rate limiting step of the chain, and the concentration of \( \text{I} \) is small compared to \( \text{Z} \). This accounts for the inability to see a spectrum of \( \text{I} \) at high temperatures and shows that the predominant radical-radical reaction for chain termination must be Eq. 5. Finally, the assay of the concentration of \( \text{Z} \) at 497°C allows calculation of the mean lifetime of \( \text{Z} \) in Eq. 5, and this was found to be 2.2 \( \times 10^{-4} \text{s} \). This is the mean time for terminating a chain and when combined with the mean time for completing one cycle of the chain gives an upper limit of chain length at 497°C of 230. This kinetic value is consistent with the results deduced from stoichiometry. A detailed account of this work will appear in the Journal of Physical Chemistry.

10.3.2 Photolysis and Pyrolysis of Hydrocarbons with Peroxides and Hydroperoxides (Henry Zeldes and Ralph Livingston)

A study has been started on model compounds that relate to jet fuels and is oriented towards a basic understanding of free radical reactions that lead to instability of the fuel from room temperature up through 300°C. Solid formation is of particular concern. The initial phase is a broadly based exploratory survey to search out major reaction pathways that will subsequently be examined in detail. ESR at high pressures is used with photolytic and pyrolytic methods for radical production. Of special interest is the use of peroxides and hydroperoxides as free-radical initiators.

n-Dodecane is a major constituent of jet fuels, and it is frequently used as a solvent in this work. This substance is not inert, and n-dodecyl radicals have been observed in several experiments. The ESR spectrum has been measured by preparing these radicals from a 7% solution of di-t-butyl peroxide in n-dodecane at 225°C. At this temperature the O-O bond of the peroxide is broken, and the resultant radicals very effectively abstract hydrogen from the dodecane to give the observed radicals. The spectra of n-dodecyl radicals formed by abstraction of hydrogen from the 3, 4, 5, and 6 positions are sufficiently alike that they are superimposed. The ESR parameters are \( a_o = 20.9 \text{ G} \), \( a_g = 23.9 \text{ G} \), and \( g = 2.0026 \). A fifth radical formed by abstraction from the 2-position gives a weaker spectrum and is characterized by \( a_o = 21.0 \text{ G} \), \( a_g = 24.3 \text{ G} \), and \( g = 2.0026 \). There is no evidence for the radical formed by abstracting a primary hydrogen. A similar experiment was done with n-decane with similar results. Whenever n-dodecyl radicals are reported to be present there is no evidence to indicate that it is anything other than the mixture of the five radicals.

Photolysis and pyrolysis of peroxides and hydroperoxides breaks the O-O bond, and a combination of the methods allows the ensuing chemistry to be followed over a wide range of temperatures. Photolysis is used at temperatures up to that where thermal initiation becomes rapid enough to obtain spectra. Peroxides, especially di-t-butyl peroxide, have been widely used as photolytic initiators, but very little ESR work has been done at high temperatures. Using oxygen free solutions and di-t-butyl peroxide as an initiator we have
prepared the expected radicals from neat toluene, cumene, tetralin, and n-dodecane near room temperature (photolysis) and at 225°C (thermal initiation). These are benzyl, cumyl, tetralin-1-yl, and n-dodecyl, respectively. A few experiments with dicumyl peroxide as the initiator gave the same results. Whereas these experiments gave the expected results, work with mixed hydrocarbons showed an interesting feature that will be studied in greater detail. A solution of 10% toluene in n-dodecane with the peroxide initiator showed only a spectrum of n-dodecyl upon photolysis at room temperature. The amount of toluene was not enough to see benzyl above the noise background. At 225°C the spectrum of benzyl was seen as well as dodecyl. This experiment as well as other experiments, including ones with 10% cumene in dodecane, indicate that a temperature activated process causes a higher relative concentration of radicals from aromatic hydrocarbons at higher temperatures. Final chemical products should reflect this change. An energetically favorable reaction being considered is \( \text{C}_12\text{H}_{25} + \text{RH} \rightarrow \text{C}_12\text{H}_{26} + \text{R} \) where RH is toluene, cumene, etc.

A variety of experiments have been carried out with oxygen free solutions of hydroperoxides in hydrocarbons. High concentrations of peroxy radicals, \( \text{RO}_2 \) are observed upon photolysis at room temperature. These radicals are relatively less reactive which accounts for the large steady-state concentration. If a peroxide is also present the formation of \( \text{RO}_2 \) is usually enhanced. Hydroperoxides that have been examined include t-butyl, cumene, and tetralin in solutions of aromatic hydrocarbons and also with mixed solvents including dodecane. Spectra of peroxy radicals typically broaden rapidly with increasing temperature. Several systems have been examined from room temperature to 300°C. Typical behavior is illustrated by 1% cumene hydroperoxide and 20% cumene in dodecane. Photolysis at room temperature gives a strong spectrum of cumyl peroxy radical. This spectrum broadens rapidly and disappears upon warming. It cannot be seen above 100°C. It has not yet been ascertained if the disappearance is entirely due to broadening or if there is a contribution from a decrease in concentration of the radical. There is a temperature range over which no spectrum is seen, but at 225°C, with photolysis there is a readily recognizable spectrum of cumyl. This temperature is not quite high enough to develop a spectrum thermally, but at slightly higher temperatures the stronger lines of cumyl start to appear with thermal initiation. At 300°C a moderately strong spectrum of cumyl is present. At high temperatures the behavior resembles that of peroxide initiators, although there may be important mechanistic differences. These systems will also be examined when air saturated.

10.4 Surface Enhanced Raman Scattering on Silver-Coated Teflon Sphere Substrates
(G. M. Begun, E. T. Arakawa, J. P. Goudonnet)

The study of surfaces and surface phenomena is very important to the industrial chemical world in the fields of coatings, metals, corrosion chemistry, colloid chemistry and catalysis. Different methods, such as Auger spectroscopy, low-energy-electron diffraction, electron microscopy and infrared spectroscopy, are used in characterizing surface structure. Raman spectroscopy also should be included, because the vibrational spectra obtained from this method depend on the physical or chemical changes in a molecule as affected by its environment. Raman spectra are, however, very weak except in very special cases.

Enhanced Raman spectral intensity has been found to occur when molecules are adsorbed on specific metals. This spectacular enhancement (surface enhanced Raman spectroscopy (SERS))—by factors up to 10⁶—of Raman scattering occurs with monolayers of molecules adsorbed on rough metal surfaces. SERS has been the subject of numerous papers since 1977. Although many different theoretical models have been reported for explaining this effect,
there is no general consensus as to its origin. Experimental studies have been carried out for many molecules adsorbed on a small number of substrates. Very large enhancements ($10^9$) have been found for silver substrates, and smaller enhancements have been observed on Cu, Au, Ni and Hg. Few of the current studies are directed toward accounting for the role played in enhancement by surface roughness (on an atomic or microscopic scale).

In order to use SERS as an analytical tool, we must control the unknown experimental parameters and demonstrate the routine enhancement on a variety of adsorbates. We have developed a simple experimental method for obtaining the Raman spectra of organic species adsorbed on surfaces which give SERS enhancement. The good reproducibility of the method due to the well-defined roughness of the substrate may provide a means by which theory can be tested.

The sample substrate was obtained by deposition of teflon spheres of uniform size and shape on a glass substrate of ordinary crown glass microscope slides. Several drops of a suspension of commercial teflon spheres (FEP Teflon spheres, E. I. DuPont de Nemours Co.) were placed onto the surface of the slide which was then spun to obtain a uniform layer. After spinning, the sample was baked at 75°C for 30 min. and placed in a vacuum coating unit and coated with various thicknesses of thermally evaporated metals under standardized conditions. A sufficiently thick metal film was deposited to avoid destruction of the film during doping. Silver layers 75-80 nm thick were used for our experiments. The diameter of our silver-coated spheres measured with a scanning electron microscope was 100 to 200 nm.

Slides containing the silver-coated spheres were then placed on the spinner and a few drops of dopant solution (0.2-4.0 mg/ml of adsorbant in a volatile solvent) added. After spinning the Raman spectra of the surface was examined using various frequencies of exciting laser lights.

