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for Period Ending August 31, 1978

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1. Introduction and Divisional Overview

The Chemistry Division has a staff of 157 people; 96 are scientists, 14 are technicians, 11 are secretaries and administrative personnel, and the remainder are visiting scientists and students. Our work includes physical chemistry, inorganic chemistry, organic chemistry, nuclear chemistry, and small but growing efforts in geochemistry and chemical microbiology. The three sections of the division, Inorganic and Organic Chemistry, Nuclear and Transuranium Element Chemistry, and Physical and Engineering Chemistry, reflect these broad areas of interest.

In the Inorganic and Organic Chemistry Section, a large effort exists in molten salt chemistry, with two groups involved. One of these studies covers the catalytic properties of molten salts related to coal chemistry, and the other their thermodynamic and transport properties. Another group covers organic chemistry, especially coal chemistry. Of the two groups in materials chemistry, one is studying corrosion and the other the chemistry and thermodynamics of structural materials subjected to high temperatures. One group is studying the chemical problems in the nuclear fuel cycle, both in aqueous and nonaqueous processes, and is supported by an effort in the spectroscopy of the actinide elements in solutions. The section also has a modest but important effort in the thermochemical synthesis of hydrogen.

The section on Nuclear and Transuranium Element Chemistry has two major efforts. The nuclear chemistry group concentrates on the interactions of energetic heavy ions with nuclei to study the mechanisms of nuclear reactions and the details of nuclear structure at high excitation energy and high angular momentum. The heavy element chemists study the chemical and physical properties of the actinide elements and their compounds, especially of elements from curium through einsteinium (atomic numbers 96 through 99). A recent development in this program is the study of chemistry problems that are important societal concerns: the behavior of the actinides in the environment and in nuclear waste repositories.

In the Physical and Engineering Chemistry Section, a major concern is aqueous solution chemistry involving three groups in the study of ion exchange, solvent extraction, and thermodynamics. Another four groups cover the area of chemical physics: chemical reactivity is studied photochemically, with electron spin resonance, and with atomic and molecular beams by two of these groups. A third group does crystallography by both x-ray and neutron diffraction. The Theoretical Chemistry Group and a sizable effort in heterogeneous catalysis completes the chemical physics area. Two fairly new efforts in the Physical and Engineering Chemistry Section are geochemistry and chemical microbiology. We expect both of these efforts to grow, the former because the earth is our source of raw materials and the sink for our wastes and the latter because eventually we will have to rely on renewable resources. The current emphasis in geochemistry is on high-temperature and high-pressure phase equilibria and crystallization of synthetic granitic compositions, chemical migration, and the properties of geothermal brines. In chemical microbiology, the emphasis is on production of chemicals for the surfactant flood process for increased oil production.

Though most of our work continues to be research seeking fundamental understanding of the elements, their reactions, and their compounds within the scope of the interests of the Department of Energy, we are heavily involved in research that has practical significance. These programs, which represent about a third of our work, address problems in enhanced oil recovery, nuclear waste isolation, the nuclear fuel cycle, fuel cells and batteries, uranium recovery from low grade ores, coal use, fusion reactor materials, and geothermal energy. These programs have led to several relationships with industry. The recovery of uranium from phosphoric acid has been an outstanding success; several commercial plants based on the research done at ORNL are either in operation or under construction. Interest has also been expressed in the processes we are developing to make polymers and cosurfactants for enhanced oil recovery. Our research in coal chemistry has generated considerable interest of several major oil and chemical companies. At the same time, we have continued our strong relationships with universities through visitors, colleagues, and the unique facilities at ORNL such as the High Flux Isotope Reactor.

Some of our work has changed direction during the last year, and some changes have been made that will affect our research in the following years. Our program on the precipitation and scaling of geothermal brines ended at the request of the Division of Geothermal Energy. The program on biophysical chemistry also ended during this period. We began programs in high-temperature materials chemistry and the thermodynamics of structural materials as well as nuclear waste isolation during the past year.

2. Coal-Related Research: Organic Chemistry and Catalysis

2.1 COAL-RELATED RESEARCH

2.1.1 Free Radical Reactions: 1,2-Shift of Phenyl from Oxygen to Carbon

C. J. Collins, W. F. Kozak,
W. H. Korte, and B. M. Benjamin

The importance of tetralin as a hydrogen donor in coal technology is well known,^{1,2} and we recently reported on its reactions with Wyodak and Wyo. 10, No. 6 vitrinite as well as with a series of model compounds.^{3,4,5} We observed⁴ that coal and tetralin-¹⁴C when heated at 400°C for 1 h yield traces of carbon-14 labeled α - and β -methyl-naphthalenes. Since tetralin alone yields no measurable amounts of methyl-naphthalenes, we presume that the methyl groups in these compounds originate in the coal. Treatment of several aralkyl hydrocarbons and ethers with tetralin under the same conditions also yielded, among many other products, 4-10% methyl-naphthalenes; experiments with carbon-14 labeled hydrocarbons and ethers leave no doubt that intermolecular transfer of carbon occurs in the formation of the alkyl-naphthalenes.

We report here on the reactions with tetralin at 400°C of phenetole- α -¹⁴C and phenetole- β -¹⁴C (ref. 6). In 18-h typical overall (normalized) yields based on gas-chromatographic (GC) analyses were: benzene, 11%; toluene, 11%; ethylbenzene, 11%; phenol, 47%; methyl-naphthalenes, 16%; and ethyl-naphthalenes, 4%. Gas chromatographic-mass spectrometric (GC-MS) analyses revealed⁷ traces of many other compounds. Monitoring of the radioactivity of the toluene, ethylbenzene, and methyl- and ethyl-naphthalenes from phenetole- α -¹⁴C disclosed that all four of these products contained carbon-14 and that their molar radioactivities corresponded essentially with that of the reactant phenetole- α -¹⁴C. An unexpected and surprising result from the reaction of phenetole- β -¹⁴C (1- β -¹⁴C) with tetralin (2) at 400°C was the observation that the toluene (3) contained only a trace of carbon-14, whereas ethylbenzene (4) and the alkyl-naphthalenes (5 and 6) were all labeled.

The result for toluene was confirmed by its isolation and radioactivity assay. The carbon-14 distribution in the ethyl-¹⁴C-benzene produced was determined after isolation by oxidation⁸ to benzoic-¹⁴C acid and carbon-14 determination. The results are shown in Fig. 2.1 and were checked independently through similar experiments with phenetole- α -¹⁴C (ref. 10).

Although the alkyl-naphthalenes (5 and 6) were formed through intermolecular reaction,¹¹ the mechanisms for the formation of 3 and 4 could, in principle, be either inter- or intramolecular. To resolve this question, we carried out the experiments

Fig. 2.1. Radioactivity distributions in toluene and ethylbenzene fractions obtained from heating phenetole- α -¹⁴C in tetralin at 400°C.

Fig. 2.2. Results expected for crossover reactions of phenetole- α - ^{14}C with ethyl *p*-tolyl ether in tetralin at 400°C through intramolecular (1) or intermolecular (2) processes.

defined in Fig. 2.2, in which a 50:50 mixture of phenetole- α - ^{14}C and ethyl *p*-tolyl ether was heated with tetralin at 400°C for 40 h. If toluene and ethylbenzene were formed by intramolecular processes, then only toluene and ethylbenzene should contain carbon-14, as shown in situation (1) in Fig. 2.2. If the processes are intermolecular, then all four products should be labeled (2). The *p*-xylene and *p*-ethyltoluene produced were devoid of radioactivity, signifying intramolecular processes.¹²

More than one intramolecular pathway is possible from phenetole (1) to toluene and ethylbenzene, but our data demand that any such pathway must involve a 1,2-shift (A $\rightarrow$ B) of phenyl from oxygen to carbon, possibly involving the formation of α -phenylethanol (7). We examined the reactions of α -phenylethanol (7) in tetralin (2) at 400°C and find that it does, in fact, yield toluene and ethylbenzene. Although 1,2-shift of phenyl from oxygen to carbon in a free radical intermediate has been claimed,¹³ the evidence is unconvincing and largely circumstantial. In the present work there can be little doubt that 1,2-phenyl shift occurs intramolecularly from oxygen to carbon through free radical intermediates.¹⁴

2. See the discussion of the Pott-Broche process by K. F. Schupp and H. Wien, *Angew. Chem. Int. Ed. Engl.* **15**, 341-46 (1976).

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

4. C. J. Collins, B. M. Benjamin, V. F. Raaen, P. H. Maupin, and W. H. Roark, "Organic Chemistry of Coal," American Chemical Society Symposium Series No. 71, chap. 12, American Chemical Society, Washington, D.C., 1978, pp. 165-70.

5. B. M. Collins, V. F. Raaen, P. H. Maupin, I. J. Brown, and C. J. Collins, *Fuel* **57**, 269 (1978).

6. Ethanol-1- ^{14}C and ethanol-2- ^{14}C were prepared from appropriately labeled sodium acetates according to A. Murray, III, and D. L. Williams, pp. 905-06 in *Organic Synthesis with Isotopes*, part I, Interscience, New York, 1958. The labeled ethanols were converted to ethyl iodides (H. S. King, p. 399 in *Organic Syntheses Collective*, vol. 2, John Wiley, New York, 1943) and thence to phenetole- α - ^{14}C and phenetole- β - ^{14}C through the Williamson synthesis (W. J. Hickinbottom, p. 91 in *Reactions of Organic Compounds*, Longmans, New York, 1948).

7. A Barber-Coleman 5000 gas chromatograph fitted with radioactivity (carbon-14 and tritium) monitoring accessories was used.

8. The dry combustion method with a Borkowski ion-chamber and a vibrating reed electrometer was used. The method is described in chap. 11, *Carbon-14*, V. F. Raaen, G. A. Ropp, and H. P. Raaen, McGraw-Hill, New York, 1968.

9. The method used was that of L. Slaugh, *J. Amer. Chem. Soc.* **81**, 2262 (1959).

10. Phenetole- α - ^{14}C was converted to toluene- ^{14}C and ethyl- ^{14}C -benzene (4.46 MCi/mol); benzoic- ^{14}C acid from toluene, 4.11 MCi/mol; benzoic- ^{14}C acid from ethylbenzene, 4.04 MCi/mol. The discrepancies with the data in Fig. 2.1 are due to isotope effects during the oxidations to benzoic acid. See, for example, W. A. Benner and C. J. Collins, *J. Amer. Chem. Soc.* **75**, 2308 (1953).

11. When phenetole and tetralin at 400°C [C. J. Collins, *J. Am. Chem. Soc.*, **73**, 1038 (1951)] were heated at 400°C, the alkylnaphthalenes were all of essentially the same carbon-14 content as the reactant tetralin (Corel²).

12. The *p*-xylene was identified by its GC retention times and by admixture with an authentic sample. The *p*-ethyltoluene, however, was isolated by preparative GC (Varian Aerograph, Series 2800) and identified by NMR (Varian XI-100). Radioactivity determinations were by GC fitted with a carbon-14 monitor.

13. M. F. R. Muekchey, J. G. Tucker, D. J. Williams, and J. R. Wymshurst, *Chem. Commun.*, 109 (1965). See also the review by J. W. Wilt, chap. 8, pp. 353-50 in *Free Radicals*, J. K. Kochi, ed., John Wiley, New York, 1973.

14. The carbon-14 (6%) found in the α -position of ethylbenzene (Fig. 2.11) is yet unexplained. In this connection it is significant that, in an experiment in which anisole and tetralin were heated at 400°C for 25 h, toluene and ethylbenzene were formed, among other products (GC analysis), in a ratio of about 4:1. See also J. W. Wilt and M. W. Stumpf, *J. Org. Chem.*, **30**, 1256 (1965).

2.1.2 Pyrolysis of 1,2-Diphenylethane in the Presence of Tetralin

B. M. Benjamin

The pyrolysis of pure compounds in the presence of donor solvents such as tetralin provides information that can be helpful in understanding some aspects of chemical changes that take place in the solvent refining of coal. In previous papers¹⁻³ data were presented to show which bonds break when several classes of compounds are pyrolyzed. These experiments do not afford evidence for the presence of any particular structural feature in coal, nor are they intended to imply a simplified coal model. The experiments may be used to visualize how certain structural features, which are known to be present in coal, respond (cleave, rearrange, reduce) to experimental conditions.

It has been demonstrated (Heredy, Newworth)⁴ that ethylene groups ($-\text{CH}_2-\text{CH}_2-$) connecting aromatic nuclei are one of the structural units present in coal. By employing 1,2-diphenylethane as a model for that structural unit and heating a mixture of that compound and tetralin at 400°C, it was shown that the ethylene group cleaves (but slowly) at the central C-C bond to produce toluene. The hydrogen needed is derived from tetralin, which, in turn, is converted to naphthalene. It was stated in a recent paper⁵ that (1) not enough naphthalene is obtained to account for the toluene produced and (2) 1,2-diphenylethane acts as its own hydrogen donor, a part of it being converted to stilbene. A review of our own work on the action of tetralin on 1,2-diphenylethane did not reveal the presence of stilbene in the reaction mixture.

The work was therefore repeated several times, and the products were carefully analyzed. Experimental procedures were the same as used earlier.

When 1,2-diphenylethane and tetralin (molar ratio, 1:2) were heated at 400°C for 1 h, only a trace of toluene and naphthalene was found. When heating was continued for 24 h, 36% of the parent compound was consumed, and the molar ratio of toluene to naphthalene was 1.83:1. Thus over twice the amount of hydrogen needed for the reaction was generated. No stilbene was found among the products. Figure 2.3 shows a GC trace of the product mixture in comparison with a synthetic mixture.

When stilbene was heated with tetralin (molar ratio, 1:2) at 400°C for 1 h, almost one-half the stilbene was reduced to 1,2-diphenylethane. Within 24 h all of the stilbene was reduced. 1,2-Diphenylethane heated alone (no tetralin) at 400°C for 24 h gave a product consisting of 71% toluene, 9% stilbene, 20% starting material, and other minor products. Similar heating of stilbene alone for 24 h gave 29% toluene, 24% 1,2-diphenylethane, 47% stilbene, and a black polymer as well as other products.

According to work at this laboratory, the following compounds are reduced when heated with tetralin: stilbene,⁶ 1,1,2-triphenylethylene,⁷ indene,⁸ cyclopentene,⁹ and 1-phenylcyclohexene.¹⁰ Oletins are not expected to be isolated when hydrocarbons are pyrolyzed in the presence of tetralin. If they are formed as intermediates, they are either polymerized or are reduced.

1. C. J. Collins, V. F. Raaen, B. M. Benjamin, and G. W. Kabalka, *Fuel*, **56**, 167 (1977).

2. B. M. Benjamin, V. F. Raaen, G. W. Kabalka, and C. J. Collins, *Preprints, Div. Fuel Chem., Am. Chem. Soc.*, **22**(2), 206 (1977).

3. C. J. Collins, B. M. Benjamin, V. F. Raaen, P. H. Maupin, and W. H. Roark, *Preprints, Div. Fuel Chem., Am. Chem. Soc.*, **22**(5), 98 (1977).

4. B. M. Benjamin, V. F. Raaen, P. H. Maupin, I. J. Brown, and C. J. Collins, *Fuel*, **57**, 269 (1978).

5. I. A. Heredy, A. E. Kostyo, and M. B. Newworth, *Fuel*, **44**, 125 (1965); I. A. Depp, C. M. Stevens, and M. B. Newworth, *Fuel*, **35**, 437 (1956).

6. K. R. Brower, *Fuel*, **56**, 245 (1977).

7. Product analysis was done on a Varian Series 2800 GC fitted with an 8 ft $\times$ 0.25 in. column containing 20% Apiezon on Chromosorb. For quantitative work, the response of the detector was calibrated using mixtures of known composition.

Fig. 2.3. Gas chromatographic trace of the products derived from heating 1,2-diphenylethane and tetralin at 400°C for 24 h.

2.1.3 Dehydrogenation of Coal and of Model Compounds with Benzophenone

V. F. Raaen W. H. Roark

Coal has been dehydrogenated with *p*-benzoquinone and also catalytically in the presence of phenanthridine. Brower has suggested that quinones in partially oxidized coals are responsible for the oxidation of tetralin to naphthalene; carbonyl compounds were not considered as possible hydrogen acceptors. We have reported previously^{1,2} that benzophenone is effective in removing hydrogen from coal as well as from the less-effective donor, tetralin. Benzohydrol proved to be even more reactive than benzophenone. However, the applicability of benzohydrol to the dehydrogenation reaction is complicated by the disproportionation:

Benzophenone is a very useful reagent, not only for ranking a series of hydrogen donors but also for determining the amount of labile hydrogen in coal. As a dehydrogenation reagent, benzophenone is superior to the quinones with respect to its thermal stability, low equivalent weight, and the ease with which it can be separated from its reduction product, diphenylmethane. We report here a comparative study of the dehydrogenation with benzophenone of typical donor solvents, coals, and phenols; all were studied under similar conditions. Benzene was used as a cosolvent; the reactions were run in sealed tubes (Pyrex capillaries or capped stainless-steel tubing), and the samples were not stirred. The degree of reduction of benzophenone to diphenylmethane was

Table 2.1. Hydrogen-donor ability of various compounds for the reaction $\text{Ph}_2\text{CO} \rightarrow \text{Ph}_2\text{CH}_2$ (400°C, 90 min)

Hydrogen donor (in excess)	Conversion to Ph_2CH_2 (%)
Cholesterol	39
1,2-Dihydronaphthalene	28
Tetrahydrocarbazole	28
1,2,3,4-Tetrahydroquinoline	21
9,10-Dihydrophenanthrene	20
Tetralin	17
9,10-Dihydroanthracene	13
Decalin	0

determined by GC analysis. The use of carbon-14 labeled reagents aided identification of products by means of a GC radioactivity monitor. Data were obtained under two sets of conditions: (1) short-term (1- to 2-h) heating at 400°C to determine the relative rates at which donors of the tetralin class give up hydrogen and (2) long-term (24-h) heating to determine how much hydrogen can be obtained from coal. Prolonged (20- to 24-h) heating causes 1 to 2% hydrogenolysis of diphenylmethane, which consumes two additional hydrogens. Table 2.1 gives typical data for hydrogen-donor response to short-term heating. Cholesterol is a classic example of a natural product that undergoes facile dehydrogenation, whereas its hydrogenated counterpart, cholestane, is essentially unaffected.

For the 11 coals studied, the hydrogen loss to benzophenone varies from less than 3% for anthracite to 34% for a vitrinite-rich fraction of Illinois No. 5. Table 2.2 shows that the hydrogen-to-carbon ratios in the depleted coals (anthracite excepted) range

Table 2.2. Hydrogen-donor ability of various coals for the reaction $\text{Ph}_2\text{CO} \rightarrow \text{Ph}_2\text{CH}_2$ (400°C, 24 h, Ph_2CO in excess)

Type of coal	Hydrogen removed (% of total hydrogen content)	Hydrogen-to-carbon ratio in recovered coal
Illinois No. 5 vitrinite	34	0.60
N.D. lignite, hagel seam, PSOC-246	34	0.55
N.D. lignite, zap seam, PSOC-86	31	0.55
Kentucky No. 9, PSOC-213	28	0.61
Pittsburgh seam, PSOC-293	28	0.51
A, B, D, and G, Tennessee	28	0.64
Illinois No. 6 vitrinite	25	0.58
Wyodak	22	0.73
Pocahontas, mid volume	22	0.54
Pocahontas, low volume	22	0.49
Anthracite	3.8	0.29

from 0.49 to 0.73, but most of them approach the value 0.50, which Reggel, Wender, and Raymond give as the approximate lower limit in the catalytic dehydrogenation of coal.

Phenols are also effective in reducing benzophenone but at rates that appear to be much slower than those for the hydroaromatic compounds (e.g., 1,2-dihydronaphthalene). Table 2.3 gives the results obtained by heating benzophenone separately with a large excess of each of the indicated phenols. The reaction has utility for the preparation of the dibenzofurans. The parent dibenzofuran is formed in 40% yield (based on GC information) from phenol, and α -dinaphthalene oxide is easily isolated in 80% yield when α -naphthol is heated with excess benzophenone.

Table 2.3. Hydrogen-donor ability of various phenols in the reaction $\text{Ph}_2\text{CO} \rightarrow \text{Ph}_2\text{CH}_2$ (400°C, 17 h)

Hydrogen donor (6% excess)	Conversion to Ph_2CH_2 (%)
Resorcinol	78
Phloroglucinol 2H ₂ O	68
<i>p</i> -Nitrophenol	64
<i>m</i> -Cresol	41
<i>p,p'</i> -Biphenol	39
Catechol	39
<i>p</i> -Cresol	38
Hydroquinone	38
2,6-Di- <i>t</i> -butyl-4-methylphenol	<i>a</i>
α -Naphthol	<i>a</i>

^a Instances in which the multitude of products interfered with the GC determination of the $\text{Ph}_2\text{CO}:\text{Ph}_2\text{CH}_2$ ratio.

As a dehydrogenator, benzophenone has the advantages over benzoquinone of increased stability at higher temperatures and of being reactive toward phenols. The coupling of phenolic structures in coal during the reordering and solubilization that occur when coals are heated may, in a similar way, account for the formation of dibenzofuran and alkyl dibenzofurans that are present in the liquids from solvent-refined coal.

Acknowledgments. We thank the Consolidation Coal Company, Reading Anthracite Company, and Pennsylvania State University for many of the coal samples.

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2. I. Reggel, I. Wender, and R. Raymond, *Fuel* 47, 152 (1968).

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2.1.4 The Pyrolysis of Tetralin

B. M. Benjamin - V. F. Rader
E. W. Kaganan - C. J. Collins

The pyrolysis of tetralin has been studied at 500°C. The pyrolysis products resulting from the decomposition of 1-¹⁴C-tetralin were analyzed by ¹⁴C-NMR spectroscopy to determine the carbon redistribution in these substances. Some results were confirmed by experiments with ¹⁴C-labeled compounds. Under the conditions employed, carbon scrambling is observed only in the aliphatic portion of the products. The primary mode of decomposition of tetralin proceeds via homolysis of the 1-8a bond. An equilibrium between tetralin and naphthalene plus hydrogen does not take place in the absence of a catalyst.

In earlier publications¹⁻³ we reported the results of pyrolysis of a large number of compounds which contain coal-related structural features in the presence of the donor solvent, tetralin. Since the appearance of that work the question has been asked several times, "What happens to tetralin under similar pyrolytic conditions?"

We now report the results of our study of the pyrolysis of tetralin using a combination of ¹⁴C labeling, ¹⁴C labeling, NMR, GC, and MS. Our experimental conditions differed somewhat from those of Penninger in that, in some of the experiments, we did not add an atmosphere of hydrogen gas; in others both gaseous hydrogen and coal were present.

Products of pyrolysis of tetralin. When tetralin was heated at 400°C for 1 h, a trace was converted to naphthalene and 1-methylindane. If the heating was continued for 18 h at 400°C, about 1% decomposition occurred. However, when tetralin was heated at 500°C for 1 hr, extensive decomposition was observed, with only about 25% of the tetralin remaining. Naphthalene was the major product, and small amounts of 1-methylindane, indane, ethylbenzene, and toluene were formed. Yields were not determined because they change, depending on the time and temperature of heating. Between 1 and 30%

each of several other compounds were present. Utilizing GC-MS, these compounds were identified as benzene, *o*-xylene, methylethylbenzene, *n*-butylbenzene, 2-methylindane and α - and β -methyl-naphthalene. Trace amounts of numerous other compounds were detected, among which the following could be identified: *n*-propylbenzene, two other C₉ benzenes, α - and β -ethylnaphthalene, 1- and 2-ethylindane, the three binaphthyls, and chrysene. The last four compounds represent condensation products with higher molecular weights than the starting tetralin.

The binaphthyls are probably derived from the pyrolysis of naphthalene. The pyrolysis of naphthalene alone is reported to give 1,1', 2,2', and 1,2'-binaphthyl. We confirmed that these were the major products when naphthalene was heated at 500°C for 1 h. About 1% of the naphthalene was converted, and the 2,2' isomer was formed in the highest yield.

The gas fraction produced when tetralin was heated to 500°C contained 35% hydrogen, 45% methane, 31% ethane, and 13% propane. Propene and butane were also detected in smaller amounts. The products of pyrolysis of tetralin over porcelain chips at 700°C and "ambient pressures" have been reported. A larger proportion of condensation products were formed under those conditions.

Pyrolysis of ¹³C labeled tetralin. The reaction described in the foregoing paragraph was repeated at 500°C, using tetralin-1-¹³C (ref. 8), and the major components of the product mixture were separated by preparative gas chromatography. Samples of tetralin (1), naphthalene (2), 1-methylindane (3), indane (4), and toluene (5) were obtained. The

distribution of the label in these substances was determined by quantitative integration of their ¹³C NMR spectra (see Experimental), and the results are presented in Tables 2.4 and 2.5. The tetralin-1-¹³C was synthesized from Br¹³CO₂ by an adaptation of the Collins procedure⁸ and was diluted with tetralin containing ¹³C in natural abundance to give two samples that contained 5.5 and 43.5% carbon at C-1 respectively.

The data in Table 2.4 refer to the products derived from the low ¹³C abundance (5.5%) tetralin. The ten-carbon compounds, tetralin (1), naphthalene (2), and 1-methylindane (3), possess the same ¹³C content as the starting material. In this experiment the labels in 1 and 2 appear to be confined to position C-1, but in 3 to be equally distributed between the benzylic methylene (position C-3) and the methyl group. The indane and toluene spectra reveal that their formation is accompanied by loss of about one-half the label of the original tetralin. In none of the products except naphthalene is any carbon-13 above the natural abundance level found in the aromatic nucleus. Thus within the error limits of the integrations, a simple distribution of the label emerges as indicated in scheme 1, Fig. 2.4. Naphthalene arises from direct dehydrogenation of tetralin, but the label distributions in 3, 4, and 5 specify that the rearrangement of tetralin proceeds by cleavage of the 1-8a bond.

The low-level carbon-13 enrichment used in this experiment limits the determination of the label distribution to an accuracy of 5-10%. Because multiple measurements of the signal area in the spectrum of 1-methylindane consistently revealed a

Table 2.4. Carbon-13 chemical shifts and abundances of the products of 1-¹³C tetralin pyrolysis^{a,b}

Compound	1		2		3	3a	3b	4	4a	4b	5	5a	5b
	δ	C (%)	δ	C (%)	δ	C (%)	δ	C (%)	δ	C (%)	δ	C (%)	δ
C-1	29.3	100	127.7	100	39.3			32.8	50	0	117.5		
C-2	23.2		125.6		35.7			25.3			129.3		
C-3					31.4	50					138.5		
C-3a					143.4			143.8					
C-4					124.0			124.1			125.6		
C-4a	136.7		133.2										
C-5	128.8				125.8			125.7					
C-6	125.1				125.8								
C-7					122.9								
C-7a					148.3								
CH					19.8		50				21.3	50	0

^aChemical shifts expressed on the TMS scale: $\delta^{13\text{C}} = \delta^{13\text{C}}_{\text{TMS}} + 76.9 \text{ ppm}$

^bPercentages for C refer to that fraction of the initial (5.5%) ¹³C label at C(1) of tetralin

Table 2.5 Site distribution of the C(1) ^{13}C label of tetralin in selected pyrolysis products

Compound	1	1a	1b	2	3	3a	3b	3c	3d	4	4a	4b	6	6a	6b
	a	C(1)		a	C(1)		C(1)				C(1)		C(1)		C(1)
1-1	29.3	96		127.7	100	39.3			5		42.8	44		144.0	
C-2	23.2		4	125.6		34.7			2	25.3		2		127.6	
C-3						31.4	48							128.7	
C-3a						143.4				143.8					
C-4						124.0				124.1				125.4	
C-4a	136.7			133.2											
C-5	128.8					125.8				125.7					
C-6	125.1					123.8									
C-7						122.9									
C-7a						148.3									
CH						19.8		45							
α CH													28.9	29	
β CH													15.6	11	
Total label		100%			100%			100%			46%			40%	
Lost label											54%			60%	

The percentages refer to that fraction of the initial (43.5%) ^{13}C label at C(1) of tetralin ($\pm 10\%$). Unique isotopic species of the compounds are designated by *a*, *b*.

small inequality in the area of the methyl and C-3 resonances and a small area increase over the natural abundance level at the benzylic methine—comparable to the error in area measurement—the pyrolysis and analysis were repeated using tetralin-1- ^{13}C with a 43.5% ^{13}C content at C-1. The label distributions in 1, 2, 3, 4, and ethylbenzene (6) isolated from this experiment are presented in Table 2.5.

The order-of-magnitude increase in the sensitivity of the area measurements confirms that the label does not appear in the aromatic nuclei. In contrast, scrambling has occurred in the recovered tetralin; 4% of the label is now found in the 2 position. The label in 1-methylindane (3) is distributed over all four aliphatic carbons. Although 45% of the label is found at the methyl carbon and 48% at the benzylic methylene carbon, the remainder is unequally distributed between the methine (5%) and the methylene carbon at C-2 (2%). Indane (4) contains 46% of the starting label distributed over both the 1 and 2 carbons. Ethylbenzene (6) retains the smallest fraction (40%) of the original label and is found at the 1 and 2 carbons in a 3:1 ratio. A series of pathways that accommodate the observed scrambling pattern in recovered tetralin and 1-methylindane (3) is shown in scheme 2, Fig. 2.5.

Inspection of the label retention and distribution in ethylbenzene (6) cautions that, at least for those substances whose formation entails loss of carbon, a simple interpretation of the data is not justified.

Fig. 2.5. Scheme 2.

Some fraction of these substances may arise by radical coupling, not solely by degradation of higher molecular weight materials.

Pyrolysis of ^{14}C -labeled intermediates. A group of experiments were done in which ^{14}C labeled intermediates other than tetralin were pyrolyzed. Product analyses were accomplished using a gas chromatograph equipped with a radioactivity monitor. In these experiments no attempt was made to determine the location of the labeled carbon atoms in the products. The position of the labels can be inferred only in relation to synthesis procedures or to results determined previously using ^{14}C . The earlier report that tetralin can be derived from naphthalene under pyrolytic conditions in an atmosphere of hydrogen was of interest. To test that reaction under our condition, we heated a mixture of ^{14}C labeled naphthalene and nonradioactive tetralin at 400°C and also at 540°C for 1 h and analyzed the products for ^{14}C content. Although extensive decomposition occurred at the higher temperature and the quantity of naphthalene increased, the remaining tetralin contained absolutely no detectable radioactivity. The only ^{14}C labeled product detected was naphthalene. The reactions were also done in the presence of vitrinite (from Illinois No. 6 coal); again, the tetralin was not radioactive.