Figure 10.11(a) shows the Raman spectrum from a 0.1-M phthalic acid solution in distilled water with 100 mw of 633 nm incident light. In Fig. 10.11(c) we show the Raman spectrum of a layer of phthalic acid deposited from 0.01 M solution and excited by 30 mw of 633-nm laser light. This spectrum shows sharp lines due to SERS from phthalic acid, although the original

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**Fig. 10.11. Raman spectra of phthalic acid.**

(a) 0.1 M. solution in water 633 nm excitation, 100 mw. (b) 0.01 M. solution adsorbed on a 75 nm silver film deposited on teflon sphere dispersion on glass. 514.5 nm excitation, 30 mw. (c) Same as (b) but with 633 nm excitation, 30 mw. (d) Solid phthalic acid powder. 633 nm excitation, 100 mw.
solution concentration and the laser power were weaker than in Fig. 10.11(a). The spectrum shown in Fig. 10.11(b) was excited by 30 nW of 514.5-nm light on the same sample used in Fig. 10.11(c). We observed here several strong broad peaks. Fig. 10.11(d) shows the Raman spectrum of solid phthalic acid powder excited by the 633 nm laser line from the dye laser.

Similar experiments were conducted on phthalic acid adsorbed on a gold film evaporated on a silicon substrate. The spectra did not show any characteristic phthalic acid lines at all with either the 514.5 or the 633-nm exciting frequencies.

The broad bands in the spectra excited by 514.5-nm laser light resemble spectra previously observed in the same range by J. C. Tsang, et al.\textsuperscript{3} in Raman scattering on Ag surface and were attributed by these workers to Raman scattering from amorphous carbon. Since our silver coatings were deposited in a vacuum system employing oil diffusion and backing pumps, carbon compounds may be present in minute quantities and be decomposed to amorphous carbon by the laser radiation. The Raman spectrum of silver-coated teflon spheres doped with graphitic carbon also showed considerable similarity to that of Fig. 10.11(b).

Thus the characteristic spectra features observed between 1350 cm\textsuperscript{-1} and 1600 cm\textsuperscript{-1} for 514.5-nm excitation light may be due to Raman scattering from an amorphous carbon layer.

We repeated these experiments with benzoic acid and nitrobenzoic acid. The spectra were similar to the phthalic acid spectra and showed sharp lines in the SERS spectra when excited by 633-nm light and broad maxima in the 1300-1600 cm\textsuperscript{-1} range in the spectra when excited by the 415.5-nm laser line.

Thus we have shown that Raman spectra can be obtained reproducibly from molecules adsorbed on a film of Ag coated on teflon spheres using 633-nm exciting light. This method constitutes a good tool by which Raman spectra of very dilute substances can be obtained and by which vapor-deposited silver films can be characterized.

1. Health and Safety Research Division.
2. Participant at Oak Ridge National Laboratory from Laboratoire de Photoélectricité, Faculté des Sciences Mirande, B. P. 138, 21004 Dijon Cedex, France.
11. THEORETICAL CHEMISTRY

11.1 Collisional Detachment of Electrons from H- (O. H. Crawford)

Three-body systems are receiving high priority in chemical physics today. One of the problems of current interest in this area is electron detachment from H- in high-velocity collisions, since this process probes the dynamics of the H- system, where correlation and exchange are important.

Recently, Duncan and Menendez\(^1\)-\(^5\) have measured the energy distributions at various laboratory scattering angles \(\theta\) of electrons ejected from H- in collisions with rare gases. Near 0° they observed a cusplike peak of electrons having the same speed as the H-. With a He target, they found\(^4\) a second peak at about 30 eV lower electron energy. The cusplike peak disappears rapidly with increasing angle, leaving the lower-energy peak, which shifts up in energy at higher angles. The peak separation (in the laboratory system) is independent of H- beam velocity, but depends on target species.

Menendez and Duncan\(^1\)-\(^4\) suggested that the broad and sharp groups of electrons are due to single and double electron loss (SEL and DEL), respectively. Franz et al.\(^6\) argued that both features can be accounted for by SEL alone, and later workers\(^7\)-\(^8\) have supported this conclusion. However, the physical basis for the occurrence of two peaks in the SEL remained obscure, and it was not previously determined whether they have the same dependence on angle, beam energy, and target species, as do the experimental features.

We showed\(^9\) that the broad and sharp features are due to electron ejection into \(s > 0\) and \(s = 0\) continuum states, respectively, and that interference between these two groups of states is appreciable. Figure 11.1 shows a comparison between theory and experiment. The dependence of the theoretical SEL peak energies upon angle, beam energy, and target species is in harmony with experiment. A contribution to the experimental intensity from DEL (leaving H+)\(^1\),\(^4\) is not ruled out.

This work was supported by the Air Force Office of Scientific Research.

11.2 Chemical Kinetics of Bimolecular and Unimolecular Processes

11.2.1 Theoretical Investigation of Vibrational Energy Transfer in Polyatomic Molecules

(D. W. Moir, J. R. Stine)

The problem of energy flow in polyatomic systems is exceedingly complex. As is well known, complex motions can occur even in model systems of two degrees of freedom. This complexity has caused most of the effort to date to be devoted to understanding model systems of two degrees of freedom.

These Hamiltonian systems can display two types of classical motion — stochastic and quasiperiodic. Various methods have been developed to distinguish between these two types of motion; the construction of the Poincare surface-of-section has proved particularly useful. Here the surface-of-section appears as a random scattering of points for the stochastic trajectory and a well-ordered locus of points for the quasiperiodic trajectory. Another useful method for distinguishing between the two types of motions is the calculation of the power spectrum. Here a stochastic trajectory results in a spectrum with many broad lines, whereas the quasiperiodic trajectory gives a spectrum with a few sharp lines.

These methods have been applied primarily to systems with two degrees of freedom, for which the trajectory is either totally quasiperiodic or totally stochastic. A polyatomic system will have \( n \) constants of the motion (where \( n \) is the number of degrees of freedom) at low energies, and only one constant of the motion (namely, conservation of energy) at high energies. The number of constants of the motion will be between one and \( n \) at intermediate energies.

In a recent paper, we presented a numerical method to determine the number of constants of the motion for Hamiltonian systems. The method determines the number of stochastic degrees of freedom from the dimensionality of the surface in phase space on which the trajectory moves. This number is determined from the slope of the line produced in a dimensionality plot. Because this is a numerical procedure, some consideration has to be given to the bin size and to the number of time steps needed to establish convergence of the number of unique bins through which the trajectory travels. If the number of bins is large, then the trajectory will not have the opportunity to access all of the bins that may be available. Because the trajectory can be represented by a point moving in phase space, the trajectory has, in fact, a dimensionality of unity (a line). This situation would produce a slope of unity for the line in a dimensionality plot if an insufficient number of time steps were generated. On the other hand, if the number of bins per direction were too small, then all the bins in phase space could be accessed and any trajectory would appear to be ergodic. These are extreme cases, and, in fact, a considerable range of bin sizes is available such that a valid slope in the dimensionality plot can be obtained.

We have assumed here that the dimensionality plot should yield an integer value for \( k \), i.e., the Euclidian or topological dimensionality. Indeed, within the error limits of the calculations, the least-square slopes agree with the theoretical values. It is known, however, that non-integer values for dimensionalties are possible for various physical systems. In fact, the value of \( 2n-k \) calculated here represents the Hausdorff-Besicovitch dimensionality. If the trajectory travels on a multi-dimensional surface that is not "well-behaved", the dimensionality of this surface \( (2n-k) \) would not necessarily be an integer but would be greater than the topological dimension. Currently we are applying this new technique to a fully dimensional model of water and to a classical model of infrared multiphoton absorption.

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11.2.2 Semiclassical Study of Infrared Spectra
(D. W. Noid, M. L. Koszykowski,1 J. R. Stine2)

Recently, we obtained from a classical trajectory the power spectrum of any classical mechanical variable.3 It was shown that the spacings of the quantum mechanical vibrational eigenvalues agree well with those deduced from the classical vibrational frequencies, in the classically quasiperiodic regime. It was also shown that in the classically chaotic regime a line spectrum was obtained, while in the chaotic regime the spectrum was “dispersed”.3

We used a zeroth-order Hamiltonian to define semiclassically the initial conditions (the “eigentorus”) for the trajectory used to obtain the classical autocorrelation function. The Fourier transform of this correlation function then provided the power spectrum. We also showed for one spectrum that good agreement with quantum mechanical results for the spectral intensity could also be obtained.

In deducing the spectrum from a classical trajectory we first calculate the classical autocorrelation function by averaging the quantity of interest, such as the dipole moment \( u(t) \) over the appropriate ensemble. The reduced classical spectral intensity \( I \) is then given by the Fourier transform of the autocorrelation function:

\[
I = \frac{1}{2\pi} \int \langle u(0) u(t) \rangle e^{i \omega t} dt
\]

In the quasiperiodic regime, the ensemble needed to obtain the spectral frequencies consists of an ensemble of trajectories, but we showed that a single trajectory can suffice when an equivalent formula, given later, is used.

Recently we used this method to obtain from classical trajectories the spectrum of OCS. The anharmonic force field and the dipole moment function given for OCS are in Ref. 4. The Hamiltonian used is given by Eqs. 29-31b of Ref. 5 for a nonrotating molecule. The dipole moment function taken from Ref. 4 was devised there by fitting the calculated \( |u_{nm}|^2 \)s to experimental integrated bend intensities (using equations in Ref. 4), employing a potential different from the present one.

The initial conditions were chosen semiclassically by using the zeroth-order Hamiltonian. Hamilton's equations were solved by using a standard program for solving coupled differential equations. The \( u(t) \) was calculated from the trajectory.

In another study6 we found that the semiclassical WKB method has applicability for deducing the dipole-moment function from experimental intensity data. The Fourier series for the time-dependent dipole-moment converges very rapidly and is a significant improvement over the Taylor series for the internuclear distance dependent dipole moment function. The simple semiclassical equations are also of value for interpolation and extrapolation of the dipole-moment matrix elements and hence the dipole-moment function can be extrapolated, at least for some distance, past the classical turning points, whereas the Taylor series expansion diverges rapidly outside the classical turning points for the excited vibrational states.

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11.2.3 Semiclassical Calculation of Bound States

(D. W. Noid, M. L. Koszykowski, R. A. Marcus)

We have compared the quantal and classical/semiclassical behavior at an isolated avoided crossing. If one plots two vibrational energy eigenvalues of a molecule versus a perturbation parameter the curves may intersect or, if the two states are suitably coupled by the perturbation, undergo an avoided crossing. Such avoided crossings can produce local changes in a spectrum, on one hand, and offer a way of substantially mixing nodal patterns of the two states, on the other. If a particular state participates simultaneously in many (i.e., "overlapping") avoided crossings, it takes on a statistical behavior, which is expected to expedite energy redistribution in a wave packet for an isolated molecule, and should generate, as well, an irregular. To study the behavior at an isolated avoided crossing we considered the following Hamiltonian:

\[ H = \frac{1}{2}\left(p_x^2 + p_y^2 + \omega_x^2x^2 + \omega_y^2y^2\right) - \alpha x^3 - \gamma y^3 + i\omega_x x^2 y - \omega_y x y^2 \]

with \( \omega_x = 3 \omega_y = 3 \). Without the \( x^3 \) and \( y^3 \) terms, the two eigenvalue versus \( \lambda \) plots considered below would intersect only at \( \lambda = 0 \). The \( i\omega_x x^2 y - \omega_y x y^2 \) term produces eigenvalues versus \( \lambda \) plots of different slopes. Because of the commensurability of \( \omega_x \) and \( \omega_y \) and the smallness of the perturbation (\( a = 0.02, b = 0.005 \) to 0.01 and \( \lambda \) varied from 0 to approximately 0.1) a nearly exact 3:1 classical resonance occurs as some \( \lambda \) in this range. At this \( \lambda \) and at nearby \( \lambda \)'s, one expects a strong distortion of the classical motion. Plots of these \((0,3)\) and \((1,0)\) quantum eigenvalues versus \( \lambda \) are given in Fig. 11.2. Two wave functions for a \( \lambda \) far-removed from the \( \lambda \) at the avoided crossing are plotted in Fig. 11.3, while those for the \( \lambda \) at the avoided crossing are given in Fig. 11.4. One sees the expected mixing of the two nodal patterns in the latter. To quantize this trajectory, we use methods described previously. The Poincare surface-of-section results are recorded for \( p_y \) versus \( y \) each time the trajectory crosses the line \( x = \) constant (in the present case, we used \( x = 0 \)) in a particular direction (e.g., \( x > 0 \)).

We then calculated the path integrals

\[ \phi P_x \, dx = 2\pi \left( n_1 + \frac{1}{2} \right) \]

and

\[ \phi P_y \, dy = 2\pi \left( n_2 + \frac{1}{2} \right) \]

and by a simple interpolation located the eigentrajectory.

A comparison of quantal and semiclassical eigenvalues for the \((0,3)\) and \((1,0)\) states are given in Table 11.1 for \( b = 0.005 \).

In following the behavior of the energy of each semiclassical state \((0,3)\) and \((1,0)\), we observed that it passes through the region of the avoided crossing instead of showing an energy level repulsion there. The present semiclassical method ("primitive semiclassical",掌门人 分享
Fig. 11.3. Plot of the square of wave functions for Fig. 11.2 at $\lambda = 0.01$.

Fig. 11.4. Plot of the square of the wave function for Fig. 11.2 at the avoided intersection ($\lambda = 0.055$).
Table 11.1. Comparison of quantum and semi-classical eigenvalues for the (0,3) and (1,0) states.

<table>
<thead>
<tr>
<th>b</th>
<th>λ</th>
<th>$E_Q$ (0,3)</th>
<th>$E_{SC}$ (0,3)</th>
<th>$E_Q$ (1,0)</th>
<th>$E_{SC}$ (1,0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.005</td>
<td>0.01</td>
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<td>4.987</td>
<td>5.002</td>
<td>...</td>
</tr>
<tr>
<td></td>
<td>0.03</td>
<td>4.9983</td>
<td>4.999</td>
<td>5.007</td>
<td></td>
</tr>
<tr>
<td>0.05</td>
<td>0.011</td>
<td>5.010</td>
<td>5.011</td>
<td>5.012</td>
<td></td>
</tr>
<tr>
<td>0.055</td>
<td>0.013</td>
<td>5.013</td>
<td>5.013</td>
<td>5.013</td>
<td></td>
</tr>
<tr>
<td>0.060</td>
<td>0.015</td>
<td>5.016</td>
<td>5.015</td>
<td>5.014</td>
<td></td>
</tr>
<tr>
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<td>0.028</td>
<td>5.027</td>
<td>5.019</td>
<td></td>
<td>5.019</td>
</tr>
</tbody>
</table>

*The five values labeled a in this column are averages of the following respective pairs: (5.0092, 5.0128), (5.0114, 5.0147), (5.0132, 5.0169).

bSmallest $J_\lambda \sim 3.12\times$ instead of $J_\lambda \sim 3\times$.

i.e., no uniform approximation) does not yield the splitting and so in the vicinity of the avoided crossing comparison, indicated by an a in Table 11.1, is made with the mean of quantum eigenvalues for (0,3) and (1,0) states.

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11.3 Systematic Derivation of Chemical Procedures for Transforming Surplus Hazardous Chemicals to Useful Commercial Products

(C. K. Johnson, W. E. Thiessen, M. N. Burnett)

Chemical procedures are required for detoxifying surplus hazardous chemicals such as obsolete chemical agents stockpiled for military deterrence. These reactive chemicals can be disposed of by incineration, transformation to inactive wastes or transformation into chemicals which can be used commercially. The present research applies systems-analysis knowledge-engineering principles and non-numerical computational chemistry methods to this chemical demilitarization problem. Two separate approaches were tried to find commercial products and plausible chemical reaction pathways from the organic phosphorus and organic sulfur chemical agents.

The first method was to implement a computer program FSECS, written at the University of California, Santa Cruz, to generate a large family of plausible products using a reaction library of 600 general chemical reaction types. This "reaction-driven" approach produced limited success because of the large amount of work required to evaluate the commercial potential of each candidate product.

The second approach used the FSECS program to aid in the generation of a few composite generalizations representing all reaction product possibilities. These composites were used as queries in searching a compilation of commercial chemicals produced and sold in significant volumes. An analysis of the commercial uses of the chemicals corresponding to the search queries produced a number of commercial application areas which were evaluated for chemical product requirements and usages. A network of plausible reactions then was constructed interconnecting the starting chemicals with chemical product possibilities in those application areas. Extensive literature search for known reactions of related molecules was carried out to evaluate the chemical feasibility of the reaction network pathways.

Our "product-driven" method led to several promising new products which might be produced from the methylphosphonate agents GB (Sarin) and VX including

(a) flame retardants for plastics and fibers,
(b) lubricating oil additives,
(c) several insecticides and herbicides,
(d) surface active agents, and
(e) solvent extractants for actinide elements in nuclear wastes.
Promising products which might be produced from the mustard vesicant agent HD include
(a) macrocyclic thio ethers for metal extraction,
(b) allyl sulfide which is used in the flavoring industry, and
(c) dihydrothiophene which is used as a chemical feedstock.
The techniques derived for this problem are applicable to a broad range of situations in which systematic enumeration of alternative products that can be produced from any surplus reactive chemical is required.