The reactions described in the foregoing paragraph were repeated in a stainless-steel-tube bomb using an initial hydrogen pressure of 900 psi. Hydrogenation of ^{14}C labeled naphthalene did not

occur at 400°C . At 500°C a trace of ^{14}C -labeled tetralin, about 0.1%, was detected in the products whether vitrinite was present or absent. When the pyrolysis was done in a batch autoclave (300 ml) at 400°C and an initial hydrogen pressure of 1850 psi, the recovered tetralin did not contain carbon-14, even when coal that contained about 30% mineral matter was present. The decomposition products normally derived from tetralin were not radioactive and thus were not derived from the labeled naphthalene.

Because 1-methylindane is present in significant amount in the pyrolysis products of tetralin, we investigated its role in the reaction sequence. The labeled species 1-methylindane-1- ^{14}C was prepared. It was mixed with nonradioactive naphthalene or with vitrinite, and the mixtures were heated at 400°C for 18 h. The results are summarized in scheme 3, Fig. 2.6. The fact that tetralin ^{14}C is isolated from the reaction mixtures supports the finding that 1-methylindane and tetralin undergo conversion.

Summary. It appears from our experiments that, in the absence of a suitable catalyst (added or from coal) or in the absence of a suitable solvent mixture, the hydrogenation of naphthalene to tetralin is extremely slow. Tetralin is a component of the recycle liquids and is believed to be derived from naphthalene, although there is no direct evidence for this. Because of the many variables to be considered, we conclude that the role of tetralin and naphthalene in donor solvents used in the solvent refining of coal should be thoroughly and intimately investigated. We suggest

Fig. 2.6. Scheme 3.

that the use of ^{14}C and ^{13}C labeling experiments can help to clarify the problems.

Acknowledgment. The authors are greatly indebted to Paul H. Maupin and W. Howard Roark for technical assistance in preparing intermediates.

2.1.5 Indole Alkaloids of *Rauwolfia reflexa*. The Structures of Rauflexine and Reflexine

F. W. Hagaman

The structure of two indole alkaloids isolated from the leaves of *Rauwolfia reflexa* was recently reported. One of these compounds, $\text{C}_{21}\text{H}_{23}\text{N}_2\text{O}$ (M^+ 336), mp 154–155°C, was identified as the known alkaloid 'purpeline' (**1a**), mostly based on its chemical conversion into mitoridine, as indicated by superimposable IR spectra. The second base, $\text{C}_{21}\text{H}_{23}\text{N}_2\text{O}$ (M^+ 338), mp 260°C (dec.), a new alkaloid designated reflexine, was assigned structure **1b**. The relationship between **1b** and **1a** was established by NaBH_4 reduction of the latter to yield a product identical (mp mmp, superimposable IR) to **1b** (Fig. 2.7).

In connection with continued structure analysis of the alkaloidal components of *Rauwolfia* species, the ^{13}C NMR spectra of several ajmaline-type bases were examined. This study reveals that the aromatic substitution pattern assigned to the indolic bases from *R. reflexa* requires revision. The NMR analysis establishes that the structure of reflexine is represented by formula **1c** and that the substance

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10. $Y=H$, $Y'=OCH_3$, $R, R'=O$
 D. $Y=H$, $Y'=OCH_3$, $R=H$, $R'=OH$
 C. $Y=OCH_3$, $Y'=H$, $R=H$, $R'=OH$
 6. $Y=OCH_3$, $Y'=H$, $R, R'=O$

Fig. 2.7. Indole alkaloids isolated from *Rauwolfia reflexa*.

originally identified as purpeline is, in fact, a new alkaloid, now designated rauwolfine (1d).

2.1.6 Surface Properties of Coal: Bruceton

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A well-documented sample of high-volatile A-bituminous coal (120-140 mesh) was obtained from argon storage for analysis. The original sample (BCI), obtained from the Bureau of Mines operation in Bruceton, Pennsylvania, was ground, sieved, and vacuum dried (100°C) prior to sealed storage in dry argon. Microgravimetric sorption studies were employed to study the amount and nature of sites available for reaction with various gases. The sorption isotherms of N_2 (-196, 78°C), CO_2 (-78, 0, 23°C), and SF_6 (0°C) were analyzed by the classical BET procedure to calculate apparent specific surface areas of 3.9, 144, and about 0 m²/g (BCI) respectively. This disparity between CO_2 and N_2 sorption capacities (36-fold) is often observed for coal and has been attributed to two phenomena: either (1) the microstructure of coal has constricted at the lower temperature and/or (2) there exists a large activation energy for diffusion such that N_2 diffusion is so slow that it

cannot be detected. Our analyses of CO_2 sorption (-78 to +23°C) showed no detectable constriction in this range which could account for N_2 exclusion at -196°C.

Kinetic analyses of CO_2 sorption-desorption showed that the process is second order (probably each CO_2 reacting with adjacent sites either on a surface or across a channel) and does not follow any classical diffusion mechanism. We calculate an activation energy for the sorption to be about 13 kcal/mol for CO_2 . If a comparable activation energy were in play for N_2 , we would be able to see at least the decreased rate. Prolonged exposure to N_2 did not reveal additional sorption of N_2 . We propose that the semirigid structure of the coal yields to allow the enhanced uptake of CO_2 , which strongly interacts with the functional groups in the coal. Mass spectrometric and calorimetric analyses of vapors released and subsequent wetting showed two regimes of reaction. Treatment below 100°C removes sorbed H_2O and CO_2 . Higher temperatures remove more strongly bound H_2O , CO_2 , and hydrocarbons (C_2 , C_3 , and C_4). At 175°C considerable HCl and aromatics are released. Surface wetting mechanisms elucidate the structural and chemical changes wrought in these thermal treatments. The results given here are available in more detail.²

1. School of Chemical Engineering Practice, Massachusetts Institute of Technology.

2. D. G. Sundberg, M. J. Abadi and M. S. Giroux, *Surface Properties of Coal*, ORNL-MIT-264 (May 16, 1978).

2.1.7 Surface Properties and Reactions of Coal: Illinois No. 6

E. L. Fuller, Jr. L. A. Field
M. M. Alger A. J. Papadopoulos
O. K. Chow R. D. Wang
M. Z. Khan S. M. Senkan

A sample of high-volatile A-bituminous (Illinois No. 6) coal was ground, sieved, and stored in dry nitrogen for these studies. Apparent specific surface areas (BET) were calculated for N_2 (-196°C), CO_2 (-78°C), and H_2O (20°C) to be 2.8, 128, and 68.2 m²/g respectively. Potential theory applied to the sorption isotherms over the entire range of 2×10^{-4} P_0 to P_0 (vapor pressure of the condensed bulk phase) revealed the trends and thermodynamics of the process. The energetics and extent of adsorp-

tion of the gases depend solely on the molecular properties (polarizability, dipole moments, etc.) of the sorbate per se. The semirigid structure seems to yield in proportion to the attractive forces between the sorbate and the polar functional groups and aromatic π structure. Thus the "surface area" one calculates depends entirely on the gas used in the sorption analyses. There is no real, well-defined surface area and/or pore structure for this coal. This is bolstered by kinetic analyses in which chemical (sorbate-site) interactions were seen to prevail with very little diffusional limitation in play.

This coal also has two types of sorbed H_2O and CO_2 inherent in the original material: (1) loosely bound material released below $100^\circ C$ in vacuum and (2) strongly bound H_2O and CO_2 released in ever increasing amounts up to about $200^\circ C$. Aliphatic (C_2 , C_3 , and C_4) hydrocarbons are desorbed at temperatures above $120^\circ C$, and aromatics and sulfur (H_2S , SO_2 , COS , etc.) are released above $160^\circ C$ in vacuo. The energetics and kinetics of wetting these materials (subjected to the above temperatures in vacuo) reflect the structural and chemical changes induced. A structural expansion accompanies the dehydration (25 – $100^\circ C$), which allows more rapid uptake of water. Treatment at higher temperature progressively restricts the access of water, as noted by the heat of wetting observed as a slow process. Details and an extended discussion have been published.² As a means of assessing the contribution of mineral matter and pretreatment, the above results were essentially duplicated for a sample of the same origin and ground in liquid water and washed extensively.¹

1. School of Chemical Engineering Practice, Massachusetts Institute of Technology.

2. M. M. Alger, O. K. Chow, and M. Z. Khan, *Surface Properties of Coal*, ORNL-MIT-266 (May 16, 1978).

3. L. A. Fields, A. J. Papadopoulos, and R. D. Wang, *Surface Properties of Coal, Part 2*, ORNL-MIT-270 (June 21, 1978).

2.1.8 Chemical and Structural Analysis of Coal: Wyodak

E. L. Fuller, Jr.	J. F. Orrick ¹
R. N. Caron ¹	J. L. Roux-Buisson ¹
K. J. Fallon ¹	S. M. Senkan ¹

A potential need exists for American subbituminous western coal reserves, and it is desirable to understand how weathering, transportation, and grinding affect the structure and chemistry of coal.

We studied dry ground Wyodak coal (<200 mesh) by examining the nature of chemical species evolved upon vacuum outgassing, the nature of water in coal, the mechanism of gas adsorption, and the physical structure. A mass spectrometer was used to identify the chemical species outgassed from 25 to $340^\circ C$. The sample was obtained at the mine face just after exposure, sealed from atmosphere, and stored in N_2 prior to grinding in N_2 . No exposure to reactive vapors (i.e., O_2 and H_2O) or elevated temperatures ($>30^\circ C$) was permitted prior to these analyses. Calorimetry was employed to determine the heat of immersion of outgassed samples in liquid water. Nitrogen, ammonia, carbon dioxide, carbon monoxide, and water were individually adsorbed and then desorbed at various temperatures and pressures in a microgravimetric sorption system. Water was the primary species outgassed (95–99%), and the amount of evolution was virtually independent of temperatures above $25^\circ C$. Carbon dioxide was the other major species, with its evolution increasing with temperature, indicating an activation barrier. Total gas evolution decreased for smaller particle sizes, suggesting the release of gases during the particle reduction (grinding) process. Hydrocarbon evolution was observed for vacuum outgasings above $100^\circ C$ for only the larger particle sizes (30–40 mesh). An aqueous heat of immersion of about 120 J/g was measured for the outgassed samples, which was insensitive to outgassing temperature. The high value reflected a large concentration of polar functional groups.

A water isotherm at $20^\circ C$ indicated 24% uptake at P/P_0 equal to 1, and an apparent surface area (BET) of 274 m²/g. Sorption data were well correlated by a second-order chemical kinetic model but did not fit a diffusion model. Corresponding experiments for N_2 ($-196^\circ C$) and CO_2 ($-78^\circ C$) showed sorption capacities commensurate with apparent areas of 2.62 and 200 m²/g respectively. The CO_2 and N_2 kinetic data were somewhat complex. It appears that there are two second processes in play. More detailed kinetic analyses of these experiments are warranted to elucidate the relative contributions of site interactions and diffusional processes. Further details and discussions are available².

1. School of Chemical Engineering Practice, Massachusetts Institute of Technology.

2. R. N. Caron, K. J. Fallon, J. F. Orrick, and J. L. Roux-Buisson, *Surface Properties and Reactions of Coal*, ORNL-MIT-273, in press (1978).

2.1.9 Submicron-size Mineral Component of Vitrinite

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C. S. Yust

Some coal minerals are known to be able to catalyze coal conversion to liquids and gases. It is commonly assumed that coal conversion processes occur via thermal pyrolysis with the formation of free radicals and ions, which are subsequently stabilized by reaction with hydrogen, hydrogen donors, or other moieties from coal. Although coal minerals are being studied for catalytic value and other properties, we have not found a discussion of the disposition of the mineral matter in coal macerals. We recently made observations of submicron-size mineral matter in a vitrinite maceral from an Illinois No. 6 coal.

Fragments of vitrinite were microscopically separated, thinned by ion bombardment, and examined by transmission electron microscopy. Photomicrographs of the macerals showed a profusion of mineral particles in the size range below 1 μm . The particles, many of which displayed growth or cleavage forms, were in the size range from the limit of resolution (about 4 nm) to about 100 nm and included particles of a wide variety of habits. Most of the mineral particles that were observed on the photographs were approximately equiaxed rather than acicular or platy. Because of the fine size and intimate mixing of the mineral particles in the macerals, we believe that we are observing primary minerals in the coal. Our x-ray diffraction results on vitrinite suggest that the principal mineral components are illite and kaoli-

nite as well as quartz and some CaCO_3 . A microprobe analysis showed that some of the unknown minerals contained iron and titanium. Little pyrite was observed in this size range.

Because the possible catalytic effectiveness of such particles is a function both of their dispersion in the matrix and of their size distribution, we measured the sizes and numbers of particles in three photographs of vitrinite. We estimated the relative thickness of the maceral from the optical density of the photographic print. We assumed the thickness to include the range of 100-1000 nm. The average diameter was estimated from measurements of the particle diameters from two or three portions of each field. The particles appeared to be of two principal sizes, a large number of small particles less than 30 nm and a much smaller number of larger particles, the largest of which had dimensions of about 0.2 μm . Particles in the size range below 30 nm account for about one-third of the total surface area of 0.3 m^2/cm^2 of vitrinite. The weight fraction of minerals derived from these data, 0.015 kg per kilogram of coal, may be compared with that obtained by Mukherjee and Chowdhury.⁴ These authors had collected a sample with a specific gravity of ≤ 1.3 having an ash weight fraction of 0.017 for an Assam coal that contained 91.2% vitrinite. Mukherjee and Chowdhury assumed that much of the mineral matter was submicroscopic in character.

From the data reported in Table 2.6, the surface area of the submicron-size mineral matter appears to be significantly large and may be expected to induce or promote a variety of catalytic reactions involving coal. Iron and titanium minerals are also expected to serve as hydrogenation catalysts, and

Table 2.6. Summary of derived data on vitrinite minerals*

Mineral surface area per unit of coal	
Small particles, < 30 nm	$0.10 \pm 0.04 \text{ m}^2/\text{cm}^2$
Large particles, > 30 nm	$0.19 \pm 0.14 \text{ m}^2/\text{cm}^2$
Total specific area	$0.20 \pm 0.15 \text{ m}^2/\text{cm}^2$
Small particle concentration	$243.0 \pm 56.0 \mu\text{m}$
Average diameter, small particles	$9.8 \pm 1.1 \text{ nm}$
Weight fraction of minerals	$0.015 \pm 0.007 \text{ kg of minerals/kg of coal}$
Mineral surface area per unit weight of minerals	$45 \pm 22 \text{ m}^2/\text{g}$

*Error limits are based on 90% confidence level.

Assumed densities: vitrinite, 1300 kg m^{-3} ; minerals, 3200 kg m^{-3} .

the aluminosilicates may serve as decomposition catalysts for reactions involving carbonium ions. Further work on these possibilities is in progress.

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4. D. K. Mukherjee and P. B. Corradini, *Fuel* 55, 4 (1976).
5. P. H. Green, D. C. Cloninger, A. Spackman, B. L. Lovell, A. David, and R. Barnes, *Fuel* 54, 34 (1975).
6. W. P. Heynes, S. J. Gossens, and A. J. Forness, *Prepr. Pap. Nat. Meet. Div. Fuel Chem. Am. Chem. Soc.* 16(2): 1 (1972).

2.2 CATALYSIS

2.2.1 Molten Salt Catalysts. I. Purification and Structural Properties of Catalysts

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H. L. Yakel¹

This section summarizes two studies of the inorganic and structural chemistry of molten salt catalysts. The first study is concerned with the purification of zinc chloride and the crystal structure of the purified material. Molten zinc chloride is the hydrocracking catalyst used in the Conoco process for making gasoline from coal. This catalyst is unusually effective for this purpose because of its high selectivity for distillate hydrocarbons. At present the mechanism by which $ZnCl_2$ catalyzes hydrogenation reactions is unknown, and it has not been possible to investigate this mechanism in a meaningful way because of the unavailability of pure $ZnCl_2$. The available forms of this substance always contain significant amounts of H_2O or hydrolysis products.

We have largely solved the problem of reducing these impurities to an insignificant level, and in our initial study of the properties of the purified compound, we found that it has a crystal structure that is different from the several previously reported for H_2O -contaminated material.

The second study is concerned with the coordination equilibria of $NbCl_5$ dissolved in $KCl-AlCl_3$ melts of various compositions. These molten solutions are expected to be dual-function Lewis acid redox catalysts, and their coordination equilibria are expected to govern the molecular

mechanism by which both their Lewis acidity and their redox properties are controlled. A noteworthy feature of this study was the use of potentiometry, optical absorption spectrometry, and Raman spectrometry in concert to give a more complete picture of coordination equilibria in the melt than would have been possible with the usual single-instrument approach.

Zinc chloride. Structures of three crystalline modifications of zinc chloride have been reported by Brehler¹ and by Oswald and Jaggi. All three are based on pseudo-close-packed anion lattices in which zinc ions occupy tetrahedral interstices. In the α and γ modification, anion layers have a cubic ABCABC... (cc) sequence, but in the β modification, a four-layered... ABCBACB... (c2c2) sequence is followed. The reported methods of preparation for these materials leave little doubt that all three are significantly contaminated by water.

We developed two methods of preparing $ZnCl_2$ crystals that are largely free of water and hydrolysis products. One method starts with high-purity zinc metal and anhydrous HCl and proceeds through synthesis and crystal-growth steps under anhydrous conditions. The other method begins with commercial reagent-grade $ZnCl_2$, which contains substantial water and hydrolysis products and achieves purification by vacuum distillation. The detailed steps in these procedures have been published.

Crystals prepared by both procedures have the same structure, which is different from those previously reported. Exposure of these crystals to H_2O transforms them into one of the forms already established for the H_2O -contaminated material.

The structure of the anhydrous compound consists of an orthorhombic lattice (space groups $Pna2_1$) with an hexagonal sequence of close-packed chloride ion layers lying normal to C in which zinc ions occupy holes with a tetrahedral coordination that differs from ideal in a barely significant way. These tetrahedra share corners but not edges or faces. The average $Zn-Cl$ distance of 2.273 Å corresponds to the shortest of those reported by Brehler¹ and is about equal to the sum of tetrahedral covalent radii for the atoms. The $Cl-Cl$ distances within $ZnCl_2$ tetrahedra approach the minimum expected for an ionic radius of 1.81 Å, but those between tetrahedra are several tenths of Angstroms longer.

$NbCl_5$ in $KCl-AlCl_3$ melts. The coordination of $Nd(V)$ was investigated for dilute (0.1-0.3 F)

... of KCl and ... range from 46.78 to ... This narrow ... acid titration curve for KCl (a Lewis ... and $AlCl_3$ (a strong Lewis acid) in which the ... measure of Lewis basicity) changes from ... ultraviolet absorption spectroscopy showed that ... is present as two species whose concentra- ... composition dependent potentiometric ... using concentration cells with ... chlorine electrodes yielded the ... of the concentration of ... that the concentration of ... and related the equilibrium constants of the ... reaction $NbCl_5 \rightleftharpoons NbCl_4 + Cl_2$. Raman ... spectroscopy yielded the principal frequencies ... determined for $NbCl_5$ and $NbCl_4$... systems and showed no other frequencies ... could be attributed to either $Nb(V)$ species ... Measurements of the vapor-liquid distribution ... coefficient of $NbCl_5$, made by ultraviolet spectro- ... copy, confirmed the model equations obtained by ... potentiometry.

1. Technical University of Denmark, Lyngby
2. Metals and Ceramics Division, National Bureau of Standards, Gaithersburg, Maryland
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4. H. R. Oswald and H. Lögner, *Helv. Chim. Acta* **43**, 22-27 (1960)
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2.2.2 Molten Salt Catalysis. II. Reactions of $SbCl_5$ in Melts

- A. S. Dworkin
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L. L. Brown
J. Brynestad
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L. O. Gilpatrick
M. J. Poutsma

Molten $SbCl_5$, like $ZnCl_2$, is a very effective hydrocracking catalyst for converting coal into oil. Although too expensive for commercial use, $SbCl_5$ has many advantages over commercial catalysts. In our laboratory studies of the hydrocracking mechanism, we are using it for that purpose. In our report we described preliminary results for anthracene (I) and naphthalene (but

not as phenanthrene) dissolved in $SbCl_5$ under an inert atmosphere. Our studies of anthracene and the following reactions are summarized in the following summary. We find that 1 in solution in molten $SbCl_5$ undergoes spontaneous disproportionation at temperatures as low as 100°C. The oxidation steps consist of Scholl reactions in which aryl-bound hydrogen is lost with the formation of 1,9-bianthracene (IV) and 2,9-bianthracene (V) as major products plus small amounts of 1,2-bianthracene (VI), anthra[1,2-*a*]aceanthrylene (VII), dibenz[*a,h*]perylene (IX), and other oligoanthracenes (but not symmetric bianthracenes). Most, if not all, of the hydrogen released converts other anthracene molecules into 9,10-dihydroanthracene (III) and, at a much slower rate, into 1,2,3,4-tetrahydroanthracene (II). The catalytic role of the solvent's Lewis acidity is evident from the fact that the addition of a few mole percent of a strong chloride ion donor, KCl or $(C_2H_5)_4NCl$, reduces the reaction rates by a large factor.

The fact that anthracene serves as an efficient hydrogen acceptor for its own Scholl reactions is a novel aspect of Friedel-Crafts chemistry. Usually when Scholl reactions occur in the absence of oxidizing agents, it has been supposed (without evidence) that gaseous hydrogen is liberated. Our results demonstrate an alternative. Also, we are the selectivity for asymmetric

previously been prepared, and the
 a Lewis acid as SbCl_5 serves
 analyze Scholl reactions, for which
 AlCl_3 are normally employed.
 obtained by ^1H -NMR spectra of the
 reactions proceeded and by conven-
 and work-up procedures following
 of a run.

on rates were found to be independent of
 concentration of I over the range 2 to 10
 whereas an increase in temperature of less
 increased the rates by a large factor.
 the effects are illustrated in Fig. 2.8.
 based on ^1H -NMR measurements made
 reactions proceeded. Figure 2.9 shows
 based on quench and work-up that illustrate
 rates of formation of the four principal
 products over an extended time period.
 mechanisms proposed for Scholl reactions are of
 types depending on whether or not they
 generate radical cations (in addition to arenium ions)
 intermediates. Both types of mechanisms can be
 extended to include the hydrogenation reactions in
 condensation/hydrogenation type of disproportion-
 condensation. The exact role of the catalyst is not
 adequately accounted for by these mechanisms.
 Strong Lewis acids like AlCl_3 will, of course,
 generate adventitious proton sources, which can
 then protonate arenes to form arenium ions.

ORNL-DWG 78-19360

Fig. 2.8. Effect of the initial concentration of anthracene and the temperature on the rates of formation of 9,10-dihydroanthracene (II) and 1,2,3,4-tetrahydroanthracene (III) in molten SbCl_5 . The weight of total organics (equal to the initial weight of anthracene) remains invariant throughout the experiment.

Fig. 2.9. Rates of disappearance of anthracene and formation of the four principal products at 130°C; initial concentration 10 mol % anthracene in SbCl_5 . The weight of total organics (equal to the initial weight of anthracene) remains invariant throughout the experiment.

However, the source of electron acceptors required to generate radical cations remained, until recently, entirely obscure apart from such gratuitous assumptions as adventitious electron acceptors activated in unknown ways by the catalyst.

Recently we obtained experimental evidence that molten SbCl_5 can react with anthracene and naphthalene so as to generate either catalytic or massive amounts of the corresponding arenium and radical cations. These reactions occur without the aid of adventitious substances.

These results make it quite clear that there exists in liquid SbCl_5 a previously unrecognized sequence of oxidation-reduction reactions involving hydrogen transfer between aromatics. The synthetic utility and mechanisms of these reactions continue under investigation.

1. Chem. Div. Annu. Prog. Rep. Mar. 31, 1977, ORNL-5297, p. 6.
2. Scholl reactions are reviewed in H. L. Jones and R. A. Osteryoung, "Organic Reactions in Molten Tetrachloroalum-

nate Solvents," pp. 121-76 in *Advances in Molten Salt Chemistry*, vol. III, F. Baerstein, G. Marmantov, and G. P. Smith, eds., Plenum, New York, 1978; and in V. I. Balaban and C. D. Nenitzescu, "Glenidrogenation, Condensation of Aromatics (Scholl and Related Reactions)," pp. 979-1047 in *Frontiers in Organic Chemistry*, vol. 11, part 2, G. A. Olah, ed., Interscience, New York, 1964.

3. Most prior research on the behavior of polycyclic aromatics in liquid SnCl_4 was done at 74-90°C (ref. 4) where we found that anthracene disproportionates quite slowly. Some research at higher temperatures (ref. 5) encountered unspecified reactions. No prior effort to separate and identify reaction products has been reported.

4. Chemistry in molten SnCl_4 is reviewed in F. C. Baughman, "Inorganic Acid Chlorides of High Dielectric Constant (with Special Reference to Antimony Trichloride)," pp. 129-65 in *The Chemistry of Nonaqueous Solvents*, vol. IV, E. J. Lagowski, ed., Academic, New York, 1976.

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2.2.3 Activation-Deactivation of "Cobalt-Molybdate" Catalyst

E. I. Fuller, Jr.

Commercial application of cobalt-molybdate hydrotreating catalysts requires "activation" prior to use and maintenance of this state during the reaction. This activation usually involves exposure to hydrogen to reduce the catalytic components, molybdenum and/or cobalt. This study was performed to elucidate the kinetics and mechanism of the reduction and reoxidation processes microgravimetrically. To study the details, we found that one must preoxidize the sample with O_2 gas at 400°C to remove the inherent carbonaceous material from the catalyst (a well-defined second-order process). Subsequent exposure to hydrogen at 400°C leads to a third-order mass loss as the reduction proceeds. The H_2O evolved in the process is retained on the surface and acts as an inhibitor. Detailed reduction-oxidation, hydration-dehydration analyses at 400°C lead us to propose the following mechanism for the synergetic reaction of the cobalt and molybdenum and the "inert" support, $\gamma\text{-Al}_2\text{O}_3$. At 400°C H_2 reduces both Mo^{6+} and Co^{3+} to Mo^{3+} and Co^{2+} , and the Co^{2+} entity is stabilized in the process by forming a structure akin to cobaltous acid. Oxygen will reoxidize both the cobalt and molybdenum complement, whereas H_2O oxidizes the molybdenum component only. The oxidized form (+3) of the cobalt tends to dissolve into the Al_2O_3 substrate.

We conclude that the role of cobalt is to facilitate the reduction of the molybdenum and also to maintain a reduced catalytically active state in the presence of a trace amount of H_2O vapor, which is extremely difficult to exclude from process streams.

2.2.4 Characterization of Porous Catalysts and Catalyst Supports

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M. J. Abadi, W. F. Sung,
S. M. Senkan

A silica (6%) promoted catalyst was studied in its commercial pelleted form (1.8-in. right cylinders), which is a good catalyst in its own right and is often used as a support for other catalysts (i.e., "cobalt-molybdate" hydrotreating). In our continuing program pertaining to heterogeneous catalysis for clean energy production, we have noted interesting catalyst-support interactions and have needed the base data for the support itself. The BET surface area (calculated from N_2 sorption isotherms) ranged from 175 to 205 m^2/g for vacuum outgassings ranging from 25 to 400°C due to more extensive removal of bound water from between the crystallites within the matrix. Microgravimetric and mass spectrometric data showed that the N_2 capacity is directly proportional to the amount of this surface hydration. Detailed analyses of the N_2 isotherms show that the extraction of water relaxes the structure to allow virtually free access with no microporosity or "high-energy" sites being generated. This matrix structure flexes at higher pressures under the influence of the capillary forces of the condensed (liquid-like) nitrogen. The amount and mechanism of capillary flexing is virtually independent of the bound water content.

Mass spectrometric analyses of outgassing at temperatures up to 400°C showed two regimes where desorption (Elovitch) kinetics prevail. Below 200°C no appreciable temperature coefficient is noted for the rate of desorption. In contrast, above 200°C the rate data are strongly temperature dependent. Heats of immersion of these outgassed samples reflect the changes induced and enable us to calculate thermodynamic enthalpies for the three hydration processes: $\Delta H = -64.73$ kcal/mol (hydroxylation of residual surface alumina, 350-450°C in vacuo); $\Delta H = -27.13$ kcal/mol (bridge hydration of silica surface, 200-350°C in vacuo); and $\Delta H = -39.61$ kcal/mol (complete hydration of silica surface, 25-200°C in vacuum). More details and comparison with cobalt-molybdate catalyst are available.

¹ School of Chemical Engineering Practice, Massachusetts Institute of Technology.

² M. J. Abadi, C. I. Geary, and W. F. Sung, *Surface Properties and Reactions of Catalysts*, ORNL-MIT-261 (May 16, 1978).

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

E. H. Taylor, W. C. Waggener

We reported last year that a proposed method for measuring the tangential component of the force between an adsorbed molecule and a solid surface was feasible and that preliminary results showed interesting differences between the behavior of different gases with a nickel surface. In the intervening year we have designed and ordered components for an ultrahigh vacuum system for conducting such experiments with clean, well-characterized surfaces. The major components are on hand and will be assembled in the next few months.

Our original (and present) set-up does not allow us to clean or characterize the adsorbing surface, and it is therefore unprofitable to try to draw any detailed, quantitative conclusions from the preliminary experiments. Nevertheless, we have continued to use the simple apparatus to explore other systems and variables in preparation for future work under adequately refined conditions.

We performed a blank experiment in which the ribbon was of nickel alone (no gold backing) and observed no deflection change between helium and H_2O -saturated helium. We expected this result, but it is a necessary confirmation that the previous observations did not result from some anomaly in the equipment.

We performed successive treatments of a nickel-gold ribbon with H_2O and with H_2 (using helium

Fig. 2.10. Deflection-time curves for a nickel-gold ribbon adsorbing H_2 after prior adsorption of O_2 . Ribbon flushed with helium between O_2 and H_2 treatments. ●, first experiment; ○, duplicate experiment performed 288 h later.

Table 2.7. Deflection of a bimetallic ribbon by adsorbed gases.

For a ribbon with gold backing and a nickel surface, after O_2 treatment.