2. Chemistry Department, University of Tennessee.
12. NUCLEAR WASTE CHEMISTRY

Several research topics in the Chemistry Division are directly related to chemical problems of nuclear waste. Safety analysis of nuclear 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 through the geologic formation to the accessible environment. If the repository is located in a dry salt formation, one of the proposed host geological media, then the change of permeability of the formation through consolidation of the polycrystalline salt is of considerable interest. The research described in Section 12.1 addresses this problem. Prediction of the interaction of migrating nuclides with the host formations is dependent upon knowledge of the chemical speciation of the nuclides. In Section 12.2, research is described concerning the effects of valence states of the nuclides upon sorption of these nuclides on the formation minerals. In particular, the reduction reaction of Np(V) to Np(IV) is discussed. This type of information is used by the Nuclear Regulatory Commission (NRC) in safety analyses of the performance of proposed repositories. In the remaining sections, other types of chemical support for the NRC's assessment activities are described.

12.1 The Effect of Water in Salt Repositories

(C. F. Raes, Jr., L. J. Gilpatrick, E. G. Kitts, H. P. Bronstein, A. K. Shor)

This project was terminated during the reporting period. The following is the abstract of the final report.

Additional results confirm that during most of the consolidation of polycrystalline salt in brine, the previously proposed rate expression applies. The final consolidation, however, proceeds at a lower rate than predicted. The presence of clay hastens the consolidation process, but does not greatly affect the previously observed relationship between permeability and void fraction. Studies of the migration of brine within polycrystalline salt specimens under stress indicate that the principal effect is the exclusion of brine as a result of consolidation, a process that evidently can proceed to completion. No clear effect of a temperature gradient could be identified. A previously reported linear increase with time of the reciprocal permeability of salt-crystal interfaces to brine was confirmed, though the rate of increase appears more nearly equal to the product of $\alpha A\Delta P$ rather than $\alpha A\Delta p^2$ ($\alpha$ is the uniaxial stress normal to the interface and $A\Delta P$ is the hydraulic pressure drop). The new results suggest that a limiting permeability may be reached. A model for the permeability of salt-crystal interfaces to brine is developed that is reasonably consistent with the present results and may be used to predict the permeability of bedded salt. More measurements are needed, however, to choose between two limiting forms of the model.

1. On loan from Chemical Technology Division.

12.2. Valence Effects on Sorption of Nuclides on Geological Materials

(K. E. Meyer, W. D. Arnold and 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. Determination of these interactions requires
that the valence state of the nuclide be known. If the valence state is not known, then there can be no confidence in use of the data for safety analysis. Methods are therefore being developed to determine and control the valence state of the nuclides, and these methods are being used in experiments that are designed to investigate interaction between nuclides and minerals.\(^1\)

12.2.1. Methods of Valence State Determination and Control

There are a number of ways of determining the valence state of a nuclide in solution. The most direct and positive method, the spectrophotometric method, is applicable only if the concentration of the species is high enough. At the low concentration levels of interest to assessment of nuclide migration, indirect methods such as solvent extraction and coprecipitation must be used. These methods assume that valence state determinations carried out at high concentrations, which can be verified by spectrophotometric methods, can be applied to low concentrations.

The most convenient method for work at low concentrations is solvent extraction. For the determination of the valence states of Np, we used thenoyltrifluoroacetone (TTA), 10% by volume in xylene, to check for the presence of Np(IV), which is extracted from 1 M HCl solution with high distribution coefficients. The presence of Np(VI) is determined by solvent extraction with tri-n-octylamine (TOA), 10% by volume in xylene, from 4 M HCl. We have spent considerable effort testing and confirming these procedures for the low concentrations of Np that we investigate, 10\(^{-10}\) to 10\(^{-12}\) M Np. The bases of these procedures have been described in Ref. 2. For work with technetium, we use tetraphenylarsonium chloride to test for the presence of the pertechnetate ion, TcO\(_4^-\), the most likely species of Tc(VII) in our studies.

In order to adjust the valence state of a species, either chemical or electrochemical methods may be used. We have developed and are using an electrochemical method of controlling valence states of species in solution. With this technique, the solution is pumped through a porous electrode which is set to a potential which will effect the desired valence adjustment. The solution then passes through a column which contains the adsorbent, and then it is recirculated through the porous electrode. This procedure assures that essentially all of the nuclide is at the appropriate valence state and that any redox couples in solution are in equilibrium at the potentials set on the electrode. The entire apparatus is contained in a controlled-atmosphere box filled with argon to prevent oxidation of any reduced species by atmospheric oxygen.

In order to detect whether or not the nuclide adsorbed on a material is reduced or oxidized, the valence state of the sorbed species must be determined. This can be done by leaching the material with dilute acid and by immediately carrying out valence state analysis by solvent extraction. This procedure must be carried out as quickly as possible in the controlled atmosphere box to minimize any possible redox reactions.

12.2.2. Adsorption of Np

Using the techniques described in Section 12.2.1, we have investigated sorption reactions of Np(V) on various minerals. Neptunium(V) exists primarily as the ion NpO\(_2^+\) up to about pH 9, and generally large, singly-charged ions are not adsorbed strongly by most minerals. Migration rates of Np would therefore be much slower if Np(V) were reduced to Np(IV) which forms insoluble hydroxides and oxides at the pH range of interest to nuclear waste.

Because basalt is one of the proposed host minerals for a nuclear waste repository, it is of particular interest, and we have carried out
a large number of interaction experiments between basalt and Np(V) at about 10^{-11}M. The porous electrode technique described above was used to insure that the Np was initially present as Np(V). In the experiments, the concentration of the neptunium in the solution slowly decreased with time. Valence state analysis of the sorbed neptunium showed that most of the neptunium on the surface of the basalt was Np(IV). The basalt was then placed into air-saturated solutions free of Np, and the concentration of Np in the solution was monitored with time. After several weeks, the concentration of the Np in the solution appeared to be at a steady state and only a small percent of the Np originally present on the basalt was in the solution. This observation suggests that the reduced neptunium was very tightly bonded to the basalt. It is of some interest that if a potential-pH diagram is used to predict speciation under these conditions (air-saturation), the stable form of Np should be NpO_2^+ provided that the Np(IV) can be considered to be present in the oxide NpO_2. Either there are kinetic factors controlling speciation in this case, or the adsorbed species of Np(IV) cannot be considered to be NpO_2.

12.2.3. Sorption of Technetium

Because ^{99}Tc has a half-life of 200,000 years and because it is normally present as the anion, TCO_4^-, under oxidizing conditions, it is considered to be potentially one of the more hazardous nuclides in nuclear waste. However, if reducing conditions are present it should be reduced to a lower oxidation state, probably Tc(IV), which forms a reasonably insoluble oxide. Because deep geological formations are usually reducing, it is therefore likely that the technetium will be present as a reduced insoluble form and that its concentration in solution may be controlled by the solubility of the reduced species. However, it still remains to be determined whether these reactions actually occur as predicted by these thermodynamic considerations.

We are therefore carrying out experiments similar to those above with Np. The experiments with Tc are more difficult because the chemistry of the lower valence states of Tc is not well-known. Our results so far have not been reproducible; in some cases, the Tc concentration in the solution is lowered and in others it is not. At present we have no explanation for these effects.


12.3. Uncertainties in Assessment of Long-Term Collective Dose and Health Effects from Geologic Disposal of High-Level Waste

G. D. O'Kelley, R. E. Meyer, D. C. Kocher

Work on this topic in the Chemistry Division has focused on geochemical considerations of significance to licensing actions by the U.S. Nuclear Regulatory Commission (NRC) concerning high level nuclear waste repositories. Activities have involved various considerations of the proposed NRC rule on disposal of high-level radioactive wastes in geologic repositories, published as part 60 of Title 10 of the Code of Federal Regulations (10 CFR 60). Our initial task was to assist the NRC by addressing technical issues involving geochemical and related uncertainties in the public comments addressed to NRC concerning 10 CFR 60. In a similar advisory capacity, we participated in a review of the Hanford site characterization report, chapter 16, "Performance Assessment Issues and Plans," and related material in Chapters 12-15.
As required by law, the Environmental Protection Agency (EPA) recently published proposed environmental standards for management and disposal of spent nuclear fuel, high-level and transuranic radioactive wastes. Such standards are needed to provide a suitable framework for the technical criteria embodied in the NRC rules 10 CFR 60 and would be implemented by the U.S. Department of Energy under its statutory responsibilities. At the request of the NRC a review of the proposed EPA standard was carried out, and a letter report of comments was prepared for NRC use.

The proposed NRC regulations for geologic repositories credit contributions to the performance of a high-level waste repository by "favorable" geochemical conditions, but there are no quantitative performance objectives directly concerned with geochemistry. However, geochemical considerations must surely be included in performance assessments for evaluating compliance with an EPA standard, and such studies are likely to be quantitative. Geochemical considerations also can lead to development of better methods for studying prospective repository sites and an improved understanding of retardation factors, redox conditions, speciation, and the complicated relationships between them.