Gas (at 1 atm)	Net deflection (microns)	Experimental deflection (microns)	Control deflection (microns)
H_2	0.8	0.8	0.8
H_2O	0.6	0.6	0.6

between the active gases) and found that the detailed shapes of the deflection-time curves were remarkably reproducible. This result is illustrated for a slightly more complicated case in Fig. 2.10, which shows the results of two experiments in which the ribbon was exposed successively to He , O_2 , He , and H_2 . In these recent experiments we have allowed each change in gas to reach a nearly steady state (no more than about $5 \mu\text{m}$ change in deflection per day) before proceeding to another change.

We have looked at a different metal, copper, and at nickel prepared by evaporation (rather than the commercial nickel foil). Table 2.7 shows the sense of the deflections observed with different gases. The different result obtained with the evaporated nickel was confirmed in an experiment with a new ribbon from commercial foil. A positive deflection was again observed, but this was changed to negative when nickel was evaporated onto the nickel side and the ribbon was again exposed to H_2 .

The calculation of a surface tension from a bending experiment is complicated by the effects of gravity. The simultaneous effects of surface tension, elasticity, and gravity lead to an integro-differential equation of forbidding aspect. We have solved it by an iterative balancing of torques along the length of the ribbon and can now convert deflections to surface tensions.

These results confirm our earlier conclusion that interesting and potentially useful information about adsorption and catalysis can be obtained in this way.

J. Chem. Div. Annu. Prog. Rep. Mar. 31, 1977, ORNL-5297 (September 1977), p. 11

2.2.6 Catalysis and Energy Systems—A Discussion of Catalytic Reactions and Materials Science¹

R. A. Strehlow

It is difficult to overestimate the importance of catalysis in chemical technology. Catalytic processes

utilized in the chemical and petroleum refining industries account for well over 20% of the gross national product. Of the chemical compounds that are produced at a rate greater than 10⁶ lb. year, more than 80% are produced by catalytic processes. Production of sulfuric acid by the contact process since the beginning of the century, the synthesis of ammonia, the oxidation of ethylene to form ethylene oxide, and many other continuous catalytic processes are employed throughout the world. Hydrodesulfurization, cracking, hydrocracking, and reforming are carried out catalytically on a very large scale in petroleum refining. It is probable that, in the new energy systems now being planned or studied, catalysis will play a large part.

The materials requirements for catalytic processes are of two types: (1) the selection of materials for chemical reactors which will be increasingly often designed to operate in new and hostile environments and (2) the set of scientific aspects of the behavior of materials which bear on catalysts and catalytic processing.

Various sources of fuel are being considered for the future energy flow in the United States: uranium, gas, coal, oil, shale, waste, solar, geothermal, and water. Applications of catalysis are being contemplated for virtually all of these fuels. The general advantage of catalysis is the possibility of achieving a higher efficiency in the use of energy, obtaining interconversions under milder conditions than would be otherwise readily possible, and increasing the options available for mixing energy resources. Because much catalytic processing, particularly in the petroleum industry, requires high temperature and high-pressure application of materials, improved catalysts would permit less stringent demands on materials as an additional motivation.

Coal liquefaction studies involve a large amount of catalyst development work. Most catalyst studies are directed at improvement of commercial catalysts, particularly of the cobalt-molybdenum catalyst system. In this application, carbon and mineral deposition on the catalyst can deactivate the catalyst in some tens to hundreds of hours, requiring replacement or chemical processing of the catalyst. Research now being conducted is directed toward catalysts with larger pore sizes, which may be more resistant to these deposits or be more readily reactivated. At this time, however, the desired characteristics of a better catalyst have not been well defined.

Coal liquefaction by hydrogenation has been accomplished without using added catalyst. It is

generally believed that the mineral matter in coal has catalytic value, and research in this area of coal structure is being conducted. Work at this laboratory has found in a common coal a profusion of aluminosilicate particles in the size range below 2×10^{-6} m, which offers a significant surface area for reaction. Thus it is possible that coal conversion to gas by hydrogenation may also be catalyzed by coal minerals.

The gasification of coal involves a reaction of coal with water to form a carbon monoxide-hydrogen mixture. The use of catalysis has been studied for this process. Alkali-metal compounds and calcium compounds added to the coal have been shown to be catalytically active. No mechanism has yet been established.

The synthetic versatility of catalytic processes using a carbon monoxide-hydrogen mixture cannot be emphasized too strongly. The production of gasoline by the Fischer-Tropsch process uses an iron catalyst. The production of aldehydes by a homogeneous catalysis using $\text{H}_2\text{O}(\text{CO})_2$ dissolved in a hydrocarbon and followed by a nickel or cobalt metal catalysis is used to form a wide variety of organic compounds. Although these applications of the coal gasification product mixture are not themselves part of an energy system, they do bear most strongly on the process economics of large-scale processes in which product CO-H_2 may have a chemical as well as a fuel market.

Because great emphasis is placed on "clean" energy in the new systems proposed for deployment as well as in old systems, increased attention has been directed toward catalysis that occurs incidentally to the burning of fuels. The catalytic effects of boiler tubes and of other materials on the various reactions of sulfur oxides are significant in the burning of fuels, even those that contain only small amounts of sulfur. The extent to which sulfur trioxide is formed in gas streams and on metal surfaces has been related to the catalytic effect of iron oxide on the formation of SO_3 in the superheater surface temperature range.

The use of nuclear process heat at high temperatures has been under study in the Federal Republic of Germany, Japan, United States, and the United Kingdom. The conclusion of many workers is that the energy contained in high-temperature helium can be used successfully for coal gasification and other fossil-fuel conversion processes using steam reforming.

The use of the reforming reaction (1) in which hydrogen and carbon monoxide are reformed from methane (hydrocarbon) by steam permits a storage of heat energy as hydrogen gas. Reaction (1) is endothermic by about 0.2 MJ/mol (50 kcal/mol). Any catalytic or noncatalytic reaction using hydrogen, such as synthesis of ammonia or methyl alcohol, may be coupled to the reforming reaction as a secondary process. Alternatively, the product of the reforming step may be treated with a nickel catalyst to release the heat for such applications as coal hydrogenation or hydrogasification.

The above is by no means a complete listing of the catalytic reactions that will probably become increasingly important as new mixes of energy sources develop. It does, however, serve to show the range of reactions in which catalysis is expected to have a significant role. The scientific questions on catalysis, their selectivity, deactivation or useful life, and activity are numerous and will continue to be important in energy research.

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2.2.7 Angle-Resolved Polarized Ultraviolet-Photoemission of Molecules Adsorbed on Ni(111)

P. A. Agron, T. A. Carlson,
W. B. Dress, J. O. Thomson

The data collection of angle-resolved photoelectron spectra of oriented benzene molecules on Ni(111), using $P_{\parallel}$ (parallel) and $P_{\perp}$ (perpendicular) polarized HeI radiation is currently in progress. A monolayer of benzene is adsorbed on a clean and annealed nickel single crystal, cut and polished to expose the (111) face. A number of ionization peaks are resolved with the polarized radiation in the region from 2 to 12 eV below the Fermi energy. Group theoretical considerations are applied to the data to identify the molecular orbitals giving rise to the ionization peaks and to ascertain the orientation of the benzene molecule on the Ni(111) surface. A successful analysis will yield the coordination site symmetry of the adsorbed molecule. A similar analysis will likewise be tested with the angle-resolved photoemission spectra collected previously of

phenyl mercaptan (ϕ -SH) sorbed on the face of a single crystal of copper.

Angle-resolved photoemission data of CO on Ni(111) have been obtained with $P_{\parallel}$ -polarized HeI radiation. The data for $P_{\parallel}$ polarization are under reexamination at an incidence angle of 45° .

Angle-resolved photoemission spectra observed with C_2H_2 and of NO adsorbed on Ni(111) indicated extensive decomposition at 300 C. An improved liquid nitrogen cooling system is now designed to continue studies of molecular species at lower temperatures. Besides following shifts in the molecular binding as a function of temperature, that is, from the physisorbed to the chemisorbed state, positive assignment of bands to particular molecular orbitals is readily made by comparison of the condensed-state spectra with that of the gas phase.

1. Department of Physics and Astronomy, University of Tennessee, Knoxville

2. P. A. Agron et al., *Chem. Phys. Atmos. Phys. Rep. Mar. 31, 1977*, ORNL-5297 (September 1977), p. 11

2.2.8 Statistical Analysis of Adsorption Processes

F. L. Fuller, Jr., F. L. Miller,
V. R. R. Uppuluri

Mathematical analyses and computer simulation of the site-oriented adsorption of polyatomic molecules on crystallographic lattice arrays have been shown to be limited. The fractional coverage can be calculated by statistical analysis when no surface mobility exists, as one finds in many cases of chemisorption. This study has been devoted to a kinetic and thermodynamic study of the process. Classical sorption kinetics do not apply because the model is not that of association of mobile spherical molecules by purely dispersion forces. The rate of sorption is broken into three general regimes, depending on the degree of coverage: (1) low-coverage regime: nearly classical rate found, decreasing with number of precovered sites; (2) intermediate range in which the rate decreases more rapidly due to steric and exclusion factors; and (3) high-coverage region in which the rate of adsorption decreases much more rapidly due to extensive exclusion and decreases to zero 10-15% before classical, mobile full coverage is achieved.

The results correlate well with experimental results for systems in which the model is applicable (i.e., H₂O on oxides, H₂ on Ni). That is to say, in systems of high energy adsorption, each sorbate molecule interacts with adjacent sites, and the surface mobility is low. Current studies are directed to the analyses of kinetics and thermodynamics of the surface structural rearrangement (migration) in transforming from the

statistical limit to the well-ordered state of full coverage.

1. Mathematics and Statistics Research, Computer Science Division, Union Carbide Nuclear Division, Oak Ridge, Tenn.

2. *Chem. Div. Annu. Prog. Rep. Mar. 31, 1977, ORNL-5297* (September 1977), p. 10.

3. Aqueous Systems and Geosciences

3.1 AQUEOUS SYSTEMS

3.1.1 Thermodynamics of Mixed Electrolytes at High Temperatures by the Isopiestic Method: NaCl-KCl and NaCl-CaCl₂

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

The vast majority of practical and/or naturally occurring aqueous electrolyte solutions contain more than one solute. However, experimental studies on such mixed electrolyte systems at temperatures other than 25°C are very limited. Osmotic and activity coefficients for aqueous solutions of the pure electrolytes KCl and CaCl₂ over the temperature range 110 to 200°C are available from our previous isopiestic study.¹ In view of these circumstances, we have completed isopiestic measurements on the two mixed electrolyte systems NaCl-KCl and NaCl-CaCl₂ over the temperature range 100 to 200°C. In addition to being important components of natural systems, the systems measured represent examples of mixtures of a 1-1 electrolyte with a 1-1 and a 2-1 electrolyte. Since analysis of the NaCl-CaCl₂ is not complete, the remainder of this discussion is limited to the NaCl-KCl system.

Osmotic coefficients for the mixtures were calculated from the isopiestic molalities in equilibrium with pure NaCl solutions. Osmotic coefficients for the standard NaCl solutions were obtained from Silvester and Pitzer.² Pitzer's equation³ for the osmotic coefficient of a mixed electrolyte solution was fitted to the data, using a general least-squares computer program. The osmotic coefficient ϕ of a mixture of two 1-1 electrolytes, MX and NX, can be described as

$$\phi = (1 - y)\phi_{MX}^0 + y\phi_{NX}^0 + y(1 - y)m\theta_{MX} + y(1 - y)m^2\psi_{MXNX}$$

where ϕ_{MX}^0 and ϕ_{NX}^0 are the osmotic coefficients of pure MX and NX, respectively, at a molality m

(equal to the total molality of the mixture). y is the mole fraction of NX, and θ and ψ are mixing parameters whose values are determined from a least-squares fit to the experimental data. In practice, ϕ^0 is a mathematical expression containing three adjustable parameters determined from data for the pure electrolyte only. It should be pointed out that the data can be described to about 1% (standard deviation ~ 0.01) without any mixing parameters, that is, $\theta = \psi = 0$. Inclusion of the parameter ψ did not improve the fit over that obtained by using θ alone. Consequently, we have set ψ equal to zero. Using the parameter θ , the standard deviation of fit (in the osmotic coefficient) ranged from 0.0025 at 110°C to 0.0044 at 201°C.

Fig. 3.1. Activity coefficients for NaCl and KCl in mixtures at indicated mole fractions of KCl

Activity coefficients for both NaCl and KCl in the mixed electrolyte solutions were calculated using the pure electrolyte parameters, the mixing parameter θ , and Pitzer's equations. Activity coefficients γ are shown in Fig. 3.1 as a function of molality and composition at 110 and 200°C. Over the temperature range, the activity coefficients (and osmotic coefficients) showed a monotonic decrease with increasing temperature and became much less dependent on molality at the higher molalities. The activity coefficient (and osmotic coefficient) of NaCl is much more dependent on composition than that of KCl. The trace activity coefficients (e.g., infinitely dilute NaCl in KCl) of NaCl and KCl are very nearly equal over this temperature range. The ability to describe the NaCl-KCl system with only one mixing parameter in Pitzer's equation is equivalent to Harned's rule. Excess free energies of mixing calculated from the mixing parameter θ were, to a very good approximation, independent of temperature. Our results, although not directly comparable, are consistent with the isopiestic study of Robinson² at 25°C.

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3.1.2 Fluorosilicate Equilibria by a Potentiometric Method from 0 to 60°C

R. H. Busey, R. E. Mesmer

There is evidence that the fluoride ion has a dramatic effect on the kinetics of the polymerization of silicic acid in solution. This fact has been attributed to possible fluoride complexing, and such behavior could have importance in silica scaling from some geothermal brines. Currently, there is no convincing evidence for the existence of the numerous conceivable fluorosilicate species that might form. This study was conducted as part of our basic research program on the physical chemistry of geothermal solutions, and a potentiometric method was employed. The cell was similar to that employed previously, consisting of a solid-state fluoride ion electrode to observe the free fluoride ion concentration and two quinhydrone electrodes as the reference electrode and the hydrogen-ion-indicating electrode.

Titration experiments were conducted at 0, 25, and 60°C on solutions containing 0.001 *m* Si(OH)₄ and

0.001 to 0.609 *m* fluoride in 1 *m* NaCl. Hydrochloric acid solutions were injected incrementally, and the potentials of both indicating electrodes were observed. Equilibrium occurred rapidly, and the results are expressed in terms of the average number of hydrogen ions $\bar{n}_H$ and fluoride ions $\bar{n}_F$ consumed in the following equilibria:

A large number of such conceivable equilibria exist if the coordination number of silicon is allowed to be variable from four to six.

The results of experiments at 25°C are shown in Fig. 3.2. As the pH decreases the $\bar{n}$ values approach maximum values, which, in the presence of sufficient fluoride, are six and four for $\bar{n}_H$ and $\bar{n}_F$, respectively. Also, the ratio of these two quantities remains at 0.67 (dashed line, Fig. 3.2), within the estimated error throughout the experiment in 0.009 *m* fluoride, indicating that SiF_6^{4-} is the only significant species

Fig. 3.2. The average number of hydrogen ions $\bar{n}_H$ and fluoride ions $\bar{n}_F$ consumed per silicic acid in Eq. (1) at 25°C in 1 *m* NaCl at three concentrations of total fluoride.

present. By a least-squares analysis of all the data, some improvement in the fit is obtained by including one additional species whose composition is not uniquely defined.

The absence of a regular sequence of fluoride complexes in this system, as compared with the analogous fluoroborates and most metal fluoride systems, is attributed to the change in coordination in going from Si(OH)_2 to SiF_6^{2-} . From the low temperature data it is possible to estimate the stability of the SiF_6^{2-} complex at 200–300°C and to show that the position of occurrence of the fluoride complex shifts toward more acidic media as the temperature increases; that is, the stability of SiF_6^{2-} with respect to Si(OH)_2 decreases as the temperature is increased. These results demonstrate that, at any temperature in this range, there is no significant complexing by fluoride ion at free fluoride concentrations of less than 0.01 *m* at pH values greater than 5, which encompasses most natural waters except particularly acidic mine waters.

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3.1.3 Thermodynamics of Ionization in Deuterium Oxide, D_2O and D_2PO_4

R. E. Mesmer, D. L. Herting¹

Data from precise potentiometric measurements made earlier in the program on the ionization equilibrium of D_2O and the neutralization reaction of D_2PO_4 from 50 to 300°C in 0.2 *m* KCl were analyzed and published.²

The ionization behavior of D_2O and of weak acids in heavy water are of interest as a part of the theoretical basis for understanding ionization and solvent isotope effects. Also, heavy water has significant practical application in the nuclear industry in Canada and elsewhere as a coolant and moderator in the CANDU reactors.

We have reexamined the data of Shoesmith and Lee³ on the ionization of D_2O along with our data in 0.2 *m* KCl and other precise data at low temperatures and have presented derived thermodynamic parameters with estimates of the propagated errors. We have also made measurements on the ionization behavior of D_2PO_4 in 0.2 *m* KCl to 293°C and have estimated the activity coefficient term for correction to infinite dilution from the data on water ionization.

The following expression gives the $\log Q$ for the ionization of D_2O from 0 to 300°C in KCl solutions to 1 *m*.

$$\begin{aligned} \log Q_{D,O} = & (3.00767 \times 10^4) T + 90.1291 (n T \\ & - 9.20168 \times 10^{-2} T \\ & - 2.16454 \times 10^5 T^2 - 577.563 \\ & + (2A \sqrt{I}) (1 + \sqrt{I}) \\ & - 0.0157 \delta I - 1.91138 I \\ & + 4.12485 \times 10^{-2} IT^2 \\ & + 4.45058 \times 10^{-4} IT^2 \\ & - 0.235872 FI \end{aligned} \quad (1)$$

where *A* is the Debye-Hückel coefficient in heavy water and *F* is the ionic strength function introduced by Pitzer,⁴

$$F = [1 - (1 + 2I^{1/2} - 2I) \exp(-2I^{1/2})] / 4I \quad (2)$$

The equilibrium isotope effects for the ionization of D_2O and of D_2PO_4 are shown in Fig. 3.3. The effects decrease slightly with increasing temperature, and

Fig. 3.3. The variation of $\log K$ for the ionization of water and of H_3PO_4 with temperature at the saturation vapor pressure.

their magnitudes can be correlated with the corresponding equilibrium constant in light water. A correlation for selected data on the ionization reactions of HSO_4^- , H_2PO_4^- , H_2PO_3^- , HCO_3^- , and H_2O is given by the relationship (independent of temperature)

$$\log (K_{HA} / K_{DA}) = 0.155 - 0.0515 \log K_{HA} (\text{cor}) \quad (3)$$

where the maximum deviation from the line is 0.15, the average deviation is 0.05 unit, and $\log K_{HA} (\text{cor})$ is a statistically corrected value for the ionization constant.

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3.1.4 An Equation for the Ion Product of Water, 0-1000°C, 1-10,000 Bars¹

W. L. Marshall

Needs have arisen for a general equation to describe the ionization behavior of water over wide ranges of temperature and pressure. Those concerned with mechanisms of corrosion as well as chemistry of steam generators may require accurately calculated values of the ion product of water K_w in the temperature (300-600°C) and pressure (100-500 bars) ranges of interest. Chemical oceanographers may wish to calculate the ion product in water at both low and high temperatures and pressures but with corrections for dissolved salts. Similarly, hydrothermal geochemists are interested in a quantitative description of the ionic behavior in interpreting behavior of geothermal solutions. To the aqueous electrolyte chemist, quantitative knowledge of K_w provides additional information for interpreting aqueous electrolyte behavior.

There are many determinations of K_w at saturation vapor pressures and at temperatures up to 310°C, reviewed recently by Sweeton, Mesmer, and Baes.² However, values at very high pressures and high temperatures are much less abundant because of the experimental difficulties.

Nevertheless, the available determined values were correlated by the previously observed straight-line relation for ionization equilibria at constant temperature. For water, $\log K_w$ is plotted against $\log$ density d . The slope k of the above relation changes

with temperature but appears to approach a constant value as the temperature rises. The basic equation is

$$\log K_w = \log K_w(d=1) + k \cdot \log d \quad (1)$$

where $\log K_w(d=1)$ and k are functions only of temperature.

The observed values of $\log K_w$ (based on units of molality) of Sweeton, Mesmer, and Baes² along the liquid-vapor curve (0-300°C) together with those of Quist³ at 400-800°C and at pressures up to 4,000 bars were extrapolated (or interpolated) to corresponding values at a density of 1 g cm^{-3} . The values of $\log K_w(d=1)$ obtained are plotted against $1/T(^{\circ}\text{K})$ on Fig. 3.4 to produce almost straight-line behavior from 0 to 800°C. These values were used to obtain an equation for the temperature dependency of $\log K_w(d=1)$ in Eq. (1).

The combined equation found to fit essentially all of the experimental values is given as

$$\log K_w = A + B/T + C/T^2 + D/T^3 + (E + F/T + G/T^2) \log d \quad (2)$$

where T is in $^{\circ}\text{K}$ and values for the parameters are

$$\begin{aligned} A &= -4.098 \\ B &= -3245.2 \\ C &= +2.2362 \times 10^4 \\ D &= -3.984 \times 10^7 \\ E &= +13.957 \\ F &= -1262.3 \\ G &= +8.5641 \times 10^5 \end{aligned}$$

Fig. 3.4. Logarithm of molal ion product of water at density of 1 g cm^{-3} ($\log K_w$) plotted against $1/T(^{\circ}\text{K})$; 0-1000°C; curve calculated by Eq. (2).

Table 3.1 compares some calculated with determined values of $\log K_a$.¹²⁻¹⁴ We observe good agreement with the values of Sweeton, Mesmer, and Baes¹² at 0-300°C at saturation vapor pressures. In addition, calculated values for $\log K_a$ at high pressures are within the experimental uncertainties of the determinations. Of great interest is the agreement with values of Hamann and Linton¹³ at extreme pressures up to 71,000 bars and at temperatures up to 373°C. Their measurements were not used for determining the parameters of Eq. (2) and are far outside our stated range of 10,000 bars for application.

Table 3.1. Representative differences between some calculated (with Eq. (2)) and observed values of $\log K_a$.

A, based on units of molality

Researcher	T, °C	Maximum pressure (bars)	Average difference
Sweeton, Mesmer and Baes (1974)	0-300	Saturation vapor pressure	+0.015
Whitfield (1972)	5-35	2,000	+0.015
Hamann (1963)	25	2,026	+0.005
Linn, Kryukov (1974)	18-72	7,845	0.25
Quist (1970)	300-500	4,000	0.15
Hamann, Linton (1969)	25	7,500	+0.09
	250	40,000	0.13
	304	50,000	0.20
	373	71,000	0.32

Deviation at maximum pressure

Equation (2) may also be used to generate values of other thermodynamic functions, ΔG , ΔH , ΔF , ΔS , and ΔF° , at related temperatures and pressures. By differentiation at constant pressure, the equation yields an enthalpy of ionization (ΔH) of 13.30 kcal mol⁻¹ at 25°C and saturation vapor pressure, which may be compared with values by calorimetry of 13.336 kcal mol⁻¹ at 25°C by Vanderzee and Swanson,¹¹ 13.340 kcal mol⁻¹ by Sweeton, Mesmer, and Baes,¹² and 14.0 kcal mol⁻¹ by Quist⁶ by similar interpretations as here.

After the above and other considerations, we believe that Eq. (2) describes $\log K_a$ (molal units) within ± 0.03 unit at pressures up to 10,000 bars when the temperature is below 250°C. At temperatures from 250 to 1000°C and pressures up to 10,000 bars, the equation may still provide accuracies of

± 0.03 to 0.05 unit, although upper limits of uncertainty at this time should probably be ± 0.05 to 0.3 unit of $\log K_a$.

1. This work will form the basis for an internationally approved release (agreement) on the accepted values for the ion product of water. This release will be made by the International Association for the Properties of Steam (IAPS) of which the author is a member of the working groups. A publication will appear shortly.

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3.1.5 Oxide Solubilities and Thermodynamics of Metal Ions at High Temperatures. $\text{Al}(\text{OH})_3$

B. F. Hitch, C. F. Baes, Jr.
R. E. Mesmer

Data on the solubility of hydroxides and oxides as a function of pH is potentially the best source for obtaining thermodynamic data on the metal ions and particularly their mononuclear hydrolysis products $\text{M}(\text{OH})_2^{2+}$ at high temperatures.¹ Our attention at the outset of this program has been directed toward crystalline gibbsite $\text{Al}(\text{OH})_3$ in the temperature range 25 to 90°C. A column approach was selected for the equilibrations, and the crystals were sized to minimize the surface-free energy contribution to the solubility.

Material from Alcoa Company (hydrated alumina C-331) was selected because of its purity and appropriate particle size. The average particle size of the grade was 10 μm . This material was mechanically sieved by means of a sonic sifter to obtain particles mostly in the 10- μm to 40- μm range. Although this was a laborious task, it was more successful than the attempts at separation by elutriation. The platinum-lined and Teflon columns used in the study contained about 76 g of gibbsite, and the flow rates were in the range of 0.5 to 2.0 ml/h.

Basic region. We were most successful in attaining equilibrium in the base region first by saturating a 0.01 *m* NaOH in 1 *m* NaCl solution and then by equilibration with a solution having the original composition of 0.8931 *m* Na⁺, 0.7959 *m* Cl⁻, 0.01876 *m* Al³⁺, and 0.07836 *m* OH⁻. The free hydroxide concentration was calculated based on the assumption that the dissolved aluminum was present as Al(OH)₃. The quotient for the equilibrium with the aluminate ion from 25 to 90°C is described by

$$\log Q_{\text{eq}} = \log ([\text{Al(OH)}_3] [\text{OH}^-]) \\ = 3.6074 - (1398.17) / T (\pm 0.03) \quad (1)$$

where *T* is in kelvins. These values are close to those obtained by Apps² in dilute solutions, indicating a small salt effect.

Acidic region. The pH in the acidic region was measured with an accuracy of about 0.03 unit, using a 0.001 *m* HCl standard. We can estimate from determinations in the pH range 3.6–4.0 at 60°C that

$$\log Q_{\text{eq}} = \log ([\text{Al}^{3+}] [\text{H}^+]) \\ = 7.20 \pm 0.15 \quad (2)$$

This value agrees with an estimate from thermodynamic data. More precise measurements should be made in this region and extended to higher temperatures.

Neutral region. In the neutral region of pH where the minimum in solubility is observed, the precision of the aluminum colorimetric method was limiting. After concentrating solutions on a cation exchange column and eluting with 0.5 *m* NaOH, upper limits of the aluminum concentrations in the range 3×10^{-7} – 2×10^{-6} *m* were set between 25 and 90°C. These values represent an upper limit for the reaction,

These results are at least an order of magnitude lower than previous estimates but are considered tentative because of questions about the reliability of the analytical method in this range.

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3.2 GEOSCIENCES

3.2.1 High-Pressure, High-Temperature Phase Equilibrium and Crystallization Studies of Model Magma Systems

M. T. Naney

Phase relations and crystal growth characteristics of two synthetic granitic compositions have been investigated at pressures of 2 and 8 kilobars and at temperatures ranging from 550 to 1200°C, using the sealed capsule technique. The influence of the component H₂O on phase relations was studied by adding water to each anhydrous granitic composition in amounts ranging up to 20 wt % for each isotherm investigated. Oxygen fugacity in samples containing an aqueous vapor phase was fixed at values appropriate for the magnetite stability field (Ni-NiO $\rightarrow$ Fe₂O₃-Fe₃O₄) by the experimental apparatus.

The main emphasis of phase equilibrium experiments was directed toward obtaining information on the stabilities of ferromagnesian silicate phases when they coexist with feldspars (plagioclase: CaAl₂Si₂O₇-NaAlSi₃O₈ crystalline solutions and alkali feldspar: KAlSi₃O₈-NaAlSi₃O₈ crystalline solutions), quartz (SiO₂), and H₂O-vapor undersaturated silicate melts of granitic composition. Some of the most common rock-forming ferromagnesian silicates [orthopyroxene (Mg,Fe)₂(SiO₃)₂; clinopyroxene (Ca,Na,Mg,Fe²⁺,Fe³⁺)(Si,Al)₂O₆; hornblende (Na,K)Ca₂(Mg,Fe²⁺,Fe³⁺,Al³⁺,Si,Al)₅O₁₂(OH)₂; biotite K₂(Mg,Fe²⁺)(Al,Fe³⁺)(Si,Al)₂O₁₀(OH)₂; and epidote Ca(Fe²⁺,Al)O(OH)(Si₂O₇)(SiO₃)] were synthesized in these experiments.

One informative method of presenting the phase equilibrium data obtained during this study is illustrated in Fig. 3.5. This pseudobinary plot (temperature vs *X*_{H₂O}) conveniently shows isobaric (2-kilobar) changes in phase assemblage relationships as functions of temperature and the weight fraction of water added to the anhydrous seven-oxide component (SiO₂, Al₂O₃, FeO, MgO, CaO, Na₂O, K₂O) granite composition. Four of these diagrams have been constructed to summarize graphically the results of experiments made at 2 and 8 kilobars, using synthetic granite and granodiorite compositions.

Crystal growth processes were investigated using the same granite and granodiorite compositions used in phase equilibrium studies. Homogeneous silicate liquids were generated by heating samples to hyperliquidus temperatures at 2 and 8 kilobars. Crystal nucleation and growth were promoted by

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Fig. 3.5. Two-kilobar temperature vs wt % H₂O phase assemblage diagram for the synthetic granite composition (R1 + 10 MI). Opx = orthopyroxene, Cpx = clinopyroxene, Bt = biotite, Pl = plagioclase, Af = alkali feldspar, Q = quartz, L = silicate liquid, and V = aqueous vapor. Numbered fields shown in this diagram represent the phase assemblages: Opx + Cpx + Pl + Af + Q + L, Opx + Cpx + Bt + Pl + Af + Q + L, Bt + Pl + Af + Q + L, Cpx + Bt + Pl + Af + Q + L, Opx + Cpx + Bt + Pl + Af + Q + L, Cpx + Bt + Pl + Af + Q + L, Opx + Cpx + Bt + Pl + L, Opx + Cpx + Bt + L, Opx + Cpx + Pl + L, Opx + Cpx + L, and Opx + Bt + L.

undercooling these homogeneous liquids 100 to 500°C in single or multiple steps.