With these considerations as background, a letter report was prepared for the NRC on the role of geochemical factors in the assessment and regulatory processes. The factors considered were chosen on the assumption that the agent most likely to mobilize radionuclides and disperse them into the environment is water. The report did not address the chemical mechanisms for leaching nuclides from the waste form by groundwater but was concerned with the chemical behavior of nuclides dispersed in a groundwater in contact with a solid geologic medium. The topics discussed included sorption by solids, oxidation-reduction processes, speciation and the roles of hydrolysis and complexation, solubility, polymeric species and colloid formation, and the applicability of models used to simulate repository performance.


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 chemical species on health effects from radionuclides in high-level waste. In the past, the potentially large variability in exposure, dose and risk arising from the differences in chemical forms of some nuclides has been largely ignored for purposes of simplification and convenience in general approaches to radiological assessments.
The present study is intended only as an initial evaluation of this complex problem and, hence, will be limited to a critical review of the pertinent literature and an identification of research needs. The current task concerns only Sr, Hp, Pu, and Am.

A computer search has been carried out on the Chemical Abstracts data base for the years 1967-1982 and on the U.S.D.O.E. data base for the years 1976-1982. Approximately one-third of the titles discovered showed potential relevance to the subject matter of this study. We are presently examining these selected references in detail to determine those which will be most useful in constructing a data base specifically for this project. A data-base management system is being designed for the ORNL POP-10 computer which will assemble the selected data in a useful bibliographic form for rapid access to information concerning the speciation of the elements of interest in various groundwaters.


12.5. An Evaluation of Retardation Parameters for Nuclide Migration in Geological Media
(J. S. Johnson, Jr., C. G. Westmoreland)

This is a new program funded by the Nuclear Regulatory Commission in the Chemical Technology and Chemistry Divisions. Its objective is experimental evaluation of critical solubility and adsorption parameters advanced by the Department of Energy to describe retardation of nuclides in flow through form ions of ground water containing nuclides leached from high-level repositories. Initial emphasis in the Chemistry Division will be on technetium in basalt environments. Activity so far has been limited to planning and acquisition of equipment.

12.6 Geochemical Review and Evaluation of Nuclear Waste Documentation
(D. R. Cole)

Geochemistry is an important factor in nearly all phases of the safety assessment of a high-level waste repository. The lifetime of the waste package will be strongly influenced by the near-field geochemistry, whereas the far-field geochemistry and hydrology will control the release of radionuclides to the biosphere after canister breach and groundwater infiltration. The overall purpose of this program is to give technical assistance to the Nuclear Regulatory Commission (NRC) in establishing what additional geochemical information about a candidate area will be required in order to assess and determine how much credit a particular candidate area can receive for geochemical retardation in performance assessments conducted in licensing.

Specifically, this program is to provide technical assistance to the NRC in the following areas:

(1) collect and review the NNE geochemical database(s) for candidate areas for radioactive waste repositories,

(2) review and evaluate the geochemical portions of the NNE site characterization reports,

(3) analyze the NNE program for characterizing the geochemical aspects of potential repository sites, and

(4) provide short-term geochemical technical assistance, which includes reviews of specific publications and presentations and the development and review of draft technical material for inclusion in NRC documents.

The results of the document review and evaluation are transferred to NRC in the form of reports that address the validity of the technical approach as well as the validity of geochemical data, algorithms and interpretations. Recommendations (with justifications) are made that can be used by the NRC as an aid in the identification and resolution of a particular geochemical issue.
13. ENHANCED OIL RECOVERY


Research in enhanced oil recovery, primarily oriented toward micellar floods, has been underway for several years, under the sponsorship of Oil, Gas, and Shale Technology, Department of Energy. One area, the search for cheaper and more abundant chemicals for the process, was suspended early in the period covered by this report. Residual work toward microbiological production of cosurfactants is outlined in 13.4. The other main area dealt with the fundamental chemistry of floods, originally from an ion-exchange point of view. Equilibria between formation minerals and aqueous brines was one topic. Phase and interfacial properties of aqueous-hydrocarbon systems in the presence of low-equivalent-weight organic salts was another. Interests of this program broadened to include high-equivalent-weight amphiphiles, both ionic and nonionic in the surfactant range and the structure of micellar and microemulsion solutions, from small-angle neutron scattering. Examples of recent results in these areas are given in 13.1-13.4.

13.1 Small-Angle Neutron Scattering of Micellar and Microemulsion Systems

Three aspects of small-angle neutron scattering (SANS) make it a particularly appropriate technique for study of the aggregates present in micellar and microemulsion systems. The accessible momentum-transfer range \( q = \frac{4\pi}{\lambda} \sin \theta \), where \( \lambda \) is the wavelength of the neutrons and \( 2\theta \) the scattering angle, in contrast to the scattering of visible light, allows measurements where the particle scattering function \( P(q) \) is less than unity, and information on size and shape of individual aggregates of the size of interest here (10 to several hundred Å) may be inferred. In comparison with x-rays, the scattering power of hydrogen isotopes is very high, and useful signals from the systems of interest can be obtained. Further, the scattering of H and D is very different, and use of deuterated components or of components selectively deuterated in parts of the molecule allows study of details of structure of aggregates.

The chemistry of these systems is complicated, and there is disagreement concerning models of micelles, and even more concerning microemulsions. We outlined in the last report of this series preliminary studies of several types of systems of interest to us. Subsequently, we have emphasized study of relatively simple systems, which are nevertheless of intrinsic interest, in order to develop techniques for analysis of more complicated systems.

Scattering intensity of a dispersion of particles is proportional to the product of a scattering function, \( P(q) \), which depends on the size, shape, and internal structure of the particles, and a structural factor, \( S(q) \), which is a function of the interparticle spatial arrangement. Two of the examples of results to be presented deal with application of two different structural factors, one pertinent to scattering by fluctuations which occur in the vicinity of critical points, and the other pertinent to charged aggregates. The third example compares scattering from a partially deuterated and wholly protiated surfactant.

13.1.1 SANS of a Non-Ionic Surfactant as a Function of Temperature

Aqueous solutions of surfactants of the class \( \text{CH}_3(\text{CH}_2)_x(0(\text{CH}_2)_2)_y\text{OH} \) frequently split into two phases with increase in temperature. Scattering of visible light increases many times over on approach to the lower consolute temperature \( T_c \), that of the phase split at the concentration where the immiscibility occurs at the lowest temperature). Usually, the increase
in intensity has been taken to indicate an increase in micelle size with temperature. Recently, Corti and DeGiorgio\(^4\) have interpreted such observations on solutions of C\(_{12}\)E\(_6\) (\(x = 11, y = c\) in the above representation) as indicating the approach to a critical point, by micelles approximately invariant in size.

Critical behavior is of considerable interest in micellar flooding, because of the hypothesis\(^5\) that proximity of critical end points are to a major extent the sources of low interfacial tensions favorable for oil recovery. SANS should be a useful technique, because at large values of \(x_c\), where particle scattering functions are less than unity, intensity arising from critical fluctuations will not seriously interfere.

We\(^6\) have measured scattering from 0.029 M C\(_{12}\)E\(_6\) in D\(_2\)O from about 15° to 45°C, below the phase split temperature, in D\(_2\)O, 47.4°C.

Figure 13.1 gives examples of the results. Intensities merge at high \(x_c\), but there is a sharp increase with temperature at low angles.

We have compared two models for the results. One, for particle growth, assumes cylinders; the other postulates scattering by spheres plus critical scattering, represented by an Ornstein-Zernike structural factor. The critical hypothesis gives a satisfactory fit to the results (Figure 13.2) substantially better than the cylinder model. Radii of the spheres (27-28.5 Å) from least-squares fits were relatively invariant with temperature. The radii of the cylinders were approximately the same, but less constant than those of the spheres. Parameters were better defined with the critical plus spheres model. The variation of the correlation length of critical fluctuations, \(\xi\), and of zero angle intensity from critical scattering as a function of
Fig. 13.2. Fit to scattering at 43.8°C by spheres plus D2 model. The inset shows the residuals (computed minus experiment, divided by error).

\[
\frac{d^2}{d^2}(N) = \frac{1}{1 + K^2} (P(K))_{\text{exp}} + N_0 V_0 (P_0 - p_0) (P(K))_{\text{exp}} + B
\]

\[
(P(K))_{\text{exp}} = \left( \frac{3 \sin KR - KR \cos KR}{KR^2} \right)^3
\]

\[\xi = t_c - t\] are consistent with expectations from \( t_c \) approach to a critical point (Fig. 13.1). The critical exponents evaluated from the slopes were approximately those expected from classical, rather than modern, theory, perhaps because our highest temperature was substantially less than \( t_c \). In any case, the SANS values of critical correlation length agreed about as well as could be expected with those from light scattering. In general, SANS supports the conclusions of Corti and DeGeorgio.