Results of these experiments contrast sharply with those obtained in phase equilibrium experiments. Crystallization experiments indicate that the mineralogy of an igneous rock may be strongly influenced by its cooling path. Plagioclase, alkali feldspar, and quartz appear at temperatures at least 200°C below their equilibrium stability limits or are completely absent in products of crystal growth experiments. In addition, the ferromagnesian phases in crystal growth and phase equilibrium experiments may be different. For example, hornblende and clinopyroxene coexist in products of crystal growth experiments

but not in products of phase equilibrium experiments. It is suggested that the contrasting phase assemblages observed in the two types of experiments result from differences in nucleation rates for framework and ferromagnesian silicates, enhanced by competition between phases for components of the melt common to both types of phases.

These types of experiments provide information about phase relations and crystallization of silicate systems over a wide range of P-T-X conditions appropriate for silicic magmas (natural silicate melt ± crystals). The data obtained will be necessary for modeling the behavior of magmas if used for production of thermal energy or chemicals and for designing "synthetic rock" ceramic host materials for incorporation and permanent storage of nuclear waste. In addition, these experiments provide background studies for further experimentation (1) with more complex systems (e.g., partitioning and solubility of economically important elements—U, Th, W, Sn, and Mo—in silicate melts to obtain information about the genesis of ore deposits associated with igneous rocks) and (2) to obtain physical property measurements in silicate melts (e.g., viscosity and diffusivity).

Principal efforts during the past year have been directed toward designing and setting up two experimental facilities: (1) one-atmosphere furnaces with capability for controlling oxygen fugacity at high temperature (1400°C) and (2) a high-pressure (60,000 psi), high-temperature (1400°C) facility with capability for controlling oxygen fugacity.

1. The preceding discussion is based on research conducted by M. L. Nancy at the Tuttle-Jahns Laboratory for Experimental Petrology, Department of Geology, Stanford University, Stanford, Calif., for a Ph.D. dissertation.

3.2.2 Precipitation and Scaling in Dynamic Geothermal Systems

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

An existing 100-gpm titanium loop was modified¹ to provide a facility for studying the formation of silica precipitates and their properties and fates as a function of brine composition, temperature, and flow conditions. Simulated silica-saturated geothermal waters are prepared by circulating part of the loop flow (~1 gpm) through a bypass column filled with amorphous silica powder. A second ~1-gpm stream is circulated through a heat exchanger in

which dynamic scaling studies are conducted. The heat exchanger was divided into five consecutive segments so that successive temperature intervals could be instrumented to monitor changes in heat transfer characteristics; selective destructive examination, when desired, is also facilitated. Blind end flanges on each segment permit borescope examination of scales in situ and sampling access. The stream leaving the heat exchanger is reheated by an electrical system to replace the 40-kW heat equivalent removed at maximum ΔT and recycled.

To date, 11 runs have been carried out in this system, and the results are summarized in Table 3.2. Run 2 was directed at silica scale formation from 1 M NaCl at pH 6. Spontaneous nucleation did not occur in 183 h of operation; the system was therefore shut down and restarted twice in an effort to seed the heat transfer surfaces without success. Similar operations in a low-flow (~1-gpm) Pyrex pipe system seeded during shutdowns of several hours with subsequent rapid scaling continued in operation. A subsequent 141-h shutdown did seed the system, however, with the result that scaling rates ranging from 0.3 to 1 mg cm⁻² h were observed.

Run 3 was operated under the same conditions as run 2 to demonstrate that our cleaning procedures had adequately removed all the silica scale formed in run 2. Run 3 further demonstrated that spontaneous nucleation was not easily initiated under these conditions.

The subsequent three runs of this series showed that spontaneous nucleation was relatively rapidly initiated from 4 M NaCl at pH 7 and 650 ppm silica.

Much higher growth rates were observed at the higher temperatures, but the rates were comparable to those in run 2 at the lower temperatures.

As in the Pyrex system studies, the scales deposited at the high temperatures are much harder and more refractory (to dissolution by 4 M NaOH at 5°C) than those formed at lower temperatures. However, all require several hours for complete removal by the hydroxide treatment.

Run 5 was aborted by loop heater relay failure shortly after scaling was indicated to have begun. The heat transfer changes. The time during which the run was in progress was probably less than 1 h.

A somewhat surprising result was the amount of scale deposited in the reheater portion of the system. Total amounts deposited were comparable to those found in the heat exchangers. The results are not serious problems for removal of silica scales removed beforehand.

The possibility of seeding during shutdowns with subsequent rapid scale growth suggests that special flushing or treatment measures would be beneficial in connection with shutdowns.

Runs 7-10 were undertaken at the request of the Division of Geothermal Energy to assess the scaling characteristics of low salinity-high pH brines at lower (~500 ppm) silica concentration. Such brines, constituting the bulk of known U.S. resources, are believed more amenable to early development. Borecope examinations after each run showed spontaneous nucleation in all heat-exchanger segments, with the scale forming scattered ridges transverse to the flow direction. Growth rates were

Table 3.2. Silica deposition in dynamic loop studies

Run No.	Time (hr)	pH	SiO ₂ (ppm)	NaCl (M)	ΔT (°C)	Segment 1		Segment 2		Segment 3		Segment 4		Segment 5			
						ΔT (°C)	mg cm ⁻² (Total per hr)	ΔT (°C)	mg cm ⁻² (Total per hr)	ΔT (°C)	mg cm ⁻² (Total per hr)	ΔT (°C)	mg cm ⁻² (Total per hr)	ΔT (°C)	mg cm ⁻² (Total per hr)		
2A	143 (100h)	6.0	850	1.0	220	155	152.95		95.64			65.58		58.49			
2B	46 (98h)	6.0	850	1.0	220	160	160.96		96.67			67.58		58.59			
2C	29 (141h)	6.0	850	1.0	215	160	160.106		106.76			74.65		65.67			
3	29	6.0	800	1.0	240	170	170.110	31.4	111.1	110.78	17.4	0.6	4.60	100.0	60.45	17.7	0.6
4	14	6.0	725	1	175	138	139.107		107.76			76.51		51.36			
4	44	7.0	700	1	165	134	134.100		100.72			2.49		40.75			
5	29	7.0	650	4	180	140	140.107	9.4	132.1	100.72	5.7	0.2	12.50	5.7	30.47	2.5	0.1
6	11	7.0	650	4	198	161	161.127	32.1	127.42	127.79	6.5	0.5	79.40	21.1	49.32	2.6	0.2
7	14	7.8	500	0.5	127	107	107.89		89.67			67.46		44.42			
8	11	7.8	500	0.5	144	125	125.103		103.77			77.57		51.42			
9	10	7.8	500	0.5	152	134	134.113		113.84			82.56		62.36			
10	1	7.8	500	0.5	175	154	154.132		132.97			97.65		72.72			
Total						1036.0		1036.0		1036.0		1036.0		1036.0		1036.0	
11	20	7.8	500	0.5	140	124	124.104	0.82	104.02	97.58	0.2	0.041	77.54	0.2	56.40	0.04	0.014

^aThe pressure will temperature was 100°C for the first 100 h of the run.

^bShutdown periods to permit cleaning.

^cCleanups were not quite complete when sodium hydroxide solutions were first.

^dPhosphate molar ratio of 0.01 to 0.02 was used for Run 5. For Run 6, Run 7, Run 8, Run 9, Run 10, Run 11.

quite low, and no deleterious effects on heat transfer were observed. The higher initial ΔT s in successive runs were the result of an unexplained saturator column malfunction that necessitated increasing operating temperatures to maintain the same silica concentration level. Thus scale that formed in segments 1 and 2 in the early parts of the series redissolved at the higher-than-equilibrium solubility temperatures of run 10. The scales formed in these runs were all friable and relatively easily removed.

The last run (program terminated September 30, 1978) was carried out with 1 M NaCl but otherwise with similar conditions to the previous series. As shown, scaling "rates" increased appreciably, but the scale was still friable and not deleterious to heat transfer, suggesting that low-silica-concentration brines produce much more friable scales.

The kinetic studies described above have shown that the surface area of the scale is an important factor in the kinetics of deposition. Where samples could be obtained from the heat exchangers in the above runs, the BET areas of the deposits ranged from 0.8 to 8 m²/g. Thus the nature of the scale formed as well as its proliferation and distribution will profoundly affect the subsequent rate of growth in terms of deposition per unit area of pipe. This effect provides an explanation for the apparent discrepancy in rates between runs 2D and 11. In run 2D nucleation was promoted by deposition of very high surface-area colloidal silica from the stagnant brine with relatively uniform distribution, whereas in run 11 nucleation was isolated and probably was spreading slowly. Thus averaged rates such as those presented are quite misleading because a knowledge of the scale surface area and the pipe coverage must be a part of the rate determination.

In general, the trend in the amount of deposition with temperature is qualitatively consistent with that predicted by the rate expression derived from our column experiments. Generally, the amounts increase with temperature and reach a maximum near the saturation temperature. There are, however, insufficient data to model the combined nucleation and growth behavior observed, even for very clean brines, at this time. It was not possible to demonstrate with the loop facility the effects of the parameters identified as important in our column experiments because of the redirection of our efforts by the Division of Geothermal Energy and by the premature termination of the program.

3.2.3 Kinetics of the Deposition of Amorphous Silica by a Column Technique

E. G. Bohlmann P. Berlinski
R. E. Mesmer

The solubility in water of the most rapidly precipitating solid form of SiO₂, amorphous silica, has been investigated by Fournier to 350°C. The solubility in salt solutions is currently under study in another program at ORNL. It is generally accepted that in equilibrium with amorphous silica (and also for the more insoluble crystalline phases of silica—quartz, cristobalite, etc.) the only species of silica present in acidic solutions is monomeric silicic acid. This conclusion is based on the rapid color development in the molybdate method of analysis and also on analysis of potentiometric data in nearly saturated solutions. However, when the solution phase is supersaturated with respect to amorphous silica, polymerization proceeds with formation of colloidal particles, and ultimately amorphous silica precipitates.

The polymerization process has been studied extensively, most recently by Makrides et al., who have also reviewed the earlier work. There is now considerable information on the homogeneous nucleation step, but as yet little information is available on the kinetics of growth on existing surfaces. It is the objective of this program to provide this information as part of a program at ORNL to examine silica deposition behavior in dynamic geothermal systems from hydrothermal brines found in the western United States.

Deposition may occur in well casings, piping, valves, flash tanks (where concentrations and the degree of supersaturation is increased), in heat exchangers, on turbine blades, in holdup storage ponds, or in subsurface formations where fluids are reinjected for disposal. The latter is a serious threat to the lifetime of the reinjection well since the porosity and permeability of the formation in the vicinity of the well bore are critical factors.

In our experiments, supersaturated brines were passed through columns packed with several forms of silica (crystalline α quartz, polycrystalline α quartz, and porous Vycor). Also, adsorption on ThO₂ microspheres and titanium powder was studied under controlled conditions of supersaturation, pH, temperature, and salinity. The residence time was varied by adjustments of flow rate and column length. The silica contents in the input and effluent solutions were determined colorimetrically by the molybdate method.

The following observations have been made

1. The reaction rate is not diffusion limited in the columns.
2. The silica deposits from a solution that contains only monomeric $\text{Si}(\text{OH})_4$.
3. The deposition on all surfaces examined was self-nucleated.
4. Essentially identical deposition behavior was observed, once the substrate was thoroughly coated and the BET surface area of the coated particles was taken into account.
5. The dependences on supersaturation concentration, hydroxide concentration, and temperature were determined.

Fig. 3.6. The rate of deposition of amorphous silica on polycrystalline α quartz at 60° in 1 *M* NaCl at three pH values. On the ordinate, C is the equilibrium solubility of amorphous silica.

The empirical rate law, which describes our data in 1 *M* NaCl in the pH range 5–7 and temperatures from

60–100 °C, is

$$\frac{d[\text{Si}(\text{OH})_4]}{dt} = 0.124 \frac{[\text{Si}(\text{OH})_4]}{[\text{Si}(\text{OH})_4] + [\text{OH}^-]} \quad (1)$$

where A is the surface area in $\text{cm}^2 \text{SiO}_2$ per kilogram of water, t is in minutes, and the concentrations are in molal units. Hydroxide concentration was derived from the measured pH and the ionization quotient for water. In the expression given above, the rate constant is essentially independent of temperature. Figure 3.6 shows the effect of pH on the rate of deposition on polycrystalline quartz at 60° in 1 *M* NaCl and also demonstrates the second-order dependence on the silica supersaturation concentration. Alternatively, the rate of linear growth of an amorphous silica surface in centimeters per minute is given by

$$\frac{dh}{dt} = 3.1 \frac{[\text{Si}(\text{OH})_4]}{[\text{Si}(\text{OH})_4] + [\text{OH}^-]} \quad (2)$$

This result allows one to make estimates of deposition rates when information about the available area of amorphous SiO_2 , the supersaturation, the pH, and the temperature is known. These studies will be extended and applied in interpreting results in the dynamic system.

1. See Sect. 3.2.4 of this report.

2. A. C. Makrides, M. E. Turner, W. W. Harvey, J. Slaughter, S. B. Brummer, P. O'D. Offenhardt, and G. E. Pearson, *Study of Silica Scaling from Geothermal Brines, Final Report for Period November, 1974 to April 1977*, EIC Corp., Newton, Mass., 1978.

3. See Sect. 3.2.2 of this report.

3.2.4 Solubility of Amorphous Silica in Aqueous Salt Solutions

W. E. Marshall and J. M. Warakowski

The solubility of amorphous silica in salt solutions is of fundamental and applied interest to several disciplines. For example, in the production of geothermal energy, the deposition from hydrothermal waters of amorphous silica on heat-exchanger surfaces is a problem that might be alleviated by quantitative knowledge or prediction of the solubility of silica. Similar problems exist for the operation of steam generators in power plants. At low temperatures, considerations of oceanographic environments

may be enhanced by knowledge of silica solubilities in seawater and brines. In addition, the aqueous electrolyte chemist is interested in the effect of salt concentrations on the solubility of amorphous silica for the development of theories of electrolyte behavior.

Previously, the solubility of amorphous silica in aqueous NaNO_3 solutions was reported at temperatures from 100 to 300 $^\circ\text{C}$. These results showed that the solubility was decreased markedly by an increasing concentration of NaNO_3 . It was believed that the relative decrease in solubility of silica might be similar for many added salts and that a common, single curve might result. Or, if a common solubility curve were not found, then perhaps a single curve would be produced by plotting solubility of silica against the "activity" of water over the several salt solutions. In another approach, the use of ionic strength rather than molality of added salt could be tried. In the current study, the solubility of amorphous silica was determined at 25 $^\circ\text{C}$ in 11 salt solutions, with concentrations of each salt varying from zero to saturation. The results are interesting in that they show no common curve by any of the modes of plotting mentioned above. The interpretation of these data is not yet complete.

Runs were made in a 25.0 ± 0.1 $^\circ\text{C}$ water thermostat. Polyethylene bottles containing salt solutions and an excess of amorphous silica were rocked for periods of time varying from 5 h to 6 d. Equilibrium appeared to be established within 24 h, as evidenced by consecutive colorimetric analyses for silica by the conventional molybdate method.

Figure 3.7 shows the molar solubility of amorphous silica plotted against the molarity of added electrolyte. Each curve originates at the common solubility of silica in pure water and shows the decrease in solubility as the concentration of electrolyte increases. Most of these curves extend to the saturation concentration of the added electrolyte, that is, where two saturating solids, silica and salt, are present.

We note that the solubility decreases sharply with increasing concentration of salt, a phenomenon usually termed the "salting-out" effect. Among the several salts, there is a large divergence in effect on solubility. Moreover, the additions of Na_2CO_3 and of Na_2SO_4 might appear to indicate some complex formation in solution, which inhibits the drop in solubility with increasing salt concentration.

Similar plots of solubility against ionic strength closely merged the curves for added MgCl_2 and CaCl_2 with those for added NaCl and NaNO_3 . However, for other added salts, divergences remained. Neither did the use of activity of water in place of molarity of

Fig. 3.7. The solubility of amorphous silica in aqueous salt solutions at 25 $^\circ\text{C}$.

added electrolyte provide a common curve for all the electrolytes.

We note, however, that, of the effect of 1-1 salts, the use of KCl and KNO_3 provides essentially identical curves, as do, respectively, NaCl and NaNO_3 as well as LiCl and LiNO_3 . The cation therefore appears to produce the significant effect; and, moreover, the decrease in solubility becomes greater as published hydration numbers (of the cations) increase in the order $\text{K}^+ > \text{Na}^+ > \text{Li}^+$.

This work and the previously reported study¹ are believed to be the first extensive studies on the solubility of amorphous silica in salt solutions of very high concentrations. When the analysis of these data is complete, we hope to predict the solubility of silica in mixed electrolyte solutions at 0–374 $^\circ\text{C}$ and to provide new information on the nature of amorphous silica in contact with aqueous environments.

1. ORNL Student Research Participant, 1978.

2. W. L. Marshall, *Chem. Div. Annu. Prog. Rep. Mar. 31, 1977*, ORNL-5297, p. 22.

3.3 ADSORPTION OF INORGANIC MATERIALS ON CLAYS AND ROCK SAMPLES

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3.3.1 Techniques and Theory

In support of research on the various chemical flooding techniques of enhanced oil recovery and also

of research on nuclear waste isolation, we have been systematically measuring the distribution of solutes of interest on selected compounds typifying adsorptive components of natural formations from solutions over a wide range of ionic strength at controlled pH. The methods used include conventional batch equilibrations, column methods, and axial filtration. Emphasis has been on measuring adsorption functions with samples of montmorillonite from various sources. Adsorption functions were also obtained with samples of attapulgite, kaolinite, illite, and various rock samples.

Techniques. In our batch equilibration experiments, weighed amounts of purified and properly pretreated clay are shaken with known volumes of solution, and the reduction of concentration of the adsorbate in the solution is determined after separation of solid and solution by centrifugation. An appropriate analytical technique, atomic absorption or counting of radioactive tracers, for example, is used to determine the concentration of the solution, from which the amount of the solid is calculated. Results are expressed as distribution coefficients D , the amount of adsorbed per-unit-weight adsorbent divided by the amount of per-unit-volume solution at equilibrium.

Columns made from clays (such as montmorillonite) alone have insufficient flow rate for efficient rapid determination of exchange equilibria. We have therefore experimented with various methods of bringing throughput to reasonable levels by mixing clays with other materials of low adsorbability. Our best results so far have been obtained with a column containing 20% clay and 80% Celite (a diatomite filter aid). Generally, distribution coefficients were determined by first equilibrating the column with the solution of interest by passing a number of column volumes through it. A small amount of tracer solution was then introduced at the top of the column, and the number of column volumes required to elute the peak was determined by the position of the maximum of the peak. The distribution coefficient is calculated from the equation

$$D = (V_{\text{peak}} - i) / \rho \quad (1)$$

where D is the distribution coefficient in units of volume weight (e.g., liters per kilogram), V_{peak} is the number of column volumes required to elute the peak, i is the fractional interstitial volume, and ρ is the bed density (weight of exchanger per unit volume

of bed). In a mixed bed, corrections must be applied if adsorption by the other components is not negligible.

We are also using an axial filter to determine values of D . This system uses a cylindrical filter rotating about its axis and enclosed in a coaxial cylindrical pressure sleeve. In a typical experiment, the filter is rotated at about 2000 rpm while a known amount of adsorbent is suspended in the pressure chamber, which contains a medium whose composition is the same as the one in which the adsorption properties are to be investigated. A solution having the same composition of the one in the pressure chamber but containing also the element to be studied at "trace" level (typically 10^{-5} to $10^{-6} M$) is then introduced into the chamber, flows through the filter, and is finally analyzed. As the adsorbate is introduced continuously into the slurry, its concentration will build up to the feeding concentration at a rate that, under the proper conditions, is a function of the distribution of the adsorbate itself between the solution and the adsorbent.

Let us indicate with C and C' the concentrations in the feeding solution and in the chamber respectively. Because of the incompressibility of the system at the pressures (< 20 psi) with which we are dealing, the mass balance when a small volume dV of feeding solution is pumped into the chamber leads to the following equation:

$$C' dV = (V_c - V_{\text{ads}}) dC' + C dV + d(mDC') \quad (2)$$

where

V_c is the volume of the empty cell,

V_{ads} is the volume of the adsorber,

m is the amount of adsorber inside the cell,

D is the distribution coefficient of the adsorbate in liters per kilogram.

If C' is small enough that D is not a function of C' , Eq. (2) can be rewritten as

$$(C' - C) dV = V_c dC' \quad (3)$$

where

$$V_c = V_c - V_{\text{ads}} + mD.$$

Integrating Eq. (3) we obtain

$$\ln \phi = V_c / V_c' \quad (4)$$

Fig. 3.8. $\text{Zn}^{2+}/\text{Na}^+$ exchange on Dowex 50-W, 0.7 M Na.

and then D can be obtained from the slope of $\ln \phi$ vs V_e , where $\phi = 1 - C/C_0$. An analogous expression can be obtained when, after loading the cell ($C = C_0$), a fresh solution with $C_0 = 0$ is pumped into the cell. In this case $\phi = C/C_0$, where C_0 is the limiting loading concentration. Coincidence between the loading and eluting lines is obtained when (1) D is not dependent on C and (2) ion and particle diffusion are fast. Strong deviations from Eq. (3) are to be found when conditions 1 and 2 are not met. To check condition 2, adsorption can be studied at different flow rates and rotation speeds. If coincidence of loading and eluting occurs in a wide range of flow rates and rotation speeds, then condition 1 must be valid.

The exchange behavior of Zn (10^{-4} M) on Dowex 50-W in sodium form in 0.7 M Na⁺ at pH 5 is shown in Fig. 3.8. Flow rates for the experiments range from ~ 10 ml/min to 22 ml/min and are constant during each loading or eluting curve. As can be noted, there is no detectable effect that might invalidate conditions 1 and 2. Distribution coefficients for $\text{Zn}^{2+}/\text{Na}^+$ and $\text{Cd}^{2+}/\text{Na}^+$ exchange on the sodium form of Dowex 50-W at different Na⁺ concentrations are shown in Table 3.3. Results have been obtained with "batch equilibration" and "axial filtration" methods, and the data are expressed for kilograms of wet resins. The agreement is very good for all the solutions examined except the most dilute one. We suspect that this is due to the fact that above condition 1 is not met (loading $\approx 10\%$ of capacity), and in fact loading and eluting curves are not coincident in this case.

Theory. Our emphasis in the determination of adsorption functions by these techniques has been on the determination of the ideality of exchange over the

Table 3.3. Distribution coefficients for $\text{Zn}^{2+}/\text{Na}^+$ and $\text{Cd}^{2+}/\text{Na}^+$ exchange on Dowex 50-W

Na^+ (mol/liter)	Zinc		Cadmium	
	Batch	Axial filter	Batch	Axial filter
0.1	751 ± 24	500		
0.2	132 ± 1	127	32 ± 0.5	33
0.5	18.9 ± 0.5	17.5	2.3 ± 0.1	1.7
0.7	8.4 ± 0.2	8.2	0.91 ± 0.05	1.0
1.0	4.2 ± 0.2	4.3		

whole range of loadings. We have been interested in the extent to which these exchangers behave as ideal ion exchangers and whether there are any significant differences in behavior at micro- and macrolading of the capacity of the clay.

Consider the ion exchange equilibrium represented by the following equations:

where the bars over the terms represent adsorbed species. We may write for the equilibrium expression

$$K = (m_M^n \cdot m_A^p) / (m_A^n \cdot m_M^p) \cdot \Gamma \quad (6)$$

Here m represents the concentrations of the components in the liquid and adsorber phases, K is the equilibrium constant, and Γ is the appropriate quotient of the activity coefficients. If the capacity of the adsorber is C , then assuming no invasion of coions,

$$pm_A = C - nm_M \quad (7)$$

Here C is expressed in equivalents per unit weight. If M is present in the adsorber at trace loading, that is, at only a few percent of capacity, then

$$m_A \approx C/p \quad (8)$$

$$K \cdot \Gamma \approx D_M^n \cdot (m_A^n) [(C/p)^p] \quad (9)$$

and

$$D_M \approx [(C/p) \cdot (m_A)]^{1/p} \cdot (K/\Gamma)^{1/p} \quad (10)$$

where

$$D_M = (m_M) / (m_A) \quad (11)$$

Assuming K/I' to be constant, rearrangement of Eq. (9) and differentiation yields

$$(d \log D_{st}) / (d \log m_{Na}) = -n/p. \quad (12)$$

Thus for exchange of $Sr(II)$ with $Na(I)$, we would expect a slope of -2 at low loading when $\log D_{st}$ is plotted vs $\log m_{Na}$. For exchange of $Eu(III)$ with $Ca(II)$ at low loading a slope of -3 is expected.

If Eq. 8 is not valid, that is, if loading proceeds to the point where it is significant with respect to the capacity, then

$$D_{st} = [(C - nm_{st}) / (pm_{st})]^{p/(K/I')}. \quad (13)$$

As loading increases, the term nm_{st} becomes significant with respect to C , and the distribution coefficient decreases relative to the value at trace loading.

3.3.2 Systematic Study of Nuclide Adsorption on Selected Geologic Media

Prediction of the migration of nuclides of interest to nuclear waste requires accurate information on their distribution coefficients relative to the various groundwaters and geologic formations that might be encountered. The adsorption of these nuclides is a complicated function, both of the properties of the solid adsorbent and also of the nature of the groundwater. We are therefore systematically measuring the distribution of solutes of interest in radioactive waste on selected compounds typifying adsorptive components of natural formations from aqueous solutions over a wide range of ionic strength at controlled pH. We have emphasized measurements at high ionic strengths because high concentrations of brine are likely to be encountered in the event of water penetration into waste depositories in bedded salt deposits.

Our initial emphasis has been in the determination of the ideality of these adsorption data, that is, in the extent to which they can be described by the ideal ion exchange equations given above. To avoid complications due to hydrolysis and the existence of several valence states, we have selected for initial study the determination of adsorption functions of alkali-metal and alkaline-earth ions on montmorillonite. Because distribution coefficients are often dependent on pH, buffers were used to control the pH, and a value of pH 5 was selected for most of the measurements. At this pH, hydrolysis and precipitation are minimized, and the clays are reasonably stable.

Fig. 3.9. Distribution of $Sr(II)$ between montmorillonite and sodium chloride 0.1 M sodium acetate solutions [low loading $Sr(II)$], pH about 5.

In Fig. 3.9, results are shown for the adsorption of strontium at trace loading as a function of the concentration of sodium ion. This plot of $\log D_{st}$ vs $\log c_{Na}$ is a straight line with a slope near to the ideal slope of -2 [cf. Eq. (12)]. This plot also shows that all three of our techniques of determining distribution coefficients give essentially the same result. Loading curves for strontium on montmorillonite are shown in Fig. 3.10. These curves show that, at loadings of up to about 0.1 mol $Sr(II)$ per kilogram of clay, distribution coefficients are fairly constant as they should be if Eq. (6) is followed for constant K/I' . The capacity of the montmorillonite used in these experiments was measured to be about 0.95 equiv kg. The loading curves begin to decline at values near the capacity, as Eq. (13) predicts. The adsorption of strontium on the sodium form of montmorillonite therefore seems to follow ideal behavior. For cesium adsorption on sodium montmorillonite, nonideal loading effects are observed as shown in Fig. 3.11. In this case the

Fig. 3.10. Sr^{2+} Na^{+} exchange on montmorillonite.

Fig. 3.11. Effect of loading on distribution coefficients of Cs(I) on the sodium form of Wyoming montmorillonite ($0.5 \text{ M NaCl} + 0.01 \text{ M NaOAc}$, pH 5, equilibration for 74 h).

distribution coefficient at tracer-level loading is about 145, significantly higher than the values at the lower loadings shown in the graph. Furthermore, a gentle decline in distribution coefficient is observed as the loading is decreased.

We have investigated adsorption functions for a great number of other systems and have found the kind of near-ideal behavior observed for Sr(II) adsorption on Na-montmorillonite for many of these systems. Further, for those cases where we could compare our results with literature values, we find fairly good agreement, although there are very few results for the high-ionic-strength environments in which we are interested. Finally, although we do observe some nonideal behavior including some significant loading effects, the loading curves that we have observed do not show any sharp discontinuities in behavior so that there is the possibility of prediction of adsorption functions with a reasonable number of experiments (see also Sects. 5.17 and 5.18).

3.3.3 Selection of Multiple Tracers for Enhanced Oil Recovery Systems, DOE Oil, Gas, and Shale Technology

In support of enhanced oil recovery technology, we have been conducting a systematic search to identify those elements and ions that can be used as tracers for water flow in the chemical flooding technique of enhanced oil recovery. Our efforts so far have concentrated mainly toward use of divalent ions; Sr(II) , Zn(II) , Cd(II) , Co(II) , and Ni(II) are the ions that we have studied until now. In the study of these ions, we have been concerned with adsorption behavior as a function of total cation concentration, pH, buffer concentration, and loading of the adsorbent. We are also interested in cases in which these ions might complex sufficiently with certain anions such as chloride to form complex anions, which might have sufficiently low distribution coefficients to be useful as tracers under specific conditions. So far we have concentrated mainly on montmorillonite because its high ion exchange capacity should cause it to have a disproportionate influence on the adsorptive properties of formations, even when present in relatively low percentages.

Either conventional batch equilibration or the axial filter have been used to determine distribution coefficients for these ions. Both methods are described in previous sections of this report. We have stressed measurements at high salinities and low loading of the adsorbent because these are the conditions most likely to be encountered in practice. In some cases, however, we have investigated the entire loading range in order to aid our understanding of the system.