13.1.2 SANS from Ionic Micelles. Interpretation by the Mean Spherical Approximation

Critical scattering, as just discussed, results in a structural factor which corresponds to an increase in intensity at low angles. Repulsion between charged micelles, on the other hand, added to hard-sphere effects, results in a maximum in intensity as a function of angle. Scattering curves from several concentrations of sodium.
I-(pentylheptyl)benzene sulfonate (6-C₁₂SNa) in D₂O are an example given in the previous report. It has been shown earlier that structural factors for ionic systems can be calculated by the Mean Spherical Approximation (MSA). More recently, Hayter and Penfold have developed a MSA computer program specifically for spherical micelles. It allows fits to models comprised of a hydrocarbon core and one or two concentric shells of differing scattering power.

We have since carried out measurements of 0.055 M 6-C₁₂SNa as a function of solvent D₂O/H₂O ratio. By this "contrast" procedure, the relative scattering power of the solute and solvent is changed, and the possibility of an apparently satisfactory fit by an incorrect model is lessened. MSA gave excellent fits (Fig. 13.4) to the interaction peaks over the range measured, 57 to 100% D₂O; the model was comprised of a hydrocarbon core of 11.9Å radius, surrounded by a shell containing the remaining hydrocarbon, the aromatic sulfonate head group, the sodium ions complexed by the micelle, and water of hydration. Values of 52 ± 2 for the number of surfactant monomers/micelle and of 19 ± 1 for the micellar charge were obtained from the least-squares fit. A value of 5.8 Å for the thickness of the outer shell was derived, a number which implies a rough micellar surface.

13.1.3 SANS from a Surfactant with Counterions of Different Isotopic Composition

Although there is fairly general agreement concerning the aggregation number of simple micelles from conventional techniques, details of their structure are still controversial.
There is disagreement between groups concerning the degree of roughness of the surface, the extent of penetration of solvent, the extent of polydispersity, the shape, and the location of complexed counterions. It is hoped that SANS help resolve some of these questions. Variation of the scattering power of different regions by the monomers by selective deuteration is one approach. We present here some results of the type we believe will be helpful.

Figure 13.5 summarizes patterns measured on 0.4 M tetramethyl ammonium dodecyl sulfate as a function of D$_2$O/H$_2$O ratio. We carried out a similar set of measurements on the same compound, except that the methyls on the amine counterion were completely deuterated (Figure 13.6). Preliminary analysis by MSA indicates three-quarters of the counterions are associated with the outer shell of the aggregates. The contrast measurements also support this. Scattering goes through a minimum with D$_2$O/H$_2$O ratio, and again rises, as the coherent scattering length density in the 0.70 becomes larger than that of the solvent, because of the deuterated counterions.

In Figure 13.7, the difference in the patterns for the per-deuterated and per-protonated counterions in 106% H$_2$O is given.
Fig. 13.5. 0.4 M tetramethyl ammonium (per h) dodecyl sulfate, contrast (30°C).

Fig. 13.6. 0.4 M tetramethyl ammonium (d-12) dodecyl sulfate, contrast (30°C).
Here virtually all the signal arises from the counterions.

13.2 Phase Behavior of Aqueous-Organic Systems Containing Amphiphiles

In the previous report of this series, phase behavior of systems comprised of hydrocarbon/water/alcohol/low-equivalent-weight organic salts (protosurfactant)/NaCl was shown to be remarkably parallel to the behavior of similar systems containing high-equivalent-weight organic salts, or surfactants. Despite the fact that these sodium alkyl aromatic sulfonates and carboxylates were substituted with six or fewer alkyl carbons, and therefore would not be expected to form the micellar or other large aggregates common with their larger cousins, we observed for example, at amphiphile contents insufficient to effect a single phase, a progression with increasing NaCl concentration, other components being fixed, from two phases to three phases and back to two phases, a pattern frequently observed with systems favorable for micellar floods. Since, the studies of the systems have been extended and published. The analyses of the coexisting phases have also been carried out; because a paper summarizing them has been accepted, only a brief discussion will be included here.

The trends of distribution of components in the different phases are also parallel for surfactant and protosurfactant systems. For example, the organic salt is predominantly in the lower phase in the two-phase systems occurring at low salinity, in the middle when three phases are present, and in the upper when two phases occur at high salinity. The greater aqueous solubility of protosurfactants is reflected by appreciable amounts in lower
phases under all conditions, whereas surfactants are so concentrated in the "microemulsion" phases that frequently reports in the literature assume none in the others.

The ratio of water to hydrocarbon in the middle phase decreases with increasing salinity in surfactant-containing systems, the logarithm of the ratio being linear vs per cent NaCl in the aqueous component. Similar dependence is observed with protosurfactants (Fig. 13.9).

Distribution of the inorganic salt between the phases in two-phase systems and the lower two phases when these phases are present follows a pattern previously observed for ion exchangers. If molalities are expressed in terms of moles of ions/kg of water in the respective phases, the square root of ratio of sodium molality times chloride molality in the bottom phase to the product in the middle phase is the ratio of activity coefficients of salt in the middle to that in the bottom. In spite of the large differences in the compositions of the two phases, the value or the ratio was within a factor of two of unity in all cases.

13.3 Free Energies of Solutions of Low-Equivalent-Weight Organic Salts

In the previous report, preliminary measurements of the osmotic coefficients of protosurfactant-water and protosurfactant-water-salt solutions were described. A paper has been submitted summarizing the results on one category, the sodium alkylbenzenesulfonates. The trends can be seen in Figure 13.9, which summarizes activity coefficients inferred from our water activities and from some in the literature. In general, activity coefficients decrease with concentration more rapidly as the alkyl substitution on the solute increases. The fact that values fall below Debye-Huckel values for physically reasonable values of the distance-of-closest approach parameters indicates a strong interaction between the anions, and would be consistent with the formation of small aggregates. Large micelles typical of surfactants seem ruled out, however.

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Fig. 13.8. Ratio of weight of water to weight of hydrocarbon in the middle phase as a function of gms NaCl/gms NaCl + gms water. Composition (wt % of total system): 0 2% sodium 3,5 dilsopropyl sallylate, 4% 1-butanol; 2 4% sodium 2,5 dilsopropyl benzene sulfonate, 6% 1-butanol, water/2-n-octane wgt ratio, 1/1.
Fig. 13.9. Activity coefficients of aqueous photosurfactant solutions.


10. P. C. Ho and T. M. Bender, J. Physical Chemistry, in press.


As mentioned in previous reports, the 3 and 4 carbon alcohols added to modify properties of micellar flood surfactant solutions can be produced by bacterial fermentation of a variety of carbohydrates. The fermentations produce mixtures of 1-butanol, 2-propanol, acetone, and ethanol called neutral solvents. The availability of 1-butanol, the major fermentation product, could pose a barrier to large scale micellar flooding as it is currently in short supply. Industrially, neutral solvent components can be used as fuel extenders, industrial solvents, and as feedstocks for plastic and fiber production.

We have been interested in extending the range of materials that can be fermented to form neutral solvents, modelling the relatively complex separations of these materials, and developing improved separations methods. We have reported on a relatively simple method for selecting bacteria that form neutral solvents from wood carbohydrates, the largest collected and sterile U.S. fermentation
stream. We were able to select several organisms that were able to ferment wood molasses, a relatively difficult industrial stream which contains hydrolyzed hemicellulose, acids, lignin, furfural. Several of the organisms selected gave yields comparable to those on traditional feedstocks, such as starch. Modelling and simulation experiments used a combination of ASPEN, the advanced system for process engineering developed by M.I.T., and the modified UNIQUAC, or unified quasichemical equation of state, developed by Prausnitz and coworkers. We were able to model the system 1-butanol: acetone: ethanol: and water to provide a basis for distillation equipment and energy balance calculations. We found that the neutral solvents system has a substantially lower distillation energy requirement than does ethanol at 5% solvents w/v, a common industrial fermentation concentration. We also found that the separations equipment required for both processes was similar in sizing and layout. This information matches industrial operation of both processes. Although it is difficult, under present economic conditions, to improve neutral solvents separations costs over distillation, we have been investigating some promising solvent extraction systems, including several that are made from renewable resource products. Candidate systems appear to provide some improvement in fermentation yield.

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14. CONSERVATION PROGRAMS

The work summarized in this chapter has been sponsored by the Department of Energy through its programs in Thermal Energy Storage and in Electrochemical Energy Storage. The Thermal Energy Storage Program is managed by Oak Ridge National Laboratory, and has as its objectives the identification and development of thermal storage technologies which, when implemented, will increase the efficiency of heating and cooling systems for buildings or provide a mechanism for use of waste energy in industrial processes. Efforts in the Chemistry Division include: (1) critical survey of properties of salt hydrates with potential for use as phase change materials in low temperature thermal energy storage systems for residential heating or cooling; the survey provides a basis for recommendation of research needed to increase the effectiveness of these materials; and (2) a characterization of compounds which form clathrate hydrates with water with the aim of identifying clathrate hydrates which could be used for heat storage via the clathrate decomposition reaction which provides essentially the latent heat of fusion of ice but at higher temperatures.

The Technology Base Research Project (TBR) for Electrochemical Energy Storage is managed by Lawrence Berkeley Laboratory. The work reported here was sponsored in the Engineering-Science Research Element of TBR, whose goal is to establish scientific and engineering principles applicable to batteries and electrochemical systems. Research in the Chemistry Division, which was discontinued in October 1982, was on fundamental transport studies in mixed molten salt electrolytes such as those proposed in high temperature (~450°C) lithium-sulfur batteries. The effort consisted of qualitative and quantitative experimental verification of predictions from a model (developed in basic studies here) of the separation of the components of the molten salt mixture as a result of the faradaic, diffusional and electromigrational transport processes.

14.1. Thermal Energy Storage


(J. Braunstein)

The purpose of this task was to review the state-of-the-art of salt hydrates as phase change materials for low temperature thermal energy storage, with the objective of recommending research that would result in more practicable use of these materials. Areas for review included phase equilibria, nucleation behavior and melting kinetics of the commonly used hydrates.

A great deal of effort has been expended over the past thirty years towards the development of efficient, reliable inexpensive systems based on phase change materials, especially salt hydrates, for the storage (and retrieval) of thermal energy for residential heating. The pioneering work by Telkes stimulated, among her colleagues and in other groups, exhaustive searches of the literature and in the laboratory for compounds with phase change temperatures in an appropriate range and having high latent heats of transition, experimental investigation of properties, theoretical correlations for the estimation of unknown properties, and ingenious chemical, physical and mechanical solutions to the problems of assuring essentially reversible thermal behavior on long term cycling. Although some commercial development is now occurring, the use of phase change material thermal energy storage systems is not yet widespread. The reasons for this are no doubt primarily economic. But a major contributing factor to the economics is that solution of the problem of long term reliability has been elusive. Much of the development work has been of a short range nature, as required in the commercial sector. Relatively little effort of a basic nature has been made to answer continually recurring questions...
relating to nucleation, crystal growth, crystal melting kinetics, detailed thermodynamic analysis of phase equilibria in complex salt hydrate systems,\textsuperscript{4,5,6} analysis of nonequilibrium behavior in solution and other phenomena which bear on the effectiveness and therefore ultimately the economics of PCM-TES.\textsuperscript{7} Detailed basic studies of these phenomena that are needed are of a long range generic nature that might not justify short term commercial support, but they offer the possibility of greatly improved choice, modification and utilization of PCMs based on a better understanding of their behavior.

A list of recommendations of needed basic research has been prepared, derived largely from generic problems which have recurred in the past thirty years. A prime example of these problems is the prevention of segregation, e.g., in Glauber's salt, by stirring, by container configurations designed to assure thin layers of salt hydrate rather than large masses, by encapsulation of the PCM or by suspension. The recommended areas of research include: crystallization and melting (kinetics and structural studies); prediction of phase behavior in ternary systems (two salts plus water, two salt hydrates, or a salt hydrate and organic solvent); thermal diffusion-Soret effect for congruently melting salt hydrates in a temperature gradient; and physical properties measurements of selected salt hydrates.

\textbf{References}


\subsection{Clathrate Hydrates for Use in Dual Temperature Latent Heat Storage Systems (J. Braunstein)}

Clathrate hydrates, first reported by Sir Humphrey Davy in 1811,\textsuperscript{1} are attractive candidates for application in thermal energy storage systems. The encased "guest" molecules may bind (by van der Waals forces) ten to twenty water "host" molecules per guest in a crystalline array in which the water bond angles are only slightly distorted from those in ice.\textsuperscript{1,2} The heat of decomposition of the clathrate, per mole of water, is very nearly equal to the molar heat of fusion of ice,\textsuperscript{3,4} but the decomposition temperature may be higher. Tomlinson\textsuperscript{5} has proposed a cool storage system based on formation of the clathrate of the freon CCl\textsubscript{2}F\textsubscript{2} in the vicinity of the quadruple invariant point of the binary system H\textsubscript{2}O-CCl\textsubscript{2}F\textsubscript{2} at 12°C. Other proposed
applications of the clathration reaction include the demineralization of seawater, separation of hydrocarbons, separation of the inert gases, and more recently, their role in deposits of natural gas in permafrost regions.

The aim of this study is to review the properties of different classes of clathrate hydrates with a view to determining the feasibility of heat storage systems employing a clathrate with decomposition temperature above 30°C in a single system for dual temperature (winter heating and summer cooling) operation.

Most of the clathrate hydrates formed by gases are of the structure I or structure II types.\(^1,2\) The former have lattice constants of about 12 Å and their cages can accommodate only small molecules such as the inert gases, nitrogen, oxygen, and \(\text{H}_2\text{S}\). The latter have lattice constants about 17 Å and their cages can accommodate larger molecules such as the chlorinated hydrocarbons, freons, and the larger hydrocarbons. A strong empirical correlation is seen between the molecular size of the guest (whether expressed as molar volume, van der Waals radius, sum of bond lengths, or other index) and the reciprocal of the quadruple invariant temperature (which is essentially the intersection of the vapor pressure-temperature line of the guest with the clathrate decomposition (pressure-temperature) line on the phase diagram). The conclusion is that it is not likely that the quadruple temperatures higher than those for \(\text{Cl}_2\), \(\text{H}_2\text{S}\) and \(\text{AsH}_3\) (28-30°C) will be found. Higher clathrate decomposition temperatures are known for supercritical gases which therefore do not show an upper quadruple point, e.g., \(\text{CH}_4\), \(\text{C}_2\text{H}_6\), but the decomposition pressures are thousands of atmospheres.\(^3,9\) An elevation of the clathrate decomposition temperature in a ternary system is thermodynamically possible, but the phase diagrams are quite complex and few have been investigated.\(^10\)

Another class of clathrate hydrates consists of a number of tetraalkylammonium halide salts. These have clathrate structures in the anion occupying sites on the water lattice. These have high heats of fusion and melt congruently,\(^11\) but their mode of utilization in a heat storage system would be analogous to the use of salt hydrate phase change materials rather than to gas clathrate hydrates.


14.2 Electrochemical Energy Storage 14.2.1 Experimental Verification of Predicted Composition Gradients in Molten LiCl-KCl Battery Electrolytes by SEM/EDX and Auger Spectroscopy (C. E. Vallet, D. E. Heatherly, J. Braunstein, H. W. Dunn, L. D. Hulett, L. Heatherly, Jr., R. E. Clausing) Basic studies have demonstrated the establishment of current-induced composition...
gradients in mixed molten salt electrolytes. For example, such gradients have been measured in AgNO$_3$-NaNO$_3$ melts electrolyzed between solid silver electrodes, and predicted in mixed molten salt battery electrolytes. Composition shifts, if large enough, can produce significant deleterious effects, such as solid phase precipitation in or near the electrodes of molten salt batteries, including the LiAl/LiCl-KCl/FeS$_2$ battery. Although current-induced precipitation in the electrolyte of porous electrodes may affect adversely the utilization of reactants and the performance, there has been no direct measurement of the effect in a molten salt battery.

Analyses by atomic absorption spectroscopy (AA) and by scanning electron microscopy with energy dispersive x-ray fluorescence (SEM/EDX), demonstrated the current-induced composition changes in LiCl-KCl eutectic electrolyzed between solid LiAl electrodes, and were reported previously.

In this study, composition shifts such as those which could occur during discharge within the porous Li-Al negative electrode of an Li/S battery were observed and measured, following electrolysis and quenching, in the LiCl-KCl anolyte of a cell with Li-Al electrodes. The SEM/EDX analysis of anolyte composition shows regions in the front part of the porous electrode where pure lithium chloride precipitated during electrolysis. A composition profile in the anode and separator is shown in Fig. 14.1. Figure 14.2 is a 3-dimensional plot of the distribution of LiCl compositions on an axially cut anode section. (The anode depth distance scale is expanded tenfold for resolution.) The regions of solid precipitation accentuate the nonuniformity of current distribution, as shown by adjacent regions with no composition change. Cathodic reaction is indicated by increased KCl concentration and was observed primarily near the cell walls. Calculations with a one-dimensional model also predicted cathodic reaction at the collector in the back of the electrode. Similar inhomogeneities could have considerable effect on swelling, ohmic resistance and other properties of battery cells, and could lead to certain failure modes.