Table 3.4 shows our most recent data for Ni(II) , Zn(II) , and Sr(II) adsorption on the sodium form of montmorillonite. The axial filter was used in these determinations, and pH was controlled either by use of acetate buffer or by addition of HCl to the suspension. For the unbuffered system, the clay must first be preequilibrated with the solution until the pH remains constant at the desired level. The buffer was made up with the NaOAc concentration indicated in Table 3.4 plus enough HOAc to maintain the desired pH. These values of D show that for Sr(II) there are no discernible effects of pH change or change of acetate concentration on the distribution coefficient within the conditions shown. For Zn(II) Na(I) exchange, the results are only approximate for the values in parentheses perhaps $\pm 25\%$; for reasons that we do not understand, there were difficulties with the technique in these determinations. However, with Zn there appears to be no significant effect of

Table 3.4. Axial filter determinations of D for exchange with Na(I) on montmorillonite

Molar ratio of total cation	NaOAc	pH	Distribution coefficients, D (mol/kg)		
			Ca(II)	Zn(II)	Sr(II)
0.3	0	6.8	14	(21)	14
0.3	0.01	4.7	9	12	12
0.3	0.1	4.7	3	12.5	12
0.4	0.1	4.7	3.5	4.0	5.9
0.5	0	6.8	6.4	(16)	7.2
0.5	0.01	4.7	5.5	(6)	6.0
0.5	0.1	4.7		(7)	8
0.7	0	4.3	4.4	3.4	2.0
0.7	0	4.6	4.5	4.7	3.5
0.7	0.01	5.6	4.3	(8)	3.0
0.7	0	6.1	4.4	(11)	3.2
0.7	0	6.3		(13)	3.0
1.0	0	6.8	1.3	(10)	1.6
1.0	0.01	4.7	0.6	3.9	1.5
1.0	0.1	4.7	0.2	3.6	
2.0	0.1	4.7	0.1	1.0	0.6

*Final concentration of Na(I), Zn(II), and Sr(II) = 10^{-3} M.

acetate, but there is a pH effect because values of D increase with pH. For Ni(II) Na(I) exchange, there are indications of an effect of acetate, and the results at 0.7 M indicate no significant effect of pH. For all of these ions, distribution coefficients are quite low at the higher concentrations of Na(I), indicating possible use of these ions as tracers under these conditions of high sodium concentration.

In Fig. 3.12 we have plotted $\log D$ for Co(II) and Cd(II) vs the logarithm of concentration of Na(I) and Ca(II) for the two respective forms of montmorillonite. If there were no complexing, the ideal slopes should be -1 for Ca(II) and -2 for Na(I). Significant complexing of Cd(II) by chloride is expected, and some of our results indicate complexing by acetate. Presumably complexing is reflected in the lower values of the slopes in Fig. 3.12.

A number of loading studies have also been completed for Co(II) Na(I) exchange on montmorillonite. Loading of Co(II) on Na-montmorillonite does not show the ideal behavior observed for Sr(II) Na(I) exchange because significant decreases in the distribution coefficient are observed between loadings of about 10^{-1} to 10^{-2} mol/kg of clay. Also there are large differences in the loading of cobalt (at pH 6.5) for different sources of the same clay. These large differences are surprising and, unfortunately, show that, at 1.0 M Na(I) and pH 6.5, the

Fig. 3.12. Distribution of cobalt and cadmium on montmorillonite.

distribution coefficients are too high to be used as a tracer.

However, the results we have so far suggest the use of Sr(II), Ni(II), Zn(II), and Cd(II) for tracers in geologic environments where salinity is high and pH is not high enough to cause problems with precipitation of hydroxides or carbonates.

3.3.4 Ion Exchange Characteristics of Enhanced Oil Recovery Systems

Adsorption functions for sodium ion alkaline earth systems, such as the Na(I) Ca(II) and Na(I) Mg(II) systems, are of interest at all ratios of these ions because of the strong effect of hardness in performance of surfactants and polymers used in chemical flooding. We have therefore been determining distribution coefficients of calcium on the sodium form of (initially) montmorillonite and of sodium on the calcium form of montmorillonite over a wide salinity range. In addition, we are investigating the distribution coefficients of both Ca(II) and Na(I) for mixed NaCl-CaCl₂ solutions over the whole range from 100% Na(I) to 100% Ca(II). Our technique is to equilibrate the clay with a solution of known Na:Ca ratio several times until the clay is at equilibrium with

the solution of known composition. After the clay has come to equilibrium with the solution tracer ^{45}Ca and ^{22}Na are added and the loading of the clay determined by the isotopic dilution of each tracer. The tracers are added to separate but identical samples because it is difficult to count both of these tracers simultaneously. From these data, distribution coefficients are calculated and K/I for $\text{Ca(II)}/\text{Na(I)}$ exchange is calculated for each Na:Ca ratio. The experiment is difficult, and there is often more scatter than we would like, but certain trends are becoming evident. For montmorillonite mostly in the sodium form, results for various determinations of K/I seem to be consistent and remain reasonably constant at values of from 5 to 10 for the equilibrium $K/I = m_c m_{Na}^0 / m_{Na} m_c^0$ (all concentrations expressed as moles per kilogram of either solution or clay). As the calcium end of the range is approached, results become less reproducible, and the values tend to rise. However, as one approaches 100% calcium, that is, at very low sodium levels, K/I seems to drop sharply to values considerably lower than unity. Furthermore, we have observed a pronounced loading effect of K/I on the essentially 100% calcium form of montmorillonite as shown in Fig. 3.13. Here it is shown that K/I and K/I clay [calculated taking into account the activity coefficient ratio of Ca(II) to Na(I) in aqueous chloride solutions] are quite low at extremely low loading. As loading is increased, but still at only a small fraction of capacity, the values of K/I tend to increase sharply. Loading must therefore be controlled and known precisely at the calcium end of the composition range.

Some of our results for intermediate Na:Ca ratios must be considered as tentative because we now feel

Fig. 3.13. Effect of loading on equilibrium quotients (m_c , $\Gamma_{aq}(\text{Ca}^{2+})$, $D^0\text{Na}$) of Wyoming montmorillonite predominately in the calcium form (pH 5, equilibration for 14 h)

that there may be an error due to "ion exclusion" in the solution in the gel after centrifugation. We have until now assumed that this solution (amount determined by weight difference) has the same composition as the clear supernatant above the gel. We are currently looking into the possibility that this effect may cause errors in some of our capacity determinations. These errors could affect the magnitude of the values of K/I to some extent but should not affect the overall trends discussed above.

1. Graduate student, University of Tennessee.
2. ORAU Summer Participant from Angelo State University, San Angelo, Tex., 1978.

4. High-Temperature Chemistry and Thermodynamics of Structural Materials

The primary thrust of this program has been shifted from chemistry in support of fusion reactor technology toward chemistry of structural materials at high temperatures. Initially, we will conclude the studies of hydrogen isotope-lithium equilibria and begin studies of the thermodynamics of microphases in alloys above 500°C. Studies of tritium permeation through and steam oxidation of construction materials at high temperatures have continued. Analysis of the oxidation products from the H₂O-alloy reactions has been an increased effort and will continue. Such analysis permits identification of the oxides and the corrosion reactions, in contrast to most other corrosion studies where only weight changes are measured. Materials that form hydrides at relatively low temperatures and that release hydrogen at elevated temperatures continue to be investigated as candidate materials for extraction and/or storage of hydrogen.

4.1 EQUILIBRIA IN HYDROGEN ISOTOPE-FUSION REACTOR BLANKET SYSTEMS

F. J. Smith J. F. Land
J. T. Bell

Studies of hydrogen isotopes (H, D, and T) in equilibrium with lithium at high temperatures have been completed. The concluding phase of this work involved mixtures of protium and deuterium in equilibrium with lithium in the Sieverts region between 700 and 900°C. The results have indicated that, for mixed isotopes in the Sieverts range, the partial pressures of H₂ and D₂ can be approximated closely by the independent Sieverts relationships; that is,

$$P_{H_2}^{1/2} = K_H N_{LiH} \quad (1)$$

and

$$P_{D_2}^{1/2} = K_D N_{LiD} \quad (2)$$

in which N denotes mole fraction in the liquid lithium phase. The total equilibrium pressure is the sum of the pressures for H₂, D₂, and HD. The gas-phase equilibrium constant for the formation of HD above 700°C is 3.9, and, because this constant is

nearly 4, the square root of the total pressure can be expressed as

$$P_{\text{total}}^{1/2} = P_{H_2}^{1/2} + P_{D_2}^{1/2} \quad (3)$$

or

$$P_{\text{total}} = K_H N_{LiH} + K_D N_{LiD} \quad (4)$$

Since the data obtained with H₂-D₂ mixtures obeyed the above equation and since the equilibrium constants of the formation of HI and DI are also essentially 4, we have assumed that a similar expression for an H-T or a D-T system would be valid and that the square root of the total pressure for an H-D-T system in equilibrium with lithium could be expressed as

$$P_{\text{total}}^{1/2} = K_H N_{LiH} + K_D N_{LiD} + K_T N_{LiT} \quad (5)$$

4.2 SORPTION OF HYDROGEN ISOTOPES BY METAL GETTERS

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J. F. Land F. J. Smith

Metal getters are important for extracting hydrogen isotopes from fusion reactor blankets and for

storing hydrogen in other energy systems. Such extraction or storage systems must be capable of taking hydrogen from a process matrix and later liberating that hydrogen when the systems are heated to higher temperatures. Based on data from the literature, yttrium is a candidate for sorbing hydrogen (tritium) from liquid lithium. Since the only previous data were for the yttrium-hydrogen system, we obtained corresponding data for deuterium and tritium. We have measured pressures at various temperatures in the 700–1000°C range for each of the three hydrogen isotopes in equilibrium with yttrium, using a modified Sieverts apparatus. The hydrogen isotope to yttrium ratio ranged from 0.5 to 2.0. The results are summarized as isotherms in Fig. 4.1. Each isotherm consists of three regions. In the lowest concentration range, the hydrogen pressure rapidly increases as the H:Y ratio increases. Hydrogen dissolves in the yttrium metal and forms an interstitial solid solution. The solid solution solubility is reached near the H:Y ratio of 0.5, and the equilibrium pressures remain nearly constant up to an

atom ratio of 1.0 or greater, depending on temperature. In this plateau region, two condensed phases coexist in equilibrium: the solid solution phase and a dihydride YH_2 phase. The third region begins as the H:Y ratio approaches 2.0, that is, the formation of the dihydride.

At equal atom ratios for the two systems (H:Y = D:Y), the deuterium equilibrium pressure is higher than the hydrogen pressure except at low concentrations where the differences in the two pressures are indistinguishable. However, the mole ratio (H:Y or D:Y) is a linear function of the square root of pressure for H:Y = D:Y < 0.3; that is, Sievert's law is obeyed.

Van't Hoff isopleths for the H-Y and the D-Y systems have been constructed from the equilibrium vapor pressure data. The H-Y data are shown in Fig. 4.2. From these plots partial molal enthalpies and entropies have been calculated for the reaction of

Fig. 4.1. Isotherms for the pressures of hydrogen and of deuterium in equilibrium with yttrium metal.

Fig. 4.2. Van't Hoff plots of the equilibrium hydrogen pressures for the yttrium-hydrogen system at the atom ratio H:Y = 0.7.

hydrogen or deuterium with yttrium as functions of H:Y or D:Y atom ratios. For the plateau region where H:Y = D:Y = 0.7, the calculated thermodynamic values are:

$$\Delta H_H = H_H - \frac{1}{2}H_{H_2} = -26.1 \text{ kcal g-atom of H}$$

$$\Delta H_D = H_D - \frac{1}{2}H_{D_2} = -25.4 \text{ kcal g-atom of D}$$

$$\Delta S_H = S_H - \frac{1}{2}S_{H_2} = -16.7 \text{ cal } ^\circ\text{K g-atom of H}$$

and

$$\Delta S_D = S_D - \frac{1}{2}S_{D_2} = -16.3 \text{ cal } ^\circ\text{K g-atom of H}$$

Experiments with tritium and yttrium are now in progress in a modified apparatus with smaller quantities of metal and gas. Initial data show the tritium system equilibrium pressures to be very close to the deuterium system pressures at equal atom ratios.

4.3 PERMEATION OF CONSTRUCTION MATERIALS BY HYDROGEN ISOTOPES

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J. D. Redman J. Brynestad
W. H. Christie

Measurement of tritium permeabilities of clean metals is a continuing part of this program. Arrhenius-type equations express the permeabilities DK in terms of a permeability constant or preexponential term ($(DK)_0$) and an apparent activation energy ΔE . Table 4.1 summarizes the tritium permeability data obtained for clean metals. As the repertoire of data for tritium permeability of clean

metals increases, we will correlate the permeabilities with the type and composition of material, that is, nickel base alloys, stainless steels, refractory metals, etc.

Tritium permeation rates through each of the metals listed in Table 4.1 were determined isothermally at various tritium pressures. The dependence of rate on pressure was determined to be 0.5 ± 0.05 , Table 4.1, except for the Croloy alloy where the value was 0.60. This alloy is quite sensitive to oxidation; consequently, there may have been some inadvertent surface oxidation during the measurements.

An equation of the T - P relationship, where permeation rates can be expected to deviate from the $\frac{1}{2}$ -power dependence on pressure, has been derived from considerations of molecule-to-wall collision rates and measured permeabilities. Using sticking coefficients of 0.1, the equation obtained is

$$P = 3.25(10^{-7}) \cdot (DK)_0^2 \cdot T \exp(-\frac{1}{2}\Delta E/RT) \quad (6)$$

This relationship and the data in Table 4.1 indicate that tritium permeation rates through clean construction alloys will be $\frac{1}{2}$ -power dependent on the tritium pressure down to pressures of about 10^{-10} torr at 1000°K and to about 10^{-11} torr at 500°K . The equation is not valid for temperatures greater than 1200°K because hydrogen molecules begin to dissociate at the higher temperatures.

Studies of the effects of oxidation by steam at subatmospheric pressures to form oxide films on construction materials and to reduce tritium permeation rates through those materials have continued. Compared to the clean metals, the permeation rates are significantly reduced by oxidation with steam. The results of six long-term experiments, about 5 months each, are summarized in Table 4.2. At 660°C

Table 4.1. Permeability constants $(DK)_0$ and activation energies ΔE for tritium permeabilities DK of clean metals in the 600 – 1100°K region

$DK = (DK)_0 \exp(-\Delta E/RT)$; the value of n relates to the dependence of permeation rate on pressure

Metal or alloy	$(DK)_0$ [$\text{cm}^3(\text{H}_2, \text{NTP}) \cdot \text{mm}/(\text{cm}^2 \cdot \text{min} \cdot \text{torr}^{1/2})$]	ΔE (kcal/g-atom)	n
Nickel	0.268	12.68	0.50
Incoloy 800	0.570	16.12	0.50
Santoro 31	0.367	15.61	0.55
316 SS	0.533	16.26	0.50
406 SS	0.104	12.20	0.49
Croloy, 2% molybdenum	0.0862	11.21	0.60
Sintered tungsten (3.5% Ni, 1.5% Fe)	0.00788	14.93	0.54

Table 4.2. Factors by which tritium permeation rates through Incoloy 800 were decreased by in situ steam oxidation

Sample No.	H ₂ O partial pressure	Temp (°C)	Permeation impedance factors after		
			24 d	150 d	170 d
1	0.32	660	57	167	183
2	0.70	660	60	178	192
3	0.94 ^a	520	124	319	
4	0.94	660	151	419 ^b	
5	0.94 ^a	520	35	41 ^b	
6	0.94 ^a	725	37	148 ^b	

^aSample downstream surface was mechanically buffed and electropolished. Other samples were as received.

^bExtrapolated from shorter times.

with 0.94 atm H₂O, oxide formation reduced tritium permeation by factors greater than 300. However, at 520°C the oxidation after 24 d had reduced the permeability only by a factor of 35, and there was essentially no further change after 61 d. The oxidation had almost ceased. The temperature of this sample, No. 5, was increased at 71 d to 657°C; oxidation resumed as evidenced by a decrease in permeability (Fig. 4.3). After 90 d at 657°C (147 d total) the temperature was returned to 520°C, and the permeability was a factor of 260 below the initial value at 520°C. After only a short additional time at 520°C, oxidation again had ceased (Fig. 4.3). This experiment demonstrated that the formation of surface oxides on Incoloy 800 by steam oxidation was significantly sensitive to temperature. It also indi-

Fig. 4.3. The permeability of Incoloy 800 initially oxidized at 520°C for 61 d and then at 657°C.

cated that an oxide barrier formed at a high temperature (660°C) could be an effective barrier at a lower temperature (520°C).

Oxidation at 725°C with 0.94 atm H₂O produced effects on the tritium permeability of Incoloy 800 similar to those at 660°C. However, the impedance to permeability was not as great as that at 660°C even though the oxide layer was thicker at 720°C for a shorter oxidation time. This result suggested that oxidation at the higher temperature was faster but produced an oxide that was different from that produced at 660°C. Chemical analysis of the oxides proved this to be true, as discussed in the following section.

Apparent activation energies ΔE for tritium permeation were determined for Incoloy 800 samples that had surface oxide coatings produced at three different temperatures (Table 4.3). The ΔE values for the samples oxidized at 520 or at 660°C were essentially equal, 15 kcal/g atom; however, the value was 20.5 kcal/mol for the sample oxidized at 725°C. This higher value for ΔE could be a reflection of the differences in the chemical nature of the oxide coating formed at the higher temperature but could also be a function of the increased rate of oxidation.

Table 4.3. Apparent activation energies for tritium permeation through oxide-coated Incoloy 800

The oxide coatings were formed by in situ reaction with 0.94 atm H₂O at three separate temperatures

Temperature at which oxide coating was formed (°C)	Oxidation time (d)	ΔE (kcal/g atom)
520	75	15.8
520	221 ^a	14.5
660	77 ^b	15.4
720	77	20.5

^aOxidation between 75 and 147 d was at 660°C.

^bAn independent experiment in another apparatus.

An experimental system for measuring tritium permeation through steam generator materials is being constructed under the Magnetic Fusion Energy Program. This system will involve use of steam at pressures up to 100 atm. This system will be described in detail in the programmatic reports.

4.4 STEAM OXIDATION OF INCOLOY 800

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J. T. Bell J. D. Redman
J. F. Land W. H. Christie

The oxidation of Incoloy 800 by H_2O at high temperatures results in oxide coatings that significantly reduce the tritium permeability of the alloy (cf. Sect. 4.3). The chemistry of such oxides formed in situ varies with temperature and with the redox potential of the medium, that is, the $H_2O:H_2$ ratio. Most oxidation studies involve only measurement of weight changes; however, we are attempting to identify the actual oxides formed under various redox conditions. Two kinds of Incoloy 800 samples with oxide coatings have been analyzed by ion microprobe, x-ray diffraction, and optical microscopy. The tube samples from the permeation experiments had oxide coatings on the inside, and the curved surface was a hindrance in the analysis. These oxides were formed in long-term experiments. Hence, the second type of samples we used were tab samples that were oxidized for shorter times but under conditions identical to those in the permeation experiments.

4.4.1 Permeation Tube Samples

Oxide coatings formed in situ on Incoloy 800 duplex tubes in tritium permeation experiments were generally enriched in chromium and manganese and depleted in iron and nickel. In the bare metal below the oxide, there was a corresponding depletion of chromium and enrichment of iron and nickel. Figure 4.4 shows the ion microprobe profile for a duplex tube exposed 129 d at $660^\circ C$ to 0.94 atm steam. Although some permeation experiments were performed with tubes that were milled and electropolished prior to steam exposure and some with tubes as received, only minor differences were found in the oxides produced after the long exposure times of permeation experiments. However, the oxide formed at $720^\circ C$ had a much higher percentage of manganese oxide than the oxides formed at lower temperatures.

To characterize the oxides formed at shorter exposure times, quarter sections of duplex tubes were oxidized in an environment similar to that of the permeation experiments. Oxides formed on tubes exposed in the as-received state were similar to those found on the permeation tubes. However, quarter sections that were milled and electropolished yielded, after 31- and 144-h exposures, thicker oxides consisting primarily of iron (up to 99 at. %). After a 28-d

Fig. 4.4. Elemental composition of the metals in the oxides formed by the steam oxidation of Incoloy 800 at a duplex tube.

exposure the iron spalled off, leaving an oxide rich in chromium and manganese. The effect of precleaning by mechanical buffing and electropolishing definitely changed the oxides produced at short times; that is, the electropolished Incoloy 800 surface initially yielded iron oxides that apparently spalled off the surface at longer times with the formation of chromium and manganese oxides.

4.4.2 Tab Samples

Samples were subjected to a variety of pretreatment sequences: some were buffed and electropolished, some were subsequently vacuum annealed (1 h at $900^\circ C$), and some were then cold rolled 20%. Then the samples were oxidized with 0.94 atm H_2O at $660^\circ C$ for various times.

Electropolished tabs after short exposure times yielded oxides rich in iron analogous to electropolished duplex tubes. Unlike the duplex tubes, however, the iron-type oxide persisted at long exposure times on electropolished tabs, as shown in Fig. 4.5. It was found, however, that vacuum annealed electropolished tabs behaved similarly to the duplex tubes; that is, short exposure times produced an iron-type oxide, while longer exposure

Fig. 4.3. Elemental composition of the oxide formed by the steam oxidation of Incoloy 800 as an electropolished tab.

yielded an oxide rich in chromium and manganese. These results indicated that the electropolished material initially forms iron oxides and that annealing the electropolished material decreased the preferential oxidation of iron. Since annealing generally is associated with the effects of cold working an alloy, some samples were cold rolled 20% after they had been electropolished and annealed. Those samples produced oxides similar to those on both the electropolished and the annealed tabs; that is, the oxides were rich in iron, chromium, and manganese. It is anticipated that samples further cold worked would yield an oxide more like those on the electropolished tabs. At this point one concludes that the 660°C, 0.94 atm H₂O oxidation of electropolished or cold worked Incoloy 800 initially will produce iron oxides and that the preferential iron oxidation will diminish with time as chromium and manganese oxides are formed. Furthermore, oxidation of annealed Incoloy 800 under the same conditions will produce much less iron oxide and will produce chromium and manganese oxides at shorter times.

X-ray diffraction analysis of the various oxides showed the composition of the oxides to agree with the above conclusions. The outer layer of iron-type oxides consisted primarily of Fe₂O₃ and Fe₃O₄, and the inner layer was a spinel structure with a lattice

constant consistent with FeCr₂O₄. The chromium-type oxides were primarily hexagonal Cr₂O₃ and a spinel (cubic) close in stoichiometry to MnCr₂O₄. However, in some cases the hexagonal phase contained up to 15% Fe₂O₃, and the lattice constant of some spinel phases suggested partial substitution of nickel for manganese and chromium. These spinel structures undoubtedly contained small amounts of other cations, including aluminum, silicon, and titanium, as these species were available and are soluble in spinel phases.

Although kinetics plays an important role in oxide formation as evidenced by the apparent cation migration in these samples, the morphology of the oxides may be described in some detail on a thermodynamic basis. In Table 4.4 are presented free energies of formation of oxides considered most likely to form. Comparison of values for Fe₂O₃, Fe₃O₄, and FeCr₂O₄ and the morphology of the iron-type oxide found on electropolished tabs suggests a trend of oxide stability with location in the oxide; that is, more stable oxides form at greater depths in the oxide. This trend appears also in the case of duplex tubes: positions of peaks in Fig. 4.4 of aluminum, silicon, titanium, and manganese are in order with stabilities of their binary oxides shown in Table 4.4, with the exception of titanium. It may be

Table 4.4. Free energy of formation of oxides expected from Incoloy 800

Oxide	ΔG^0 (kcal/mol O ₂ at 900 K)	Reference
SiO ₂	74.5	a
Fe ₂ O ₃	93.5	a
Fe ₃ O ₄	98.5	a
Mn ₂ O ₃	115.8	a
Mn ₂ O ₄	127.8	b, c
FeCr ₂ O ₄	133.4	a
Cr ₂ O ₃	143.5	b, c
MnCr ₂ O ₄	148.6	b, c
SnO ₂	171.0	a
Ti ₂ O ₃	201.9	a
Al ₂ O ₃	221.5	a

a) J. P. Coughlin, *Contributions to the Data on Theoretical Metallurgy. XII. Heats and Free Energies of Formation of Inorganic Oxides*, Bureau of Mines Bulletin 542, U.S. Department of the Interior, Washington, D.C. (1954).

b) O. Kubaschewski, I. L. Evans, C. B. Alcock, *Metallurgical Thermochemistry*, 4th ed., Pergamon, Oxford, 1967.

c) O. Kubaschewski, *The Thermodynamic Properties of Double Oxides*, NPL-DCS-7, National Physical Laboratory, Division of Chemical Standards, Teddington, Middlesex, England (November 1970).

that titanium forms an off-stoichiometric oxide or a ternary oxide not considered here. In line with this trend, $MnCr_2O_4$ would form at greater depths than Cr_2O_3 ; according to Table 4.4, then, the peak in manganese at the surface, as shown in Fig. 4.4, would correspond to a binary oxide of manganese. Evidence of this was seen by x-ray diffraction in the case of the duplex tube exposed at 720°C.

The trend of location of oxide with stability is in accord with a model based on anion diffusion. The profile of oxygen concentration from the steam interface to bulk metal drops exponentially; hence, at greater depths in regions of low oxygen activity, more stable oxides are favored. Initial formation of iron rather than chromium oxide on the surface of electropolished duplex tubes is favored according to this model. It is well known that chromium oxide acts as a protective barrier to further oxidation; hence, once this oxide forms beneath the spalling iron oxide, the driving force for further iron diffusion halts, leaving a protective chromium-type oxide. The reason for persistence of the iron-type oxide on unannealed electropolished tabs is currently under investigation.

4.5 METASTABLE PHASES AND THERMODYNAMICS OF ALLOYS ABOVE 500°C

J. Brynestad H. F. Batner
J. L. Bell

The lifetimes of structural alloys are known to rapidly decrease at temperatures above 500°C. Austenitic steels (those with solid solutions of carbon) are stable at lower temperatures for long periods, but, at higher temperatures, the physical properties deteriorate, and the simultaneous formation of various carbide and nitride precipitates have been observed. The formation of these precipitates and the degradation of structural properties are directly related, but the relationship is not defined. Knowledge of the nature of the precipitates, of the thermodynamics and kinetics for precipitate formation, and of the influence on structural properties can lead to the development of high-temperature structural alloys with long lifetimes.

A Differential Thermal Effluent Gas Analysis System is being assembled for the identification and quantitative analysis of carbides, nitrides, and carbonitrides that are known to precipitate in steels (such as 2-1/4Cr-1Mo) at temperatures above 500°C for periods of months and years. Furnace systems for the preparation of well-defined alloys and instrumentation for high-precision quantitative analysis of carbon (in alloys and precipitates) will be acquired. This effort is associated closely with related work in the Metals and Ceramics Division.

1. Analytical Chemistry Division
2. G. C. Wood, *Corros. Sci.* 2, 173 (1961)

5. Chemistry of Transuranium Elements and Compounds

5.1 DOES Md(I) EXIST IN AQUEOUS SOLUTION?

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The chemical properties of mendelevium (element 101) are, for the most part, still unknown, and no direct measurements of its electrochemical properties have been published. The most stable oxidation state of mendelevium in aqueous solution is the trivalent state. Hulet et al.³ showed that mendelevium could easily be reduced to the divalent state in aqueous solution with a reduction potential⁴ E° of -0.2 V, while E° for the $\text{Md}^{3+}/\text{Md}^{2+}$ couple has been estimated from systematics⁵ as -1.66 V. By using data from cocrystallization experiments, Mikheev et al.⁶ claimed that a stable, monovalent, cesium-like ion of mendelevium could exist in ethanolic and aqueous solutions. The existence of such a monovalent oxidation state would be unique, for either lanthanide or actinide ions, and would imply that the half-wave potential for the reduction $\text{Md}^{3+} \rightarrow \text{Md}(\text{Hg})$ must be at least as negative as -3.6 V. Such a potential is in contradiction with the experimental fact that sodium amalgam reduces mendelevium to the amalgam.

The purpose of the present work was to obtain the first quantitative information on the electrochemical properties of mendelevium and then to evaluate the possible existence of monovalent mendelevium in aqueous solution. Experiments were undertaken to study the overall mechanism of reduction of Md^{3+} to the amalgam, using controlled-potential electrolysis. To deduce the oxidation states of mendelevium, the shift in the half-wave potential with the degree of complexation expected for the monovalent, divalent, and trivalent actinides was used.

Samples of 77-min ^{258}Md containing about 2×10^4 atoms were prepared by the $(\alpha, 2n)$ reaction on a 0.1-

μg target of ^{252}Es at the Oak Ridge Isochronous Cyclotron. Half-wave amalgamation potentials were measured by radiocoulometry in weak (acetate) and strong (citrate) complexing agents. The measured half-wave potentials vs the normal hydrogen electrode were -1.49 ± 0.01 V in acetate and -1.60 ± 0.01 V in citrate solutions. The results showed that the reduction of mendelevium was analogous to that of fermium, which has been shown to occur in two steps, $3^+ \rightarrow 2^+$ and $2^+ \rightarrow 0$. The half-wave potentials observed for mendelevium are believed to be characteristic of the reduction $2^+ \rightarrow 0$. Further, the shift in the half-wave potential of mendelevium caused by a strong complexing agent is too large to be explained by reduction of a cesium-like monovalent ion.

Although these experiments yielded no support for the view that monovalent mendelevium can exist in aqueous solution as a cesium-like ion, it is useful to consider whether or not Md(I) might have the properties of Ag^+ or Cu^+ ions. Experiments now in progress at Lawrence Berkeley Laboratory are designed to determine quantitatively the number of electrons involved in the observed current-potential wave and whether or not, like Ag^+ and Cu^+ ions, mendelevium tends to form strong complexes with Cl^- ions.

1. Institut de Physique Nucléaire, Orsay, France.

2. Supported by DOE contract EY-76-S-05-4447 with the University of Tennessee, Knoxville.

3. F. K. Hulet, R. W. Loughhead, J. D. Brady, R. E. Stone, and M. S. Coops, *Science* **158**, 468 (1967).

4. All potentials herein are referenced to the normal hydrogen electrode.

5. F. David, K. Samhoun, R. Guillaumont, and N. Edelstein, *J. Inorg. Nucl. Chem.* **40**, 69 (1978).

6. N. B. Mikheev, V. I. Spitsyn, A. N. Kamenskaya, I. A. Rumer, B. A. Gvozdev, N. A. Rozenkevitch, and I. N. Auerman, *Dokl. Akad. Nauk. SSSR* **208**(5), 1146 (1973).

Fig. 5.1. Absorption spectra of californium bromides.

Cf(II) absorption occurs most characteristically at $11.0 \times 10^4 \text{ m}^{-1}$. The x-ray data for both the Cf_2GdCl_7 and Cf_2GdB_7 compounds are given in Table 5.1, where they are compared with corresponding lanthanide compounds. Evidence for mixed-valence compounds with pure einsteinium is limited and consists of observing via spectrophotometry only Es(II) in (Es,La) and (Es,Gd) halide mixtures after hydrogen reduction. Attempts to obtain x-ray data on the einsteinium products were unsuccessful due to the rapid degradation of their crystal lattices by self-irradiation.

Table 5.1. Mixed valence halide compounds

Compound	Lattice dimension			
	a_0 (Å)	b_0 (Å)	c_0 (Å)	2θ
$\text{Cf}_2\text{GdCl}_7^d$	7.139	34.83	6.685	90.24
Dy_2Cl_7^b	7.110	34.68	6.634	90.23
Ho_2Cl_7^b	7.078	34.57	6.603	90.19
$\text{Cf}_2\text{GdB}_7^d$	7.619	36.97	7.040	90.18
$\text{Sm}_2\text{B}_7^{c,h}$	7.652	37.21	7.121	90.26

^dR. G. Hare, J. P. Young, J. R. Peterson, and R. L. Fellows, p. 501 in *The Rare Earths in Modern Science*, G. L. McGarthy and L. J. Rhyne, eds., Plenum, New York (1978).

^bH. Borchhausen, p. 404 in *Proc. 12th Rare Earth Res. Conf.*, Denver Research Institute, Vail, Colo., July 1976.

^cJ. M. Haschke, *Inorg. Chem.* 15, 298 (1976).

5.2.2 Tetravalent Fluorides of the Transplutonium Elements

The tetravalent state of the transplutonium elements through californium is well established. In contrast, of the corresponding electronic homologs in the lanthanide series, only terbium exhibits an oxidation state of (IV). Recently, efforts have been made to obtain solid state absorption spectra of the tetrafluorides and also to resolve some questions on the lattice parameters of these compounds. In addition, experiments have been carried out to see if EsF_4 could be prepared; to date, an oxidation state of (IV) has not been reported for einsteinium, although its III-IV oxidation potential is expected to fall between that of terbium and dysprosium.

The tetrafluorides of ^{244}Cm , ^{247}Bk , and ^{252}Cf have been prepared by treatment of the respective anhydrous trifluorides with chlorine trifluoride or fluorine at elevated temperatures. Good absorption spectra of these tetrafluorides have been obtained,

but the crystallinity of these preparations has not been sufficient to obtain high-quality x-ray diffraction films. The problem of crystallinity is due in part to the relatively low temperatures required to avoid thermal decomposition of the tetrafluorides.

The trifluorides of ^{244}Cm , ^{247}Bk , and ^{252}Cf have been prepared and characterized by both absorption spectrophotometry and x-ray diffraction. A special effort was made to characterize BkF_3 in the two crystallographic forms that have been reported.²

To date, experiments designed to yield the tetrafluoride of einsteinium have not been successful, although absorption spectra of einsteinium trifluoride have been obtained. Attempts to obtain x-ray data from any of the einsteinium products have not yielded useful data, due to the degradation of the sample's crystallinity by the intense self-irradiation. The self-irradiation may also be a factor in the preparation (or maintenance) of a tetrafluoride of einsteinium. Some unsuccessful attempts have also been made to oxidize alkali-metal fluoride salts containing einsteinium with the hope that Es(IV) may be stabilized under these conditions. Future efforts on preparing Es(IV) will emphasize this latter approach.

5.2.3 Divalent Halides of the Transplutonium Elements

The divalent states of californium and einsteinium have been prepared by reducing their trihalides with hydrogen at elevated temperatures. The products have been examined by absorption spectrophotometry and x-ray diffraction. The most recent californium dihalide to be prepared was CfCl_2 (ref. 6,12). In accord with the increasing stability of divalency in going across the actinide series (i.e., from Cf to Es), it has also been possible to prepare the anhydrous Es(II) chloride, bromide, and iodide. These compounds have been characterized primarily by their absorption spectra because the rapid crystal degradation from the self-irradiation of ^{252}Es has prevented the collection of sufficient x-ray data. Absorption spectra of EsI_2 , EsBr_2 , EsCl_2 , and EsBr_2 (for comparison) are shown in Fig. 5.2. The most recent Es(II) compound to be prepared was EsCl_2 (ref. 13), which is also the most difficult dihalide to prepare, with the possible exception of the difluoride. In general, the ease of reduction to the dihalide follows the order triiodide > tribromide > trichloride. The most intense absorption band of EsCl_2 occurs at $24.5 \times 10^4 \text{ m}^{-1}$ (not shown in Fig. 5.1), followed by bands

Fig. 5.2. Absorption spectra of einsteinium dihalides.

at 18.5 and $11.1 \times 10^3 \text{ m}^{-1}$. The strong absorption of Es(III) at $12.7 \times 10^3 \text{ m}^{-1}$ can be readily used to monitor the presence of any Es(III) in a preparation of Es(II) halide.

Future work on the dihalides will be aimed at preparing dihalides of berkelium and possibly americium. Absorption spectra of divalent berkelium halides are critically needed to fully interpret data from the parent-daughter-granddaughter studies on Es , Bk , and Cf preparations (Sect. 5.2.4). It was expected that molecular hydrogen was not capable of

reducing the trihalides of berkelium, and a few scouting experiments have confirmed this contention. Thus future attempts to prepare the dihalides of berkelium will use berkelium metal as the reductant of Bk(III) halides, for example, $\text{Bk} + 2\text{BkBr}_3 \rightarrow 3\text{BkBr}_2$.

5.2.4 Chemical and Structural Consequences of α Decay in Es , Bk , and Cf Halides

The chemical and structural consequences of α and/or β decay are being investigated with ^{253}Es and ^{247}Bk halides. These studies extend beyond the effects of such radiation to the parent compound and are concerned with characterization of daughter-granddaughter products as well. For example, consider the radioactive decay process:

If an einsteinium dihalide is prepared, the question that arises is what will be the oxidation states of the berkelium daughter and the californium granddaughter? The existence of a berkelium dihalide as a bulk phase is unknown. Numerous trihalides and dihalides of einsteinium and trihalides of berkelium have been prepared and are being stored under varying conditions of atmosphere, crystal structure, and temperature to answer this question as well as related questions involving the transfer of "heredity" during transmutation. The initial results from this on-going study have been reported¹⁴ and show that in the above-mentioned case of einsteinium dihalides, the granddaughters are the californium dihalides under our storage conditions (retention of the grandparent's oxidation state). The absorption spectra of these samples do not indicate "new" absorption peaks that can be attributed to Bk(II) . Future plans include the preparation of bulk phase berkelium dihalides to obtain standard spectra for Bk(II) (Sect. 5.2.3).

In another study, it was found that the orthorhombic form of BkBr_3 generated the daughter CfBr_3 , which retained the crystal structure of its parent. This new form of CfBr_3 has been characterized by both x-ray diffraction and absorption spectroscopy. When preparing CfBr_3 from pure californium oxide, it has not been possible to obtain this orthorhombic, 8-coordinate form; the compound normally exists in a monoclinic, 6-coordinate form.

These and other studies on parent-daughter-grand-daughter relationships are continuing.

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5. Analytical Chemistry Division.
6. *Chem. Div. Annu. Prog. Rep. Mar. 31, 1977*, ORNL-5297 (September 1977).
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8. H. Barnighausen, p. 404 in *Proc. 12th Rare Earth Res. Conf.*, Denver Research Institute, Vail, Colo., July 1976.
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13. R. L. Fellows, J. R. Peterson, J. P. Young, and R. G. Haire, p. 493 in *The Rare Earths in Modern Science and Technology*, G. McCarthy and J. J. Rhyne, eds., Plenum, New York, 1978.
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5.3 PREPARATION OF TRANSPLUTONIUM METALS¹

D. A. Damien² R. G. Haire³
J. R. Peterson⁴

Methods have been developed to prepare and analyze microgram and submicrogram quantities of the actinide metals, and recently they have been modified to yield milligram amounts of the transplutonium metals. Although it would be desirable to prepare even larger amounts of these metals (~100 mg) in a single preparation, the limited availability and the radiation levels that would be encountered prohibit the preparation of such quantities.

Two preparative methods have been used for making the transplutonium metals: (1) reduction of the actinide trifluoride with lithium metal vapor, followed by distillation of the excess lithium and lithium fluoride by-product to leave bulk actinide

metal and (2) reduction of the actinide oxide with lanthanum or thorium metal followed by distillation of the actinide metal. The first procedure is used for the less volatile actinide metals (Cm, Bk) whereas the second method has been used for the more volatile Am, Cf, and Es. During this report period, five transplutonium metals have been prepared, with the total quantities from multiple preparations being as follows: ²⁴³Am, ~100 mg; ²⁴⁴Cm, ~10 mg; ²⁴⁷Bk, ~5 mg; ²⁴⁹Cf, ~5 mg; and ²⁵²Es, ~30 µg. These metals were used for several different chemical and physical studies, some of which are described in subsequent sections, in addition to physical property measurements (crystal structure, melting point, etc.) of the metals themselves. Recently, electron diffraction patterns have been obtained from einsteinium metal which indicate that the metal is divalent.⁴ From the work on ²⁴⁴Cm metal, an fcc phase (high temperature form) was prepared that had an average room-temperature lattice parameter of $a_0 = 5.072(7)$ Å. This value is higher than previously reported for the fcc form of ²⁴⁴Cm metal [$a_0 = 5.039(2)$ Å] (ref. 5), which was disturbingly similar to the lattice parameter of CmN ($a_0 = 5.027$) (ref. 6). Additional work is planned on these metals to characterize them more completely.

1. Supported in part by DOE contract FY-76-S-05-4447 with the University of Tennessee, Knoxville.
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3. Department of Chemistry, University of Tennessee, Knoxville.
4. R. G. Haire and R. D. Bayburt, "Studies of Einsteinium Metal," *Proc. 3rd Internat. Conf. Electronic Structure of the Actinides*, Grenoble, France, Aug. 28-Sept. 2, 1978, to be published in *J. Phys. (Paris)*.
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5.4 OBSERVATION OF SUPERCONDUCTIVITY IN AMERICIUM METAL¹

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The recent availability of pure ²⁴¹Am metal, longer lived isotope, $t_{1/2} = 8 \times 10^4$ years) permitted low-

temperature physical measurements to be made on this element. Previously, resistivity measurements on ^{241}Am had been made down to 2 K, but no evidence for superconductivity was obtained.^{1,2} The use of the ^{243}Am isotope, as opposed to the ^{241}Am species, reduced the heat generated from radioactive transitions (6.3 vs 115 mW/g) and made the cooling problems less severe.

Recently, collaborative experiments with the Los Alamos Scientific Laboratory on ^{243}Am metal showed that it becomes superconducting at temperatures as high as 1.05 K (ref. 5). Five different metal preparations were used in these experiments, and spark-source mass spectrographic analyses showed that the total impurities (excluding hydrogen, nitrogen, and oxygen, which could not be determined due to the small samples available) ranged from 50 to 240 ppm. Samples of single phase, double-hexagonal, close-packed americium showed onsets of superconductivity between 0.79 and 0.55 K; the face-center cubic phase showed superconductivity at slightly higher temperatures. The superconductivity was detected by two different systems: (1) a ^4He cryostat in which the sample resided within one coil that formed part of an ac bridge and (2) a ^4He - ^3He dilution refrigerator from which the ac susceptibility of a sample coil was extracted via a lock-in amplifier.

Superconductivity in americium metal is not magnetically quenched due to its unique f electronic configuration, which produces a null magnetic moment by either Hund's rules or $j-j$ coupling. Likewise, lanthanum metal with no localized f electrons, and hence a null magnetic moment, is also a superconductor. However, a high density of states near the Fermi level, as produced by bound or nearly bound f electrons, can play a beneficial role for the onset of superconductivity. Note, for example, that other trivalent elements, Sc, Y (IIIB group), and Lu, are not superconductors.

Measurement of the critical field H_c and the electronic heat capacity coefficient γ of ^{243}Am metal has also been made.¹ A value of $2 \pm 2 \text{ mJ mol}^{-1} \text{K}^{-2}$ was obtained for γ . The critical field $H_c(0)$ was determined to be $\sim 500 \text{ Oe}$. We hope these results with americium metal will provide additional insight into understanding superconductivity in the $4f$ and $5f$ metals.

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5.5 HEATS OF VAPORIZATION OF AMERICIUM AND CALIFORNIUM METALS¹

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P. D. Kleinschmidt²

As greater quantities of the transplutonium isotopes become available, more sophisticated measurements on these materials are possible. Of special interest and importance are thermodynamic data, which can be used for understanding and comparing the chemistry of these elements. Recently, vapor-pressure measurements were made on ^{243}Am and ^{249}Cf metals, using the Knudsen effusion technique. From these data, heats of sublimation of the metals can be calculated.

The vapor pressure of americium metal had been previously measured, using the effusion-target technique and ^{241}Am (ref. 3). Due to the higher specific activity of this isotope, those data were limited to measurement of the pressure over the solid state of the metal. By using ^{243}Am metal, it was possible to extend the pressure measurements through melting and to collect data over the liquid phase. The heat of vaporization of Americium over molten ^{243}Am metal is very close to the values extrapolated from data for solid ^{243}Am metal, being 60 kcal/mol vs 65 kcal/mol respectively. Both values are characteristic of a trivalent metal.

The vapor pressure of ^{249}Cf metal has also been measured over the temperature range 500–750°C (ref. 4). At higher temperatures, the vapor pressure becomes too high for this effusion technique, even when using very small cell orifices. The vaporization of californium metal is described by the equation:

$$\log_{10} P(\text{atm}) = -(9895 \pm 34) / T + (5.675 \pm 0.039),$$

from which the heat of vaporization is calculated to be $46.9 \pm 0.3 \text{ kcal/mol}$. These data show that californium metal was trivalent over the temperature

1. Supported in part by DOE contract W-7405-eng-36 with the Los Alamos Scientific Laboratory, Los Alamos, N.M.

2. Los Alamos Scientific Laboratory, Los Alamos, N.M.

range studied, which is below the supposed trivalent-trivalent transition at $>800^{\circ}\text{C}$. The californium metal used in these experiments was initially trivalent, *dhcp* form, as determined by x-ray diffraction. Further, from the simultaneous mass spectrometer measurements, no evidence for CfO was found. Finally, californium metal has a very high volatility (usually indicative of divalency); over the temperature range studied, it is slightly more volatile than samarium metal (trivalent) but slightly less volatile than europium metal (divalent).

1. Supported in part by DOE contract W-7405-eng-36 with the Los Alamos Scientific Laboratory, Los Alamos, N.M.

2. Los Alamos Scientific Laboratory, Los Alamos, N.M.

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5.6 HEAT OF SOLUTION OF MICROGRAM QUANTITIES OF CURIUM METAL¹

D. L. Raschella² J. R. Peterson

The solution microcalorimeter, described in part in ref. 4, has been modified extensively and is reported in detail in ref. 5. The facility is operated under isoperibol conditions. The microcalorimeter is constructed of tantalum metal with a nominal volume of 5 cm³. Its energy equivalent is 24 J K⁻¹ when containing 5 cm³ H₂O. The thermal leakage modulus is 0.010 min⁻¹. A thermistor is employed as the temperature sensor. The operating sensitivity is about 1×10^{-4} K ($300 \mu\text{J}$).

A novel sample container was developed. It is fabricated from Pyrex, and its basic design is a barrel shape with thin glass membranes sealed across the two open ends of the container. Sample containers were subjected to extensive leak tests with no leaks being found in the seals or membranes. The chemical reaction is initiated by puncturing the membranes with a sharp wire.

The performance of the calorimetry system was tested by measuring the heat of solution of NBS Standard Reference Material 724a, which is tris(hydroxymethyl)aminomethane (TRIS), and magnesium metal. The results of the TRIS experiments at a concentration of 1 g dm⁻³ in 1 N HCl at 298 K yielded an average ($N = 5$) heat of solution of

$-29.606 \pm 0.063 \text{ kJ mol}^{-1}$. The literature values³ for the heat of solution of TRIS at the 1 g dm⁻³ concentration level vary by 0.3% and are slightly higher than the results obtained with the tantalum microcalorimeter. A possible explanation for our lower results is that part of a sample was trapped inside the sample container by air bubbles and thus did not contact the HCl solution. The magnesium experiments in 1 N HCl at 298 K gave an average ($N = 7$) heat of solution of $-465.965 \pm 1.14 \text{ kJ mol}^{-1}$, as compared with the 35-year-old literature value⁴ of $-465.483 \pm 0.171 \text{ kJ mol}^{-1}$. The results of these experiments demonstrate that the (present) sample containment and stirring configuration are especially appropriate for experiments with metals and somewhat less suitable for powdered samples.

The availability of some curium-248 metal, which was originally intended for use in the synthesis of curium pnictides and chalcogenides, permitted experiments with an actinide. It is important to note that this metal was not primarily intended for calorimetry; therefore, the additional steps and

Table 5.2. Data for the heat of solution of curium metal in 1 N HCl at 298 K

Investigator	$\Delta H_{\text{solution}}$ (kJ mol ⁻¹)
Bansal ^a	585.3 ± 4.2
Wallmann ^b	586.6 ± 4.2
Morss ^c	$590.4 \pm 5.9^{d,e}$
Morss ^c	$602.5 \pm 12.1^{d,f}$
Fuger ^g	614.5 ± 4.5
Raschella ^h	606.4 ± 1.8

^aB. M. Bansal, Ph.D. dissertation, University of California Lawrence Radiation Laboratory Report UCRL-16782, The University of California, Berkeley, 1966.

^bJ. C. Wallmann, J. Fuger, H. Haug, S. A. Marel, and B. M. Bansal, *J. Inorg. Nucl. Chem.* 29, 2097 (1967).

^cL. R. Morss, Ph.D. dissertation, University of California Lawrence Radiation Laboratory Report UCRL-19851, The University of California, Berkeley, 1969.

^dCritical evaluation of all data up to and including 1969.

^eHeat of solution based on the weights of the samples.

^fHeat of solution based on radioassays of the samples.

^gJ. Fuger, J. Reul, and W. Mulier, *Inorg. Nucl. Chem. Lett.* 11, 265 (1975).

^hThis work.

precautions necessary to produce high-quality, homogeneous material were not taken in all of the sample preparations. The results of the experiments performed to date in 1 N HCl at 298.1 ± 0.1 K is a "best" value of -606.4 ± 1.8 kJ mol⁻¹ for the heat of solution of curium metal. Sample sizes have ranged between 22 and 534 μ g. Additionally, a single measurement with 6 N HCl as the solvent yielded a heat of solution of -602.3 kJ mol⁻¹ for a sample weighing 110.40 μ g. The present value is compared in Table 5.2 with existing data for the heat of solution of curium metal under similar conditions (the isotope used in the other experiments cited was curium-244).

The heat of formation of Cm³⁺ was determined by extrapolating the heat of solution obtained in 1 N HCl and in 6 N HCl to zero acid concentration. This extrapolation yields a value of -607.2 ± 2.5 kJ mol⁻¹ for the heat of formation of Cm³⁺.

5.7 CHALCOGENIDES AND PnictIDES OF THE TRANSPLUTONIUM ELEMENTS¹

D. A. Damsen² R. G. Haire
J. R. Peterson³

Several pnictides (group V) and chalcogenides (group VI) of ²⁴³Am, ²⁴⁷Cm, ²⁴⁹Bk, and ²⁴⁹Cf have recently been prepared. These materials are of interest because of their special chemical and physical properties. For example, certain pairs can be chosen for study (i.e., selenium-arsenic, tellurium-antimony, etc.) which form compounds that have very similar interatomic distances but involve a modification of the bonding; chalcogens are generally dinegative, whereas pnictogens are considered trinegative in bonding. These compounds also exhibit a variety of physical properties, being semiconductors, conductors, and possibly even superconductors.

The chalcogenides and pnictides of the transplutonium elements were prepared by direct reaction of the actinide metals with the chalcogen or pnictogen element at elevated temperatures. Higher chalcogenides (i.e., MTe₂) were obtained by reacting the actinide metal with an excess of the chalcogen. Chalcogenides of lower stoichiometries (i.e., MTe, M₂Te) were prepared by thermal decomposition of the higher ones. Only the monopnictides of the transplutonium elements were formed by this preparative technique.

Previously unreported trichalcogenides, dichalcogenides, and sesquichalcogenides of berkelium and californium have been prepared and characterized by x-ray diffraction (Table 5.3). Lattice parameters are given in ref. 4. These materials have been shown to be isostructural with the corresponding lanthanide compounds.

Attempts to prepare monochalcogenides of the transcurium elements were not successful, usually

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4. *Chem. Div. Annu. Prog. Rep. Vol. 1*, 1975, ORNL-5111, p. 42.

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Table 5.3. Chalcogenides of ²⁴⁹Bk and ²⁴⁹Cf

(Cf, Bk)Te ₄	(Cf, Bk)Te ₂	ε Bk ₂ Te ₃
	(Cf, Bk)Se ₂	η Bk ₂ Se ₃
		γ Bk ₂ Se ₃
	(Cf, Bk)S ₂	α Bk ₂ S ₃
		γ Cf ₂ S ₃
		γ Bk ₂ S ₃

yielding chalcogenide mixtures of higher stoichiometries. The difficulty stemmed from controlling the exact stoichiometry (weighing, volatility losses, etc.) of reactants with μg quantities. However, the fcc monosulfide ($a_0 = 5.575 \text{ \AA}$), the monoselenide ($a_0 = 5.791 \text{ \AA}$), and the monotelluride ($a_0 = 6.150 \text{ \AA}$) of ^{248}Cm phases were obtained by using larger quantities of curium metal and chalcogenide.

The mononictides that have been prepared are listed in Table 5.4 along with their room-temperature

Table 5.4. Pnictides of Cm, Bk, and Cf

	N	P	As	Sb
$^{248}\text{Cm}^a$	5.027			
$^{248}\text{Cm}^b$	5.027	5.743	5.887	6.243
$^{248}\text{Cm}^c$	5.041	5.72	5.901	6.248
$^{249}\text{Bk}^a$	5.010			
$^{249}\text{Bk}^b$	4.95	5.669	5.833	6.192
$^{249}\text{Cf}^b$			5.809	6.165

^aD. A. Damien, R. G. Haire, and J. R. Peterson, "Chalcogenides and Pnictides of the Transplutonium Elements," *Proc. 3rd Internat. Conf. Electronic Structure of the Actinides, Grenoble, France, Aug. 28 Sept. 2, 1978*, to be published in *J. Phys. (Paris)*.

^bThis work.

^cJ. N. Stevenson, Ph.D. thesis, University of Tennessee, Knoxville, 1973.

fcc lattice parameters.^{4,6} Also included are values previously reported for some of these compounds. Additional work on BkN is needed to resolve the discrepancy in its observed lattice parameters. The parameters listed are consistent with the expected trends of larger parameters for a heavier pnictide and smaller parameters for the heavier actinide element (actinide contraction). Self-irradiation effects are likely responsible for the differences between the ^{248}Cm and ^{244}Cm pnictides.

1. Supported in part by DOE contract EY-76-S-05-4447 with the University of Tennessee, Knoxville.

Fig. 5.3. Stereoscopic view of the structure of $\text{AmTe}_{1.11}$.

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4. D. A. Damien, R. G. Haire, and J. R. Peterson, "Chalcogenides and Pnictides of the Transplutonium Elements," *Proc. 3rd Internat. Conf. Electronic Structure of the Actinides, Grenoble, France, Aug. 28 Sept. 2, 1978*, to be published in *J. Phys. (Paris)*.

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5.8 CRYSTAL STRUCTURE AND SUBSTOICHIOMETRY OF AMERICIUM DITELLURIDE

J. H. Burns D. Damien¹
R. G. Haire

A refinement of the crystal structure of americium ditelluride, AmTe_2 , was carried out because it typifies the whole series of transuranic compounds from NpTe_2 to $(\text{Bk,Cf})\text{Te}_2$, which have been prepared in recent years.² The variable amount of tellurium in the compounds and the apparent presence of two types of bonding make them interesting intermediates between metals and insulators. One detailed analysis of this structure type (anti- Fe_2As) was reported³ previously, for $\text{NdTe}_{1.8}$; and x-ray powder diffraction has been used to establish that all the transuranic analogs are isomorphous with it. We have prepared tetragonal single crystals ($a = 4.358 \text{ \AA}$; $c = 9.027 \text{ \AA}$; sp gr, $P4_2/nmm$) of AmTe_2 , by reaction of ^{241}Am metal with elemental tellurium at 500°C under vacuum, followed by removal of excess tellurium by sublimation. One such specimen was used for structure refinement employing single-crystal x-ray diffraction data.

The structure of AmTe_2 , shown in Fig. 5.3, is comprised of double, puckered layers of AmTe

composition interleaved with planar layers containing only tellurium. From this study it was ascertained that the variable stoichiometry is correlated with random vacancies at sites within the pure tellurium layers. In the crystal studied, 27% of the sites were vacant (i.e., $\text{AmTe}_{1.73}$), but it has been shown elsewhere² that the composition in all of these compounds varies somewhat with the thermal treatment.

All nine Am-Te bond lengths are about the same ($\text{av} = 3.24 \text{ \AA}$) and near to the sum of ionic radii. But within the pure tellurium layers the $\text{Te(II)}-\text{Te(II)}$ distances are only $3.08 \text{ \AA}$, a value much nearer to a covalent bond length than an ionic one. From this it is inferred that $\text{AmTe}_{1.73}$ may be semiconducting, as was found to be true of $\text{LaTe}_{1.7}$ and $\text{NdTe}_{1.8}$ (ref. 4).

1. Visiting scientist from Centre d'Etudes Nucleaires, Fontenay-aux-Roses, France.

2. D. Damien, *J. Inorg. Nucl. Chem.* **36**, 307 (1974); *Inorg. Nucl. Chem. Lett.* **8**, 501 (1972); D. Damien, A. Wogakowski, and W. Muller, *Inorg. Nucl. Chem. Lett.* **12**, 441 (1974); D. Damien, R. G. Haire, and J. R. Peterson, *Proc. Third Int. Conf. Electronic Structure of Actinides, Grenoble (1978)* to be published in *J. Phys. (Paris)*.

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5.9 X-RAY DIFFRACTION OF METALS AND COMPOUNDS AT HIGH PRESSURE

J. H. Burns R. G. Haire
D. Damien

A miniature high-pressure x-ray diffraction camera employing diamond anvils and Inconel gaskets has been used to study the structural behavior of several substances at high pressure and room temperature. The examination of transplutonium metals, begun with californium last year, was continued with the study of americium. Several samples of *dhcp* ^{241}Am metal were measured using aluminum as a pressure indicator, and a value of $\Delta V/V = -0.05$ was found at 20 kbars. This value is in agreement with values reported previously¹ and obtained by a different method. Our measurements will be extended to at least 100 kbars.

The behavior of AmTe under high pressure was examined because the nonstoichiometry suggested the possibility of a variable valence such as had been

found in samarium monochalcogenides. The compression up to about 130 kbars was measured and was found to be between that of EuTe and SmTe ; this value does not indicate that a valence change is occurring. At 100 kbars the volume is about 17% less than at 1 atm.

In the series of lanthanide sesquichalcogenides a change in structure type occurs between Gd_2Te_3 (U.S.-type) and Tb_2Te_3 (Sc-S-type); this change is attributed to the difference in size of the lanthanide ions. Hence the application of pressure might be expected to induce a structure change in one or the other of these compounds. Both Gd_2Te_3 and Tb_2Te_3 were prepared and studied by use of the high-pressure camera. Up to 120 kbars, neither exhibited a change in structure type, but they both experienced a normal volume contraction of about 11%.

1. Visiting scientist from Centre d'Etudes Nucleaires, Fontenay-aux-Roses, France.

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5.10 SYNTHESIS AND STRUCTURAL ANALYSIS OF SOME CRYPTATES OF SAMARIUM

J. H. Burns

The ion-size selectivity of certain diazapolyoxy macrobicycles (cryptands) and their capacity to form very stable complexes (cryptates) have led to numerous studies of the properties of the cryptates of monovalent and divalent cations.¹ This has been extended here to include trivalent samarium because lanthanide ions are inherently important and also serve as models with which to develop procedures for application to trivalent actinides (Am^{3+} , Cm^{3+} , etc.).

The cryptand used was 4,7,13,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane, for which the trivial name crypt-[2.2.2] has been adopted. This ligand was reacted in acetonitrile solution with $\text{Sm}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ that had been dried by refluxing over molecular sieves. Large triclinic crystals ($a = 14.82 \text{ \AA}$, $b = 8.81 \text{ \AA}$, $c = 13.25 \text{ \AA}$, $\alpha = 91.51^\circ$, $\beta =$

Fig. 5.4. Stereoscopic view of one ion pair in the crystal of $[\text{Sm}(\text{NO}_3)(\text{C}_{12}\text{H}_{16}\text{N}_2\text{O}_6)][\text{Sm}(\text{NO}_3)_2] \cdot \text{H}_2\text{O}$.

92.48° , $\gamma = 86.73^\circ$, $d_{\text{meas}} = 2.06 \text{ g cm}^{-3}$, space group $P1$) grew slowly from the solution. On evaporation in air of the remaining solution, hexagonal crystals ($a = 12.04 \text{ \AA}$, $c = 22.43 \text{ \AA}$, $d_{\text{meas}} = 1.53 \text{ g cm}^{-3}$) were obtained. The composition of the hexagonal crystals is not known, but the triclinic phase was completely analyzed by x-ray crystallography. It has the formula: $[\text{Sm}(\text{NO}_3)(\text{C}_{12}\text{H}_{16}\text{N}_2\text{O}_6)][\text{Sm}(\text{NO}_3)_2] \cdot \text{H}_2\text{O}$.

As can be seen in Fig. 5.4 there are two separate complex ions in this substance; each is doubly charged. One consists of an Sm^{2+} ion surrounded by a neutral molecule of crypt-[2.2.2] plus one NO_3^- ion, and the other contains an Sm^{3+} ion coordinated by five bidentate NO_3^- ions and one O atom from a water molecule. With the same cryptand, [2.2.2], La^{3+} is reported¹ to form a complex containing three singly charged $[\text{La}(\text{NO}_3)_2(\text{C}_{12}\text{H}_{16}\text{N}_2\text{O}_6)]^+$ ions and one $[\text{La}(\text{NO}_3)_6]^-$ ion. Thus for Sm^{2+} (radius = $0.96 \text{ \AA}$) and La^{3+} ($r = 1.06 \text{ \AA}$), their difference in size causes a different fraction of their coordination spheres to be occupied by the neutral ligand and a different number of negative ions to be attracted to fill the remaining space. The result is the formation of two bulky cations, each containing a lanthanide ion but having different net charges.