Figure 14.3 shows Auger spectra which confirmed the Li/Cl analysis of the precipitates deduced from the SEM/EDX analysis of the K/Cl ratios. Similar behavior in actual battery electrodes remains to be demonstrated; measurements of electrolyte composition, together with anal-

![Figure 14.1](image_url)  
Figure 14.1 EDX measured compositions near the electrode/electrolyte interface in the porous Li-Al anode and in the porous Y$_2$O$_3$ separator. Current = 0.252 A cm$^{-2}$; time = 4 minutes.
Figure 14.2 Measured anolyte composition in the front part of a Li-Al porous electrode, and projected composition isopleths.

Anodic reaction:
- $X_{\text{LiCl}} > 0.78$; LiCl precipitates found.
- $0.65 < X_{\text{LiCl}} < 0.78$

No change:
- $0.52 < X_{\text{LiCl}} < 0.65$

Cathodic reaction:
- $0.39 < X_{\text{LiCl}} < 0.52$ No LiCl precipitates found.
- $X_{\text{LiCl}} < 0.39$
positive electrode, and the present methods appear to be applicable.11

2. Analytical Chemistry Division, OPNL.
3. Metals and Ceramics Division, ORNL.
PUBLICATIONS AND PATENTS

COAL CHEMISTRY


1. Summer Research Participant, Notre Dame University.
2. University College of Science, Calcutta, India.
4. Department of Chemistry, University of Tennessee, Knoxville.
5. Metals and Ceramics Division.
6. Engineering Technology Division.
7. Chemical Technology Division.
AQUEOUS CHEMISTRY AT HIGH TEMPERATURES


1. Chemical Technology Division.
2. Institute of Physical Chemistry, University of Frankfurt, FRG.
4. School of Oceanography, Oregon State University, Corvallis, Oregon.
5. Chemistry Department, University of California, Berkeley.
6. Arizona State University, Tempe, AZ.

**GEOSCIENCES**


HIGH TEMPERATURE CHEMISTRY AND THERMODYNAMICS OF STRUCTURAL MATERIALS


1. Chemical Technology Division.
2. Aerospace Corporation, Los Angeles, CA.
4. Analytical Chemistry Division.
5. Carleton College, Northfield, MN.
6. Phillips Petroleum Co., Bartlesville, OK.
7. Laboratoire de Physique, Faculté de Sciences, Mirande, Dijon, France.
9. KFA, Julich, FRG.
10. Metals and Ceramics Division.
11. Tritium Research Center, Toyama University, Toyama, Japan.
12. Department of Chemistry, University of Tennessee, Knoxville, 37996.

CHEMISTRY OF TRANSURANIUM ELEMENTS AND COMPOUNDS


2. Department of Chemistry, University of Tennessee, Knoxville, TN.
3. University of Tennessee, Knoxville; part-time ORNL employee.
4. Institut de Physique Nucléaire, Orsay, France.
6. Lawrence Livermore National Laboratory.
7. Tennessee Technological University, Cookeville, TN.
8. Analytical Chemistry Division.
10. State University of New York, Albany.
11. Physics Division.
12. Physics Department, University of Tennessee, Knoxville, Tennessee.
15. Nuclear Research Centre - Negev, Beer-Sheva, Israel.
16. Present address: Battelle-Houston, Houston, TX.
18. Engineering Physics Division.
19. Instruments and Controls Division.
20. Westvaco Research Laboratory, Maryland.
21. Gesellschaft für Schwerionenforschung, Darmstadt, Germany.
22. University of Mainz, Germany.
23. Lawrence Berkeley Laboratory.
25. Los Alamos National Laboratory.

SEPARATIONS CHEMISTRY


J. H. Burns, "Solvent-Extraction Complexes of the Uranyl Ion. 2. Crystal and Molecular Structure of Catena-di-d1-r-butylphosphato-dioxouranium (VI) and Di-d1-r-butylphosphato-bis[nitrato(tri-n-butylphosphine oxide) dioxouranium (VI)]," Inorg. Chem. 21 (in press).


1. Rexnord Corporation, Milwaukee, Wis.
2. Fuel Recycle Division.
3. Chemical Technology Division.

ELECTROCHEMISTRY


1. Department of Chemistry, University of Missouri, Columbia, Missouri.
2. Department of Chemistry, Brookhaven National Laboratory, Upton, New York.
3. Department of Chemistry, Stanford University, Palo Alto, California.

CATALYSIS


1. University of Messina, Italy.
2. University of Tennessee, Knoxville, TN.
3. Universität Osnabrück, FRG.
5. Physics Division.
6. Lawrence Livermore Laboratory.
7. Northwestern University, Evanston, IL.

CHEMICAL PHYSICS


1. Solid State Division.
2. University of Oklahoma.
5. Carleton College, Northfield, Minn.
6. University of Georgia.
7. Undergraduate research participant, Fall 1973; Wooster College, Wooster, Ohio.
8. Department of Chemistry, University of Tennessee, Knoxville.
10. Instituto di Chimica Generale, Università di Roma, Rome, Italy.
14. Georgia State University, Atlanta, GA.
15. Sandia Laboratories, Livermore, CA 94550.
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17. Physical Science Laboratory, Stoughton, Wisconsin.
19. Argonne National Laboratory.
20. Ames Laboratory.
22. Freie Universität, Berlin, FRG.
25. Oak Ridge Associated Universities.

THEORETICAL CHEMISTRY


1. Consultant, Prophysica, Inc.
2. Industrial Safety and Applied Health Physics Division.
3. College of William and Mary, Williamsburg, VA.
5. Sandia Laboratories, Livermore, CA 94550.
6. California Institute of Technology, Pasadena, CA 91125.
7. Department of Physics, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada.
8. Physics Division.
9. Institute of Physics, University of Aarhus, Denmark.
10. Los Alamos National Laboratory.

NUCLEAR WASTE CHEMISTRY


1. Chemical Technology Division.
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ENHANCED OIL RECOVERY


1. Information Division.
2. Co-op student, University of Tennessee, Knoxville.
3. Present Address: Department of Chemistry, Wake Forest University, Winston-Salem, N.C.
4. Department of Chemistry, University of Tennessee, Knoxville; part-time ORNL employee.
5. University of Palermo, Italy.
6. Union Carbide Nuclear Division, Central Management Staff.
7. IERI, Environmental Protection Agency, Cincinnati, Ohio.
8. Retired.
11. Present Address: Battelle Houston Laboratories, Houston, Tex.
CONSERVATION PROGRAMS


1. Metals and Ceramics Division.
2. Analytical Chemistry Division.
3. SCUU student, 1980.
### DIVISIONAL PERSON-POWER AND FINANCIAL SUMMARY
### FY 1982

<table>
<thead>
<tr>
<th>DOE PROGRAMS</th>
<th>Funding (in thousands)</th>
<th>Scientific and technical person-years</th>
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<th>WORK FOR OTHERS PROGRAMS</th>
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<td>Dupont Co. — Molecular Structure of Coal</td>
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<td>EPRI — Sulfate Phase Studies</td>
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<td>LBL — Molten Salt Batteries</td>
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<td>US Army — Computer Assistance</td>
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<td>Miscellaneous</td>
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<td><strong>TOTAL WORK FOR OTHERS</strong></td>
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<td><strong>TOTAL FINANCIAL PLANS</strong></td>
<td><strong>$8,251</strong></td>
<td><strong>71</strong></td>
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*Approximately 4 persons worked on loan to other ORNL divisions.*
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<td>Central Research Library</td>
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<td>Laboratory Records, ORNL R.C.</td>
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<td>D. M. Jared</td>
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<tr>
<td>33</td>
<td>J. S. Johnson, Jr.</td>
<td>L. C. Ianniello</td>
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<tr>
<td>34-108</td>
<td>O. L. Keller, Jr.</td>
<td>E. L. Keller, Jr.</td>
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<tr>
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<td>R. E. Leuze</td>
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<td>110</td>
<td>R. Livingston</td>
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168. R. J. Kendall, Chief, Fundamental Interactions Branch, ER-161, Division of Chemical Sciences, Office of Basic Energy Sciences, DOE, Mail Station J-309, GTN, Washington, DC 20545
169. R. S. Maranelli, Processes & Techniques Branch, ER-162, Division of Chemical Sciences, Office of Basic Energy Sciences, DOE, Mail Station J-309, GTN, Washington, DC 20545
171. J. Y. Borous, CEA, Fontenay-aux-Roses, France
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173. M. O. Millington, P. O. Box 25063, Houston, TX 77265
174. V. C. Stawdalis, Energy and Environmental Systems, Building 362, Argonne National Laboratory, Argonne, IL 60439
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