5.11 BINDING AND TRANSITION ENERGIES IN THE ACTINIDE REGION. A COMPREHENSIVE COMPARISON BETWEEN THEORY AND EXPERIMENT¹

M. O. Krause C. W. Nestor, Jr.

The present status of experimental and theoretical binding and transition energy determinations has been reviewed. Experimental data and recent theoretical predictions are compared for the energies of the $K\alpha_1$ x rays, M series x rays, KLL Auger electrons, K, L, M , and N levels, and the $4f$ /spin-orbit splitting. A triply modified Moseley fit has been applied to the $K\alpha_1$ data reported up to now. The comparison of theory with these fitted data as well as the KLL Auger energies and $K\alpha_1$ x-ray hypersatellite energy shifts demonstrates that modern, sophisticated theoretical apparatus is capable of predicting energies of the innermost levels of interconnecting transitions to a relative accuracy of about 10^{-4} , that is, about 10 eV for the K level and about 1 eV for the L level. This finding implies that Dirac-Fock calculations that include Breit interaction and Lamb shift effects in the lowest order are adequate at this level of accuracy. However, for reliable predictions of energies for transactinide elements, a confidence level of about 1 eV in the actinide region is most desirable because of the steep rise of the magnetic and quantum-electrodynamic contributions with increasing atomic number.

Experimental level and transition energies in the intermediate and outer regions of the atoms were

¹ J. J. M. Lehn, *Acc. Chem. Res.* **11**, 49 (1978).
² F. A. Hart, M. B. Hursthouse, K. M. Abdul-Malik, and S. Moorhouse, *J. Chem. Soc., Chem. Commun.* **1978**, 549.

found to agree well with theoretical Dirac-Fock and multiconfiguration Dirac-Fock predictions in those instances in which electron correlation effects are presumably small, as, for example, the M_1 and M_2 levels or $M\alpha$ and $M\beta$ x-ray energies. However, for other levels and associated transitions, the single-particle theoretical results proved inadequate because of the presence of many-electron or electron correlation interactions. Although the most probable interactions responsible for the existing discrepancies can be inferred from analogous studies made previously with lighter elements, a full quantitative interpretation will have to await further experimentation and detailed many-electron calculations.

of the K series $5 \leq Z \leq 101$, and the three L series $12 \leq Z \leq 101$ in the energy range $1 \leq h\nu \leq 100$ keV. Special considerations were given the analytical chemist by (a) calculating $K\alpha$ and $L\alpha$ cross sections at specific photon energies frequently used in fluorescence analysis and (b) tabulating radiative rates for many x-rays of the L and M series of the elements. Additional, supplementary data were included in the report to which the following potentials are. For example, fluorescence yields and hole transfer yields were presented, as well as calculation of x-ray production cross sections for ionization by electrons, protons, and alpha particles or neutrons.

One of some 30 formulas and tables for the calculation of the cross sections for the K and L series of x-rays of the elements $5 \leq Z \leq 101$ is presented in the report.

Extended abstract of paper published in *Phys. Rev. A* 15, 101 (1977).

Computer Sciences Division

5.12 CALCULATION OF X-RAY FLUORESCENCE CROSS SECTIONS FOR K AND L X RAYS OF THE ELEMENTS ($5 \leq Z \leq 101$)

M. O. Krause C. J. Sparks, Jr.
C. W. Nestor E. Ricci

X-ray fluorescence cross sections are important in various applied fields, such as radiation transport in matter, dosimetry, and especially x-ray fluorescence analysis using either traditional photon sources or synchrotron radiation. In all cases, an accurate knowledge of fluorescence cross sections is desirable. This requires reliable values of the basic parameters that enter into the calculation of the fluorescence cross section σ_{fl} .

$$\sigma_{fl} = \sigma_{pi} \omega_i F_{ij} T_{ij} \quad (1)$$

namely the partial photoionization cross section σ_{pi} , the fluorescence yield ω_i , the partial radiative rate F_{ij} , and the Coster-Kronig yields f_{ik} contained in the hole-transfer factor T_{ij} . Until recently, accurate values have been known only for the K shell parameters (where $T_{ij} = 1$), but now reliable values have become available also for the parameters pertaining to the L subshells. Thus it has become feasible to calculate for both the K and L shells fluorescence cross sections of sufficient accuracy to be useful in the various applications of inner shell ionization by photons.

Extensive numerical and graphical presentations were made in an ORNL report for the major x rays

Fig. 5.5. X-ray fluorescence cross sections at the photon energy of the ^{241}Am excitation source. Note that the L series values do not include emission following K_{α} and K_{β} transitions when the excitation energy falls below the K edges of the elements $Z \geq 68$.

to vary smoothly with Z , but those for the L x-ray series are shown to exhibit discontinuities and undulations. These breaks in the L curves are a direct consequence of the hole transfer between the L subshells by Coster-Kronig transitions. The need for including hole transfer has been pointed out recently,¹ and a dramatic increase of the $L\alpha$ fluorescence cross section has been demonstrated for photon energies somewhat above the L_1 absorption edge.

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Calculation of X-Ray Fluorescence Cross Sections for K and L Shells of the Elements ($12 \leq Z \leq 110$), ORNL-5399 (June 1977).

M. O. Krause, E. Ricci, C. J. Sparks, Jr., and C. W. Nestor, *Phys. Rev. A*, **21**, 119-127 (1978).

EVALUATION OF FLUORESCENCE, COSTER-KRONIG, AND AUGER YIELDS OF THE L SUBSHELLS OF THE ELEMENTS ($12 \leq Z \leq 110$)

M. O. Krause

X-ray fluorescence yields for the K shell have been measured almost from the beginning of x-ray and radiation physics, and the numerous data have been compiled and evaluated repeatedly through the years. The latest evaluations of the K shell yields appeared in 1972 and are due to Bambynek et al.¹ and Burhop and Asaad.² However, no evaluation of the fluorescence, Coster-Kronig, and Auger yields for the L subshells of all elements has been presented so far, although a definite need exists for reliable values in both basic and applied sciences. For example, cross sections of ion-atom collisions are derived as a rule from a measurement of the emitted x rays and hence require in the case of L shell ionization a knowledge of the L shell fluorescence and Coster-Kronig yields. In another example, the analytical determination of heavy elements by the x-ray fluorescence method relies on, or is restricted to, the measurement of characteristic L x rays and, hence, needs accurate fluorescence and Coster-Kronig yields to be of maximum value. Finally, Auger electron spectrometry in its move from a qualitative method to a quantitative method must have reliable values of basic parameters such as the Auger yields.

In this work, the radiative and radiationless yields were reviewed and extended up to $Z = 110$ in the case

of the K shell and evaluated in the case of the L subshells for the first time in the range $12 \leq Z \leq 110$. The evaluation was based on a novel procedure, inasmuch as the entire body of information available

Fig. 5.6. Fluorescence or radiative yields for K and L shells.

Fig. 5.7. Auger yields for K and L shells.

Fig. 5.8. Coster-Kronig yields for L_1 and L_2 subshells. Total L yield is partitioned into its two components.

from the measurements of yields and related properties was utilized and mutually reconciled for optimum consistency and compatibility. Data on the following interrelated properties were included in the evaluation process: (1) fluorescence, Auger, and Coster-Kronig yields, (2) radiative and radiationless transition rates, (3) level widths, (4) x-ray and Auger line widths, (5) x-ray and Auger spectra, and (6) Coster-Kronig energies. By contrast, an earlier tabulation¹ of L_2 and L_3 fluorescence yields from $Z = 47$ to $Z = 98$ was based solely on a fit to the experimental data of that particular property. The adopted values of the yields will be presented in tabular and graphic form in the *Journal of Physical and Chemical Reference Data* early in 1979. Also included will be a reference list of the original work that appeared between 1972 and October 1977. In Figs. 5.6 to 5.8, respectively, are presented, for fluorescence yields, Auger yields, and Coster-Kronig yields.

1. W. Bambynek, B. Crasemann, R. W. Fink, H. U. Freund, H. Mark, C. D. Swift, R. E. Price, and P. V. Rao, *Rev. Mod. Phys.*, **44**, 716 (1972).

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5.14 SEMIEMPIRICAL VALUES OF NATURAL WIDTHS OF K AND L LEVELS, $K\alpha$ X-RAY LINES, AND KLL AUGER LINES¹

M. O. Krause J. H. Oliver

As in the case of radiative and radiationless yields, tabulations of level and line widths involving the L subshells have been incomplete and inconsistent with related properties until now. But unlike the K shell fluorescence yield, previous evaluations of the K level width and $K\alpha$ x-ray line width have suffered from poor knowledge of all the effects contributing to the widths and from insufficient data input. In spite of a number of previous efforts, this situation has persisted for this atomic property, which is as basic as level energies, transition energies, and x-ray transition rates.

In this first comprehensive evaluation of natural level and line widths, we took advantage of the

recently evaluated fluorescence yields² for K and L shells and Scofield's relativistic Hartree-Fock calculation³ of radiative rates. We calculated the natural width Γ_i of level i ($i = K, L_1, L_2$, and L_3) from the relation

$$\Gamma_i = \Gamma_{R,i} \omega_i \quad (1)$$

where $\Gamma_{R,i}$ is the total rate of all radiative transitions to level i , and ω_i is the corresponding fluorescence yield. Line widths were then obtained as the sums of the widths of the levels involved in the transitions.

By way of Eq. (1), the semiempirical widths are based on the same body of information that was used in the evaluation of the fluorescence yields.² Hence the width values are mutually consistent and compatible with all available data, as the theoretical radiative rates have been shown previously³ to be realistic and reliable.

Although the semiempirical values obtained from Eq. (1) ideally are natural widths of free, singly ionized atoms, they are virtually identical with the "true" observed widths in atoms in which K and L levels are deep core level. The reason for this is that chemical and solid-state effects as well as outer shell

Fig. 5.9. Natural widths of K and L levels

ionization have a negligible effect on the inner shell transition rates, which are correlated with the natural width of a level by the Uncertainty Principle. However, deviations from the semiempirical natural width values may be expected if $Z \leq 13$ for the K level and $Z \leq 30$ for the L levels and for transitions between K and L levels.

In Fig. 5.9 we show the widths of K and L levels from $Z \approx 10$ to $Z = 110$ as an excerpt from the complete tabular and graphical presentation in the *Journal of Physical and Chemical Reference Data*.

1. *J. Phys. Chem. Ref. Data* 8, in press, 1979.
2. Section 5.13 of this report.
3. J. H. Scofield, *Phys. Rev. A* 9, 1041 (1974); *A* 10, 1507 (1974).

5.15 MICROMAGNETIC SUSCEPTOMETER FOR THE ACTINIDES¹

S. E. Nave² P. G. Huray³

With the development of the Superconducting Quantum Interference Device (SQUID), a high-sensitivity magnetic susceptometer has become available for use in determining the magnetic properties of limited sample quantities. We have constructed an apparatus based on these electronics which emphasizes a large sample to the pick-up coil flux transfer ratio. At the same time we have retained the versatility of variable sample temperature between 4.2 K and room temperature and an externally applied magnetic field up to 2000 G. A cross-sectional diagram of the low-temperature part of this apparatus is shown in Fig. 4.10 of the 1977 annual progress report.⁴ In the previous year we have, however, slightly altered our sensing coil design. The pick-up coils are now wound in a "second derivative" fashion so that they respond significantly neither to changes in a spatially invariant magnetic field nor to changes in a field with constant first derivative. This geometry reduces the effect of external noise and ideally gives a persistent response only when a sample is displaced relative to the coils in the presence of an applied field. A thermally activated niobium cylinder is rigidly attached about the pick-up coils to shield them from external electromagnetic noise and to trap a stable uniform applied magnetic field.

Samples are held by G.E. 7031 varnish in a 0.2-mm cavity drilled in the side of a uniform 0.5-mm-diam gold wire. The wire is enclosed inside a quartz tube for positioning and insulation. The gold wire is held

by a copper chuck that contacts a thermal ballast containing heaters and a variety of thermometers. The chuck, gold wire, and sample may be removed through a vacuum interlock for sample exchange. The entire chuck and ballast may also be driven up or down by a motor at a rate of 15 $\mu\text{m/s}$. This displacement moves the sample through the pick-up coils and is detected by a linear potentiometer.

A series of experiments was conducted to calibrate the apparatus. In one a 60- μg sphere of lead was used to define the sample-susceptibility as $\chi = -1/\pi$ due to its perfect diamagnetism at 4.2 K. A plot of the theoretical magnetic flux per unit dipole moment of the sample Φ/μ vs position in our pick-up coils is illustrated in Fig. 5.10. Points taken from an experimental measurement Φ_{signal} vs position of the sample in our pick-up coils is also given for comparison in this figure. For a sphere the sample moment is $\mu = 3/2(\chi m)(\rho)H$, where m is the sample mass, ρ is its density, and H is the applied field. Thus $\Phi_{\text{signal}} = (-3 H m) / (8 \pi \rho) \Phi/\mu f$, where f (the flux transfer ratio) is the fraction of the sample flux coupled to the SQUID and depends on the various coil geometries through their inductances. The value of f obtained by using the response when the sample is in the geometric center of the coils is 0.0029.

For the 8.3-G measurement shown in Fig. 5.10, a maximum signal of 163 Φ_0 was obtained; $\Phi_0 = 2.07 \times$

Fig. 5.10. A plot of the theoretical magnetic flux divided by the sample moment Φ/μ (cm^{-1}) coupled to the persistent pick-up coils (also indicated) as a function of the position (mm) of a spherical sample. Points taken from an experimental measurement Φ_{signal} are also indicated for a 60- μg lead sphere in a uniform 8.3-G field.

10^{-4} G-cm². Since $\Phi_{\text{meas}} \propto \chi H/m$ it may be seen that a 0.1- μ g sample of ^{235}U metal (which has $\chi = 10^{-4}$ at 50 K) is expected to give a signal of 0.6 Φ_0 in a field of 2000 G. This measurement is accessible with our system noise level of 10^{-4} Φ_0 . For a 2- μ g actinide sample in a 2000-G field, our minimum measurement dimensionless susceptibility is thus $\Delta\chi \sim 10^{-6}$ cgs (or $\Delta\chi_c \sim 10^{-6}$ cm³/g).

With these sensitivity levels, measurements should be of sufficient accuracy so as to be limited by other uncertainties such as sample geometry, bulk and surface contamination, and reproducibility of weighing. A computer program designed to compensate for a distribution of magnetic moments has been written to deconvolute the flux vs position data. With this program we may to first order account for geometrical sample or coil irregularities.

1. Research sponsored in part by DOE contract EY-76-S-05-4447 with the University of Tennessee, Knoxville.

2. ORAU Research Participant.

3. Associate Professor of Physics, University of Tennessee, Knoxville.

4. *Chem. Div. Annu. Prog. Rep. Mar. 31, 1977*, ORNL-5297 (September 1977), p. 42.

5.16 SPECTROELECTROCHEMICAL INVESTIGATIONS OF URANIUM AND EUROPIUM IN AQUEOUS SOLUTION¹

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J. P. Young⁴

A continuing interest in the generation and characterization of unusual oxidation states of the actinides, for example, Bk(II), Cf(V), and Es(IV), has prompted initiation of a study using the techniques of spectroelectrochemistry. A preliminary study of uranium and europium in aqueous solution with a new optically transparent electrode (OTE) made of reticulated vitreous carbon (RVC) has been performed.

The RVC is a rigid network of "glassy" carbon struts with a large surface-to-volume ratio. It is chemically resistant to a wide variety of solvent systems and acts as an inert electrode in a range of about 1.2 V to -1.0 V at pH 7 (ref. 6). When sectioned into thin sheets, 0.4 mm to 1 mm, RVC exhibits high transparency throughout the uv-visible spectral region. The optical and electrochemical properties of RVC make it ideal for use as an OTE. The small volume, less than 0.1 ml, and large surface

area of the RVC-OTE are well suited for investigations of highly radioactive, microgram-size samples of the heavier actinide elements. The useful potential range of RVC can be extended into the cathodic region by coating the matrix with mercury. The RVC is also resistant to molten salts at high temperature. Molten salts can provide wide versatility as solvent media.

An RVC-OTE was constructed after that of Norvell and Mamantov.⁷ The electrode was sandwiched between two quartz microscope slides, and the edges were epoxied on three sides. This assembly is dipped into the bulk solution, and a portion of the solution is drawn up into the electrode-cell by suction. The reference and auxiliary electrodes are placed into the bulk solution. The entire assembly can be placed in the sample beam of a recording spectrophotometer from which simultaneous electrochemical and spectral data can be obtained.

Uranium was chosen for the feasibility study due to the stability of UO_2^{2+} and U^{4+} in aqueous solution and the well-characterized absorption spectrum of each oxidation state. Cyclic voltammograms of UO_2^{2+} in 1 M KClO_4 supporting electrolyte using the RVC-OTE show a single reduction (cathodic peak potential near -0.3 V vs S.C.E.; pH, <2). Spectra were recorded for various applied potentials between 0.0 V and -1.0 V vs S.C.E. The results are shown in Fig. 5.11. The loss of UO_2^{2+} absorption peaks at 415, 458, and 472 nm and the concomitant appearance of U^{4+} absorption peaks at 431, 495, 547, 647, and 670 nm demonstrate the usefulness of the RVC-OTE. Spectroscopic evidence indicates the reduction of the uranyl ion to U^{4+} .

which is an irreversible electrode reaction due to the oxygen transfer. Cyclic voltammetry, however, indicates that it is likely that the reduction mechanism is via UO_2^+ .

which disproportionates to form U^{4+} and UO_2^{2+} . The net result, however, is the same as reaction 1.

The couple $\text{Eu}^{3+}/\text{Eu}^{2+}$ was selected for study because of the low reduction potential, the stability of both species in aqueous solution, and a one-electron reduction mechanism. The reaction was shown to be reversible by cyclic voltammetry in 1 M KCl at pH 5.

Fig. 5.11. Absorption spectra of uranium(IV) and uranium(VI) at various applied potentials. A, no potential applied; B, -0.2 V vs SCE; C, 0.6 V vs SCE; D, 1.0 V vs SCE. Spectra were recorded in 1 M KClO_4 at $\text{pH} = 2$, in the RVC-OTF, path length 0.78 mm, concentration of $\text{UO}_2^{2+} = 1\text{ M}$. The overall reaction is: $\text{UO}_2^{2+} (\text{yellow}) + 4\text{H}^+ + 2e^- \rightarrow \text{U}^{4+} (\text{green}) + 2\text{H}_2\text{O}$.

Spectra were recorded at various applied potentials. The molar absorptivities for the two species are, however, orders of magnitude different. Thus with the appearance of the reduction product, the sharp spikes due to Eu^{3+} at 397 and 316 nm are almost completely engulfed by the broad-band absorption of Eu^{2+} starting at about 475 nm and extending into the uv spectral region. The experiment is conclusive in a qualitative manner, demonstrating the "in situ" generation and simultaneous spectral identification of the product.

Continuation of this work will involve the extension of the use of the RVC-OTF and other

electrodes into the realm of nonaqueous spectro-electrochemistry, utilizing both nonaqueous-organic and molten-salt media. It is expected that molten-salt media can stabilize rare and unusual oxidation states of the transuranium elements and can provide sufficient transparency for the spectral characterization of these new species.

1. Research sponsored in part by DOE contract EY-76-S-05-4447 with the University of Tennessee, Knoxville.

2. Graduate student, Department of Chemistry, University of Tennessee, Knoxville.

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

4. Analytical Chemistry Division.

5. RVC is a trademark of Chemtronics International, Inc., Ann Arbor, Mich.

6. V. E. Norvell and G. Mamantov, *Anal. Chem.* **49**, 1470 (1977).

5.17 INTERACTIONS OF ACTINIDES AND RARE EARTHS WITH GEOLOGIC MEDIA IN CONNECTION WITH NUCLEAR WASTE ISOLATION

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R. G. Haire G. D. O'Kelley

Studies have been initiated on the interaction of the rare earths and actinides with various geologic media. These studies were begun in connection with current programs of the Chemistry Division as part of a national effort concerned with waste isolation in the nuclear power industry. The first materials studied were three clay minerals, kaolin, montmorillonite, and attapulgite, which were chosen for their high ion exchange capacity.

The distribution coefficients D for La, Sm, Yb, Am, Cm, Cf, and Es were determined on these clays by batch shaking experiments. Values of D were measured in brine solutions varying from 0.25 M to 4 M total sodium, which might be characteristic of solutions resulting from a breach in a salt-bed repository for nuclear waste. The initial studies were carried out in acetate-buffered solutions at $\text{pH } 5$. Values obtained for the distribution coefficients indicate a small increase in adsorption of both the rare earths and actinides as the atomic number increases. There also appears to be very little difference in behavior between the rare earths and actinides. The change in D as a function of sodium concentration qualitatively follows the trend expected for ion exchange (Fig. 5.12). However, the slopes indicate the presence of acetate complexing and activity

Fig. 5.12. Distribution coefficient for ^{241}Am and ^{244}Cf on kaolin, montmorillonite, and attapulgite at pH 5.

coefficient effects. The most striking differences occur in the relative magnitudes of the D values for the three clays. Kaolin has very low D values in the range of 1 to 10 and montmorillonite in the range of 10 to 50. These D values are in good agreement with the respective cation exchange capacities of the two clays. However, this is not the case for attapulgite, whose D values are several orders of magnitude larger, whereas its exchange capacity is intermediate to that of kaolin and montmorillonite. Measurements of D values for Cs, Rb, and K on attapulgite showed adsorption increases going from K to Rb to Cs, which approached the americium values.

The rate of exchange of trivalent ions on attapulgite was found to be drastically different from the other two clays. Shaking experiments using kaolin and montmorillonite exhibit very rapid reaction rates so that less than 15 min is required to attain equilibrium. Experiments with attapulgite indicate two rates of reaction, one requiring 10 to

12 h and a second reaction requiring up to 9 d. In contrast, potassium and rubidium showed a very rapid exchange on attapulgite, whereas cesium displayed a two-component rate, like that of americium.

We have attributed the high specificity of attapulgite for rare earths, actinides, and cesium to geometric factors associated with relatively large channels that are peculiar to attapulgite. The high D values could be caused by ions being of the right size to fit into the channels. The two-component rates of exchange observed may be caused by a rapid exchange with sites exposed on the surface and a second slower reaction involving diffusion into the inner channels.

To obtain data more nearly representative of conditions existing in natural systems, we have measured D values at several concentrations of sodium ion as a function of pH. So far, we have measured distribution coefficients for americium and cesium on montmorillonite and americium on kaolin at values of pH ranging from 4 to 7. The D values for americium on both clays change by three or four orders of magnitude between pH 4 and 6.5. We believe that anions such as CO_3^{2-} and OH^- are responsible for these drastic changes and that CO_3^{2-} solubilities in the literature may be overestimated. This view is substantiated by the D values for cesium, which do not change with pH. It appears that, at $\text{pH} \leq 5$, the most important sorption phenomenon is cation exchange. At higher pH, precipitation seems to predominate and is surely the limiting factor in soluble species in nature.

5.18 IMPLICATIONS OF RADIATION DAMAGE IN NUCLEAR WASTE ISOLATION

R. G. Haire G. W. Beall

Recently there has been a great deal of interest in the storage of radioactive wastes and the impact, if these materials were accidentally released to the environment. The transplutonium elements that may be present in such wastes are of special interest because of their long half-lives and because most of them are alpha emitters. Interest in the behavior of naturally occurring clays with the transplutonium elements arises due to their sorptive capacities, and studies have been carried out to define the sorption behavior of these elements on different clays and minerals (Sect. 5.17). However, it is also important to

determine the stability of the clay-actinide products with regard to radiation damage and to predict the behavior of these products after exposure to radiation.

Of the three clays chosen for the sorption studies, two were selected for the radiation damage experiments. The two clays, kaolin and attapulgite, are shown in Figs. 5.13a and 5.13c and were selected because their morphologies are best suited for monitoring changes brought about by radiation. The regular needle-like structures of attapulgite and the plate-like forms of kaolin are clearly defined in this figure.

From sorption studies (Sect. 5.17), it was clear that the trivalent ions of americium through einsteinium

behaved similarly so that the sorption behavior element of one was representative of the other four elements. To provide the greatest radiation field per unit time, the damage studies were carried out using ^{252}Es (alpha specific activity = 6×10^{10} α min $^{-1}$ μg^{-1} , 6.16 MeV α). The experimental procedure was to mix appropriate amounts of ^{252}Es in 10^{-3} M HCl with each clay and periodically examine portions of the mixtures by electron microscopy. Colloidal solutions of the clays without ^{252}Es were used as controls.

The results of the study showed that the radiation destroyed the clay's morphology by generating voids in the structures, eventually leaving only fragments of the original forms. The rate of destruction was proportional to the loading; little change was seen in

ATTAPULGITE

KAOLIN

Fig. 5.13. Electron micrographs of kaolin and attapulgite before (a and c) and after (b and d) exposure to ^{252}Es .

[illegible]

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radioactive secular equilibrium, where the activity (disintegrations per unit time) of each is constant. It is equal to the activity of the "parent." However, because of the chemical differences between the different elements in the decay sequence, and because of the kinetic effects of the radioactive decay, it is conceivable that the daughters of uranium may be mobile, especially if the ore is in contact with some fluid. For example, radon is a gas and so could diffuse out of the deposit. Polonium and possibly some of the other elements could form organic compounds, whereas radium should be soluble in aqueous media. Thus one would hope to find evidence for uranium deposits by detecting nonequilibrium amounts of the radioactive daughters in samples of underground water, oil, natural gas, and particulate matter which are pumped to the surface.

If differences were found in the amounts of isotopes with different half-lives, for example, ^{214}Bi (which would be characterized by the 3.8-d half-life of its precursor, ^{214}Pb) vs 19-year ^{210}Pb vs 138-d ^{210}Po , one could infer something about the distance of the uranium deposit from the well being surveyed. Thus ^{214}Bi and ^{214}Pb would be indicative of uranium deposits close to the well, whereas ^{210}Pb and ^{210}Po would either indicate uranium sources at large

Often, uranium and its decay daughters are all contained in the same geological deposit, in a state of

PLUTONIUM AND URANIUM STUDIES

During the past decade, ORNL was engaged in a study of the fundamental photochemical reactions of plutonium. As a result of these studies, it became apparent that photochemical processes might provide useful techniques for actinide separation programs. Plutonium photochemical reactions were investigated in considerable detail, and the fundamental reactions, along with their quantum efficiencies, were published. These plutonium data suggested a simple alternate means of separating plutonium to a solution that was compatible with the Purex process. The advantage of this photochemical alternative was the elimination of bulk chemical reductants such as ferrous sulfamate and the resulting promise of a simpler separation process. This concept was demonstrated in the laboratory and subsequently patented.

Our most recent efforts have been focused on the photochemistry of neptunium. The studies were performed first in perchloric acid solutions because these are not hampered by the ligand's interfering absorption of the excitation radiation nor its subsequent photolysis. Following this study, the photolysis of

neptunium(IV) was found to be a useful process, and the hydrolytic chemistry with respect to the various experimental approaches used, and the information gained. Different terminologies used in describing the experimental procedures have often confused the understanding of the chemical processes that occur between the first hydrolysis reaction of the tetravalent actinide and its final dehydration to form the crystalline oxide. Attention has been focused on the chemical significance of the term "polymerizing," which is best defined in terms of A. W. Thomas' ol-to-oxo conversion reaction and involves simply the conversion of hydroxyl-bridged polymer links to oxygen-bridged linkages. Thorium(IV) hydrolytic reactions are included because they are analogous in many respects to those of Pu(IV) and offer a simpler chemical system for experimental study.

Figure 6.1 summarizes the hydrolytic behavior of these ions and reviews the regions where the various terms are defined. Also shown in the figure are the regions touched by the various experimental approaches and, finally, the fuel reprocessing problem area, which still requires further attention. It is remarkable to note the consistency in the hydrolytic behavior in terms of facets seen by the individual experimental approaches used.

Fig. 6.1. Hydrolysis and polymerization of the tetravalent actinides.

6.1.3 Effects of Uranyl Nitrate on the Polymerization of Pu(IV)

Interest in the effects of uranyl ions on the polymerization of Pu(IV) and hence, in the separation of actinides in fuel processing has been enhanced because of processing modifications with low-acid concentrations. Results from our research have indicated that the uranyl ion can be incorporated into the polymer and tends to terminate polymerization. Also, increased nitrate concentrations tend to promote polymerization of Pu(IV) by increasing the amount of Pu(IV) in a low-acid solution. This increase in Pu(IV) concentration results from the nitrate complexation of Pu(IV) and the corresponding decrease in acid concentration as well as the corresponding shift in the Pu(IV) disproportionation equilibrium.

The net effect of uranyl nitrate is to decrease the rate of Pu(IV) polymerization. The detailed results of these investigations have been reported in the Advanced Fuel Recycle Program Quarterly Progress Reports ORNL TM-6306, -6221, and -6092.

6.1.4 Chemistry of Fission Products in Refrigerant-12 Media

Fission products and contaminants in process off-gases can be separated and isolated by dissolution of the total gases into refrigerant-12 followed by

fractionation, distillation. Solubility, distribution, and interaction data are required for optimum design and operation of this separation process. The fuel reprocessing programs have supported investigations to acquire such data. Detailed results have been given in the AFRP and the Alternate Fuel Cycle Technologies Thorium Fuel Cycle Technology Quarterly Progress Reports ORNL TM-6306, -6221, -6092, -6429, -6307, and -6076.

The data obtained have been analyzed with respect to Hildebrand's solution theory; the results are being readied for publication.

1. Visiting scientist from Kenyon College, Kenyon, Ohio.
2. Expanded abstract of *Pu(IV) and Th(IV) Hydrous Polymer Chemistry* by G. L. Johnson and L. M. Loh, ORNL TM-6365 (May 1978).
3. I. Pokras, *J. Chem. Educ.*, **33**, 152 (1956).

6.2 RECOVERY OF NONRADIOACTIVE PALLADIUM FROM HIGH-LEVEL RADIOACTIVE WASTES¹

H. F. McDuffie

A possible method for recovering significant quantities of nonradioactive palladium from fission-product wastes requires essentially complete separation of the fission-product (radioactive) palladium from fission-product ruthenium. After the decay of ^{106}Ru via ^{106}Rh to ^{106}Pd , this nonradioactive palladium is recovered for normal commercial use.

The U.S. production of palladium has never been above 1000 kg per year vs consumption of about 46,000 kg per year. Most of the supply comes from Russia and South Africa. It has been estimated that a 400-GW(e) nuclear reactor economy will make available 2000 kg per year of ^{101}Ru at reactor fuel discharge. A substantial increase might be achieved if plutonium were recycled as fissionable material because of the higher yields of the 106 chain from plutonium. A literature search has uncovered support for three promising approaches to the required separation of palladium from ruthenium: (1) recrystallization from solution in bismuth or in zinc, (2) selective precipitation of a titanium-ruthenium intermetallic compound from bismuth followed by precipitation of a zinc-palladium intermetallic compound, and (3) dissolution in molten magnesium followed by partitioning between molten magnesium and a molten uranium-5 wt % chromium eutectic at a temperature above 870 °C. Liquid-liquid extraction appears to be the most promising method from a technological point of view, although intermetallic compound formation is much more interesting chemically. Demonstration of the practicality of the separation will contribute a positive factor to the evaluation of U.S. resumption of nuclear fuel reprocessing and plutonium recycle in light-water-moderated reactors.

1. Abstract of report to be published as ORNL TM-4754

6.3 RECOVERY OF URANIUM FROM WET-PROCESS PHOSPHORIC ACID

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6.3.1 OPAP Process Development

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

The liquid chromatographic method for analyzing OPAP was improved so that we can now detect at least 11 components in the commercial mixture. Besides MOPPA and DOPPA, we have identified

octyl phenol, trioctylphenyl phosphate, and unsubstituted phenol; the other materials remain unidentified. Two columns are used for the analysis. With a column containing strong-base anion exchange resin, nonacidic and weakly acidic materials elute with absolute methanol and are detected at 275 nm; the acidic compounds are retained on the column. Five peaks are obtained in chromatograms of OPAP with this column (Fig. 6.2). The second column contains ODS, an 18-carbon hydrocarbon bonded to silica, and is eluted with a 25% H_2O -methanol mixture containing tetrabutyl ammonium phosphate, an

ORNL-DWG 78-11307R

Fig. 6.2. Chromatographic separation of OPAP. Identification of peaks: A, trioctylphenyl phosphate; B, unidentified octylphenol impurity; C, octyl phenol; D, unidentified; E, unsubstituted phenol; 1, unidentified; 2, MOPPA; 3, unidentified; 4, unidentified; 5, octyl phenol; 6, unidentified; 7, unidentified; 8, DOPPA.

ion-pairing reagent. Chromatograms of OPAP obtained with this system contain eight peaks. We have examined a number of OPAP batches and find the same materials, with some variations in the relative amounts in each batch.

This technique was used to monitor OPAP composition changes during hydrolysis. Results with the ODS column are shown in Fig. 6.3. The OPAP sample was hydrolyzed by gently refluxing with water five successive times. Titrations of the OPAP samples indicated a loss of about 20% of the apparent concentrations of both MOPPA and DOPPA in the first contact and then a slower MOPPA loss and no DOPPA loss in subsequent contacts. The chromatograms show a substantial decrease in the size of the MOPPA peak and a slight decrease in the size of the DOPPA peak, which agrees with the

titration results. Peak 1 disappeared, with most of the loss occurring in the first contact, which could be part of the loss of readily hydrolyzable acidic material that was indicated by the titrations. Peaks 3 (unidentified) and 5 (octyl phenol) increased in size with succeeding hydrolysis treatments. On the basis of these and later stability tests, we would expect the initial loss of readily hydrolyzable material to occur in plant operation with wet-process phosphoric acid but would not expect the loss in subsequent contacts. These results also indicate that the process solvent would contain significant concentrations of octyl phenol and an unidentified OPAP impurity (peak 3).

Studies of the stability and long-term performance of OPAP are a major part of our program. In an earlier stability test with wet-process acid, a loss of uranium extraction power occurred, which we attributed to a combination of reagent poisoning with unidentified material extracted from the acid and precipitation of the extractant as a complex with ferric iron. These tests have been continued in continuous countercurrent stability tests in a pure system, that is, with purified OPAP in *n*-dodecane and reagent-grade phosphoric acid.

Significant volumes of the organic phase were lost in the stability tests. The losses, summarized in Table 6.1, were of the total organic phase and were separate from any distribution loss of the extractant. The loss rate was about 1 ml of organic phase to each liter of phosphoric acid passed through the mixer-settler array that contained two extraction stages and two stripping stages. It was slightly higher in the pure system than in the system with commercial OPAP and wet-process acid. Adding octyl phenol to the organic in the pure system had little effect on the loss rate. These losses are too large to be accounted for by spills or other mechanical means.

Fig. 6.3. Effect of hydrolysis on OPAP composition. Commercial OPAP hydrolyzed five successive times by gentle reflux with water. Analysis by liquid chromatography on ODS column.

Table 6.1. Organic volume loss in continuous tests

OPAP	Diluent	Acid	No. of extraction stages	Acid volume (liters)	Organic volume (ml)		Organic loss rate (ml/liter aq)
					Initial inventory	Loss	
Commercial, hydrolyzed	Kermac 470 B	Wet-process, green	2	529	1080	495 ^a	0.8-0.9 ^a
Purified, MOPPA + DOPPA	<i>n</i> -Dodecane	Pure, 6 M Fe	2	316	1075	351	1.1
Purified, MOPPA + DOPPA + OP	<i>n</i> -Dodecane	Pure, 6 M Fe	2	44	1080	59	1.3
Commercial, hydrolyzed	<i>n</i> -Dodecane	Pure 6 M Fe	1	72	350	47	0.6
Commercial, hydrolyzed	<i>n</i> -Dodecane	Pure 6 M Fe	1	63	540 ^b	40	0.6 ^b
None	<i>n</i> -Dodecane	Pure 6 M Fe	1	57	346	7	0.1

^aNo allowance made for spill at end of test.

^bOrganic continuous mixing, all others aqueous continuous.

We believe they were caused by the formation in the phosphoric acid of microemulsions, that is, finely dispersed droplets of the organic phase that are stable for long time periods. Several shorter term continuous tests were made with 6 *M* reagent grade phosphoric acid containing ferrous iron in a 1-stage mixer-settler to simulate the raffinate extraction stage. The organic loss rate with this system was 0.6 ml per liter of acid. It was the same with organic or aqueous continuous mixing, although physical entrainment was much lower with organic continuous mixing. Only the volume of organic remaining on equipment surfaces was lost in a test with *n*-dodecane as the organic phase, which indicates that the microemulsions do not form without OPAP being present. Although some organic separates from the acid solutions after they stand for several weeks, we have not been able so far to recover the dispersed organic from freshly generated raffinate samples.

We believe the decreased uranium extraction in the earlier continuous test was caused primarily by poisoning of the extractant with unidentified material that was extracted from the wet-process acid because this problem did not occur in the tests made in the pure system. The poison could originate in the phosphate rock or in chemicals added during processing, and it could be extracted by the major OPAP components or by one of the impurities. The poison also causes the color of the organic to darken and interferes with titration of the organic. Part of the strongly acidic hydrogens are complexed and titrate as weakly acidic hydrogens; the effect of this is to give apparent results that are high in MOPPA and low in DOPPA. The poisoned organic cannot be regenerated (in terms of uranium extraction, titration, or color) by scrubbing with mineral acids. Scrubbing with ammonium carbonate and then with acid improves the titration but does not change the uranium extraction or the color.

During part of the test with wet-process green acid, a solid complex containing iron and both major components of the OPAP reagent formed in the extraction section. The solid deposited from the organic phase; that is, the iron extracted and then the complex crystallized. It did not cause any operational problems. The solids contained DOPPA, MOPPA, and iron at a molar ratio of 1.0:0.5:0.6. Other samples, prepared here and obtained from other sources, varied in composition but contained primarily these three components. No metals other than iron were present in significant concentrations. The major factors that affected formation of the precipi-

tate in batch tests were the concentrations of ferric iron and phosphoric acid in the aqueous phase; formation increased with increasing Fe^{3+} concentration and with decreasing H_3PO_4 concentration. The acid used in the continuous test contained a high Fe^{3+} concentration of 13 g/liter. It is possible that the precipitate formation can be controlled by controlled reduction of the iron in the phosphoric acid and by maintaining the H_3PO_4 concentration at 6 *M* or above.

A large distribution loss of MOPPA to the aqueous phase occurred in the continuous tests with reagent grade H_3PO_4 . The MOPPA distribution coefficient (organic/aqueous) was about 200. The DOPPA concentration remained constant until essentially all of the MOPPA had been lost, and then, DOPPA crystallized from the *n*-dodecane diluent. The MOPPA loss was by distribution to the aqueous phase, not by degradation; chromatograms of organic samples showed that the MOPPA disappeared and that no degradation products formed. The loss rate was not affected by the presence of octyl phenol in the organic phase; it was essentially the same with commercial or purified OPAP. It was the same in the one-stage extraction system, with no stripping as in the system with two extraction stages and two stripping stages, and it was also the same with organic or aqueous continuous mixing. There was little or no MOPPA distribution loss in the test with wet-process acid, possibly because the reagent was complexed with extracted metals such as iron. This suggests that MOPPA distribution can also be controlled by controlling the oxidation state of the iron in the phosphoric acid. It will need to be balanced to minimize both the MOPPA distribution loss and the iron precipitate formation.

6.3.2 Interaction with Industry

We have had extensive interaction with industrial concerns interested in the recovery of uranium from wet-process phosphoric acid. These concerns include phosphate producers, firms interested in uranium recovery on a contractual basis, engineering firms, and reagent suppliers. There was also interaction with governmental agencies such as the Tennessee Valley Authority and the Bureau of Mines. Two full-scale recovery plants that will use the DEPA-TOPO [di(2-ethylhexyl)phosphoric acid tri-octylphosphine oxide] process for uranium recovery are currently under construction, and a third, in the engineering design stage. Future construction of two additional plants has been announced. One plant that

uses the WXP process is in commercial operation, and other companies are considering this process.

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6.4 FLOW THROUGH POROUS BODIES

6.4.1 Filtration Studies

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W. L. Griffith C. G. Westmoreland

Separations of high-molecular-weight substances from one another. The separations feasible by filtration processes have expanded enormously over the last generation. Removal of dissolved salts or other low-molecular-weight substances from water by hyperfiltration (reverse osmosis) has become an industrial-scale operation. Processes for ultrafiltration of colloids and filtration of coarser materials from liquids have become much more efficient in many cases, with the use of cross flow of liquid past the filter so as to slow the buildup of filter cake by shear at the interface.

A class of applications which still poses formidable problems is the situation in which one wishes to separate from each other two substances, both dispersed in a liquid as aggregates of different but large size. Even though filters are now likely to be available with pore sizes and pore size distributions which should in principle discriminate between the species to be separated, the filter cake or dynamic membrane that builds up in the process soon dominates behavior, and the pore size of the filter itself quickly becomes irrelevant. One more than likely ends up concentrating both substances, rather than passing one with the liquid through the filter.

We have been investigating under Basic Energy Sciences DOE support whether or not judicious selection of pore size and nature of the filter, movement of filtered solution relative to filter, and manipulation of other experimental conditions such as pressure might allow some control of this difficulty. The separation selected for evaluation is one of interest in an applied program, a biopolymer in fermenter broth from cell fragments and other constituents that might plug formations when the polymer is used for mobility control in enhanced oil recovery. Accomplishing this separation without precipitation of the biopolymer is necessary to realize full benefits of field production of the biopolymer.

It is preferable to effect it without addition of diatomaceous earth filter aids (a conventional way to remove plugging constituents) in order to keep open the option of biomass disposal as a cattle feed supplement (Sect. 7.1.2).

The possibilities of success are good. Figure 6.4 summarizes some results of filtration in a flat-plate configuration with several pore sizes in straight-through filtration without cross flow. The feed was broth, heated to 80°C to stop fermentation, subjected to a Waring blender for a few minutes, and diluted to a polymer concentration of 1 g/liter to approximate a typical injection concentration. The biomass concentration was about the same as that of the polymer. It can be seen that the flux during filtration declined rapidly as the filter cake built up. The viscosity of the filtrate also decreased with time, an indication that the polymer was being filtered out.

Slower flux decline and less viscosity loss were observed if the filtration was carried out with relative movement of filter and feed, effected either by pumping feed past the filter or by mounting the filter on a rotor and spinning it in a chamber of pressurized feed (axial filtration). The cross-flow experiments were carried out with an experimental module containing Acropor membranes in a pleated configuration provided by G. B. Tanny of the Gelman Instrument Corp. Better results were obtained if a first stage axial filtration was carried out on the axial filter with a stainless-steel screen of 125- μ m openings. Fluxes were high in this preliminary screening, 700 gpd/ft² or more, and viscosity loss was negligible.

Figure 6.5 summarizes typical fluxes obtained in axial filtration with 5- μ m Nuclepore filters of prescreened and unscreened broth. Flux decline is much less rapid than in Fig. 6.4 (without cross flow) and is less with screened feed than with unscreened. Figure 6.6 illustrates very little viscosity loss in passing through the filter. When feed that had not been prescreened was used, however, there was about a 30% loss of viscosity in filtration.

A criterion that must be met is that filtrates do not plug formations. Comparison of flux declines in a plugging test of filtrates and feeds indicates that the filtration has vastly improved the solution in this respect (Fig. 6.7). The plugging rate is probably still too high to meet oil-company criteria, but the behavior is good enough to indicate that further manipulation of conditions will likely give the desired purification.

Fig. 6.4. Filtration of glucan biopolymer from diluted fermenter broth with no cross flow; (a) flux during filtration; (b) viscosity of filtrate (shear rate, 22 s^{-1}). Acropor AN filters, $5 \mu\text{m}$.

Fig. 6.5. Fluxes in axial filtration of diluted glucan fermenter broth through $5 \mu\text{m}$ Nuclepore filters (2000 rpm , $\sim 11 \text{ ft/s}$).

Fig. 6.6. Comparison of viscosities of feed and filtrates from axial filtration (screened feed, 25°C , axial filtration through $5 \mu\text{m}$ Nuclepore).

The Nuclepore filter used in the filtration shown in Fig. 6.5 has cylindrical pores of a narrow size distribution, obtained by fission-fragment bombardment and subsequent etching. It was thought that control of filter cake on these films might be

Fig. 6.7. Screened feed for axial filtration. Flux of 1.2 l/min. Membrane for test filtrate from 5- μ m S&W pore filter used but no axial filter supporting test pressure 12 psig.

better than with the tortuous pores of comparable size in Acropor or Millipore filters. Results in tests so far seem somewhat better with Nuclepore but not enough to be clearly significant.

Some of these observations are reported in more detail in a forthcoming paper.

Porous supports for dynamically formed membranes. One of the main barriers to use of dynamic membranes in the many water processing applications for which the performance of the membranes themselves has advantages over alternatives is the dearth of suitable porous supports. The recently completed pilot-plant program on pulp-mill wastes carried out in cooperation with the International Paper Company emphasizes this deficiency. Although the ceramic-tube modules used in the tests gave encouraging purification over short times, they appeared, in contrast to our laboratory experience, to be too fragile in the industrial environment for adoption on a plant scale.

We referred in the previous annual report to encouraging results with porous stainless-steel tubes fabricated by the Mott Metallurgical Corp. Two serious objections could be raised to these supports. First, their cost might limit severely the applications feasible for them. However, recently developed modules fabricated for these tubes promise to be offered at much lower costs than those currently marketed, and the range of uses that are practical economically should be considerably broadened. Second, their pore size is too large, without use of a layer of fine particulates at the interface, for formation of membranes of good properties. In our original procedure for using particulates, a filter-aid layer was formed as a precoat by circulating a slurry. Besides involving an additional step in membrane formation, this mode required use of pumps that could pump slurries as well as complicated equipment design to assure favorable hydrodynamics for deposition. However, as we mentioned in last year's report, we have found that addition of a fine carbon black dispersion (particle size $<0.1 \mu\text{m}$) to the solution from which the hydrous Zr(IV) oxide layer is formed results in membranes of good properties without the disadvantages cited. We have since confirmed these observations and have evaluated tubes of another pore size made available to us.

In Table 6.2 properties of membranes formed with and without filter aid are summarized. On the 5- μm rating (the micron rating relates to the size of particles removed in filtration and is smaller, by perhaps as much as a factor of ten, than the pore size), results are compared for no filter aid and for a conventional precoat, preformed by circulating 25 ppm of a diatomaceous earth filter aid and 25 ppm of carbon black. It can be seen that both fluxes and salt rejections are better, both for the membrane comprised only of hydrous Zr(IV) oxide and for the membrane after the deposition of polyacrylic acid, when the filter-aid layer was present. On the 0.2- μm tubes, no precoat was laid, but 25 ppm of carbon black was added to the ZrOCl₂-containing solution during the formation of the hydrous oxide layer (in our experience, there is essentially no difference between NaCl and NaNO₃ solutions in these procedures). The rejection of this layer was lower than without filter aid, but the completed hydrous Zr(IV) oxide polyacrylate membrane again had superior properties. Presumably, the particulates prevent layers from forming too deeply in the support, make coverage better, and perhaps make the interface more even so that polarization of rejected salt in depressions is minimized.

Table 6.2. Effect of filtration on properties of membranes dynamically formed on Mott porous stainless steel tubes

Feed: 0.01 M NaNO_3 (pH 6.5) at 25°C and 100 psi

Filtration stage	Filtration fluid	NaCl conc. (M)	Before Zn(IV) coating (pH 4)		With PAA layer (pH 6.5, 70°C)	
			Flux (gpd ft ²)	Rejection (R_{NaCl} , %)	Flux (gpd ft ²)	Rejection (R_{NaCl} , %)
1	None	NaNO_3	23	25	34	66
2	25 ppm CB	NaNO_3	340	46	100	98
3	25 ppm CB present	NaNO_3	40	38	14	64
4	None	NaCl	13.5	38	14	64
5	25 ppm CB (with Zn(IV))	NaNO_3	270	49	50	78

*CB, carbonaceous earth; Johns-Manville Celmo 505, CL, carbon black, Cabot Recel SR.

In Table 6.3, results are compared for membranes formed with carbon black added to the Zn(IV) step (10 ppm in this case) on three stainless-steel elements—a 0.5- μm , a 0.2- μm , designated "old," which had been used in earlier experiments, and a new 0.2- μm tube. A 0.27- μm Sclaf ceramic tube was included for comparison. The 0.2- μm (old) was of different diameter than the other two, and the circulation velocity was 32 ft/s rather than 18 ft/s in the others. It can be seen that the membrane on the 0.5- μm tube had substantially better properties than those of the other two stainless-steel elements. In subsequent tests with kraft pulping effluents, rejections by membranes on the 0.5- μm were also generally better than those on the 0.2- μm . Reasons for the differences between the two sizes are not clear, but the discrepancy between the 0.2- μm samples suggests difficulties in control of fabrication of this type. The circulation velocities past the two samples are different enough for significant effects but are unlikely to account for such sharp variations in properties.

We have also begun to evaluate the Gelman pleated cartridge, mentioned in connection with filtration of biopolymer fermentation broth, for ultrafiltration applications. This configuration is likely to be much cheaper per square foot than tubular modules and can be operated in a mode allowing easy backwashing. Some encouraging results have been obtained with kraft bleach-plant effluents at room temperature, but problems, both with these cartridges and with a spiral-wound module of Aeropor membranes, have been encountered when temperature was raised to the range desirable for the

operation. There is no reason at present to believe that these difficulties cannot be overcome with simple design modifications. A more critical question is the quality of long-term performance on practical feeds with configurations having the rather close spacing for fluid flow which these have.

Table 6.3. Comparison of Mott tubes of different micron ratings

0.01 M NaNO_3 , pH 6.5

Filtration stage	Before Zn(IV) coating (pH 4)		With Zn(IV) coating (pH 6.5)	
	Flux (gpd ft ²)	Rejection (R_{NaCl} , %)	Flux (gpd ft ²)	Rejection (R_{NaCl} , %)
Stainless steel				
0.5- μm	130	48	36	92
0.2- μm (old)	26	31	4	7
0.2- μm (new)	265	48	14	50
Ceramic				
0.27- μm (size 1)	280	47	87	84

6.4.2 Dispersion of Miscible Fluids in Packed Beds

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The studies of the displacement of a fluid from a porous medium by another miscible fluid are of

interest in transport of nuclides from waste repositories and in enhanced recovery of oil.

As discussed in the previous annual report, the mixing that develops between two adjacent miscible fluids is affected by inertial, viscous, and gravitational forces as well as the properties of the medium. Previous investigators have studied extensively the effects of density, viscosity, and flow rate on dispersion. However, insufficient data exist on the effects of particle size. Therefore, the objective of this research is to study the effect of particle size with other variables on dispersion of miscible fluids. To simplify the analysis, spherical packing materials (glass beads) of narrow particle-size distributions were selected.

The stability of the boundary has been shown to be affected by the density and viscosity differences of the two fluids and is enhanced or reduced by other variables. For a density and viscosity favorable system, the breakthrough curve is symmetric and described by an error function [Fig. 6.8(a)] (ref. 7,8). If the error function is plotted on arithmetic probability paper, a straight line will be obtained. The dispersion coefficient can be calculated from the slope of the line [Fig. 6.8(b)] (ref. 9). For a density and viscosity unfavorable system, early breakthrough can be observed, especially with large-size

Fig. 6.8. Effluent-composition curve for miscible displacement.

particles. During the current year three student groups from the MIT School of Chemical Engineering Practice have contributed to this work. In their studies, a two-parameter mathematical model¹⁰ was used to describe the breakthrough curves for stable displacements. The apparent dispersion coefficients were determined by matching experimental data to the mathematical model.^{10,11}

Ethanol-water systems were used because they can give all four possible combinations of favorable and unfavorable density and viscosity gradients between displacing and displaced fluids. Several sizes of narrowly distributed spherical glass beads (ranging from 20 to 400 mesh) were packed in a vertical Plexiglas tube. The concentration profile in the mixing zone was monitored by passing the effluent through a Sodev densitometer.

Figure 6.9 shows the mixing length (measured from 5 to 95% of displacing fluid; see also Fig. 6.8)

Fig. 6.9. Effect of particle size and flow rate on mixing length. Equal viscosities, unfavorable density ($\Delta\rho = 0.0031 \text{ g/ml}$).

of a density favorable system (same viscosities) as a function of the downward interstitial fluid velocity for two particle sizes. No appreciable change in mixing length as a function of flow rate was observed in these systems. For a density unfavorable system with $\Delta\rho = 0.031 \text{ g/ml}$ (same viscosities), the mixing length was apparently unchanged for two small particle sizes (Fig. 6.10). However, for the largest particle size, the mixing length decreased with increased flow rate, then remained constant at higher flow rate.

Measurement of dispersion of coefficients of miscible fluids in packed columns may be affected by entrance and exit effects. Therefore, the effect of bed height on the dispersion coefficient for stable displacements was also investigated. Figure 6.11 shows the logarithm of the dispersion coefficient as a function of the logarithm of flow rate for two density and viscosity favorable systems. The dispersion

Fig. 6.10. Effect of particle size and flow rate on mixing length. Equal viscosities, unfavorable density ratio, $\Delta \rho = 0.0015$ g./ml.

Fig. 6.11. Effect of bed height and flow rate on dispersion coefficient. Particle size: 25-30 mesh (closed symbols); 31-25 wt. ethane displacing 16-25 wt. ethane downward ($\Delta \rho = 0.0225$ g./ml.); 25-30 mesh (open symbols); 16-25 wt. ethane displacing 7.5 wt. ethane downward ($\Delta \rho = 0.0125$ g./ml.).

coefficients for two bed heights with large particles (25-30 mesh) were comparable at equivalent flow rates, which indicates that end effects were negligible under these conditions. Also, the slope is close to ~ 1 , which is in agreement with that reported by Blac'well et al.¹¹ However, a significant variation in dispersion

Fig. 6.12. Effect of bed height and flow rate on dispersion coefficient. Particle size: 25-30 mesh (closed symbols); 31-25 wt. ethane displacing 16-25 wt. ethane downward ($\Delta \rho = 0.0225$ g./ml.); 25-30 mesh (open symbols); 16-25 wt. ethane displacing 7.5 wt. ethane downward ($\Delta \rho = 0.0125$ g./ml.).

coefficients with bed height was observed (Fig. 6.12) with small particles (275-300 mesh), suggesting that the end effects cannot be neglected in this case.

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7. Enhanced Oil Recovery Research

Our programs support primarily the micellar-flood approach to enhanced oil recovery. Topics evolved from long-term interest in ion exchange reactions; aqueous and aqueous-organic solution chemistry, including surfactant properties; and treatment of industrial aqueous waste streams. Research discussed in this section includes work aimed at lowering the cost of chemicals used in micellar flooding; study of the phase behavior of aqueous-organic systems pertinent to this process; and basic studies of the structure and properties of surfactant solutions. In Sect. 3 (geosciences) research on the adsorption of inorganic ions on minerals is described. The pertinence to oil recovery is twofold: (1) equilibrium involving alkali metals and alkaline earth ions affect the hardness of formation brines to which surfactants and some mobility-control polymers are sensitive and (2) conditions under which adsorption is low of ions potentially useful as tracers for water flow need to be identified. In Sect. 6, studies of the mixing of fluids of different density and viscosity in flow through packed beds are described, a subject important to the flow of oil formations.

Support for research on the adsorption of inorganic ions on minerals is shared by Oil, Gas and Shale Technology (OGST) and the Office of Nuclear Waste Isolation. Oil, Gas and Shale Technology sponsors the major part of the work discussed in this section, with significant contributions (effect of structural modifications on interfacial properties of surfactants, some of the miscibility studies, and fundamental studies of surfactants) by the Division of Chemical Sciences, Office of Basic Energy Sciences, DOE.

7.1 CHEMICALS FOR ENHANCED OIL RECOVERY

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The cost of chemicals used in micellar flooding is a major deterrent to the implementation of the approach. Requirements vary with the reservoir, the range being perhaps \$5 to \$15 per incremental barrel of petroleum, mainly for surfactants, cosurfactants, and mobility-control polymers. We have been attempting to find ways in which these costs might be lowered by using cheap raw sources of materials from waste streams or elsewhere or by finding cheaper methods of production.

7.1.1. Surfactants

In last year's annual report, initial evaluations were reported of tall oil, a by-product of the pulping of soft woods, as surfactants. Interfacial tensions between hydrocarbons and aqueous solutions, 0.1 *M* in NaCl, pH 9.5, or 0.002 *M* sodium oleate (a prominent component of tall oils and many other natural products) were found to reach a minimum value with *n*-undecane. This value, about 60 millidynes/cm, is, however, more than an order of magnitude higher than the millidyne range considered necessary for efficient oil displacement.

In this report period, the effects of many other conditions have been explored, and the results are summarized in a forthcoming paper. Concentration of sodium oleate up to 0.1 *M* had little effect on position of the minimum or on values of interfacial tension shown in Fig. 6.2 of last year's report. As

shown in Fig. 7.1, increasing pH above 9.5 increased tensions, for reasons not clear. None of the variations in salinity or in the addition of alcoholic co-surfactants resulted in tensions lower than, or as low as, the 60-millidyne value mentioned above.

Fig. 7.1. Interfacial tension vs pH.

Interfacial tensions in the presence of salts of other fatty-acid components of tall oil were, under comparable conditions, even higher as shown in Fig. 7.2. These compounds are also straight-chain 18-carbon acids and differ from sodium oleate, which has a single double bond, only in that sodium linoleate has two double bonds and sodium linolenate has three. The effect of what might be considered relatively minor differences in structure is perhaps even more striking with the *trans* isomer of sodium oleate, sodium elaidate (not a natural product), also included in Fig. 7.2.

These results as well as the frequent references in the literature to effects of branching and other structural effects on interfacial properties suggested that modification of these compounds would be interesting. In particular, substituents in the position alpha to the carboxyl might by steric influence alter sensitivity to divalent ions, thought to be especially deleterious with carboxylate surfactants. Sodium 2-ethyl-*trans*-9-octadecenoate or sodium oleate with an ethyl group on the carbon next to the carboxylate was the first of several planned compounds of this type to be synthesized.

Fig. 7.2. Interfacial tension vs alkane carbon number.

The tendency of aqueous-hydrocarbon systems containing this compound to form emulsions required addition of a cosurfactant to effect phase separations after equilibration. Three volumes of aqueous solution containing 0.01 *M* surfactant, NaCl, and 5% *n*-butanol were pre-equilibrated with one volume of hydrocarbon prior to interfacial tension measurements. With this formulation, the salinity at which lowest interfacial tension was observed was 0.5 *M* NaCl (Fig. 7.3). The interfacial tension under this condition was 0.015 dyne/cm, a factor of about 4 lower than the lowest attained with unmodified sodium oleate.

In contrast to the unmodified sodium oleate, concentration of the surfactant had a substantial effect on both the hydrocarbon for which minimum tension was attained and the value; invariance of the alkane carbon number at which minima occur (though not necessarily the magnitude of interfacial tension at the minimum) is the usual observation with pure surfactants. At 0.05 *M* 2-ethyl oleate, a middle phase appeared in equilibrations with heptane and octane, with much lower interfacial tensions than the values at 0.01 *M* surfactant (Fig. 7.4). A minimum value of about 1 millidyne was observed.

Fig. 7.3. Interfacial tension between *n*-undecane and aqueous solutions of sodium carboxylates as a function of NaCl concentration. (O) 0.001 *M* sodium oleate, 5% *n*-butanol, Δ 0.001 *M* sodium oleate, no added alcohol, pH = 9.8.

Fig. 7.4. Interfacial tensions between alkanes and aqueous solutions of sodium oleate and of sodium 2-ethyl oleate. Measured under the same conditions, 0.5 *M* NaCl, pH 9.8, 30 $^{\circ}$ C, 5% *n*-butanol, 3 volumes aqueous pre-equilibrated with one volume hydrocarbon.

There appeared to be less effect of Ca(II) addition to aqueous solutions of the substituted oleate than to solutions of the unsubstituted oleate under the same conditions, to judge from turbidity (Fig. 7.5); similar comparisons were seen on Mg(II) additions. Additions of Ca(II) to low-concentration formulations of the surfactant, if anything, lowered and broadened the minimum as a function of the alkane carbon number (Fig. 7.6). With 0.002 *M* Ca(II), a third phase

Fig. 7.5. Effect of Ca(II) on solutions of several surfactants.

Fig. 7.6. Effect of Ca(II) on interfacial tensions between aqueous-alkane phases. Initial aqueous 0.01 *M* sodium 2-ethyl oleate, 0.5 *M* NaCl, 5% *n*-butanol, pH 9.8, three volumes aqueous pre-equilibrated with one volume *n*-alkane, 30 $^{\circ}$ C.

appeared, and an interfacial tension much less than without the divalent ion was observed. At 0.004 M Ca^{++} , the middle phase was not apparent, but the interfacial tension was not deleteriously affected by the hardness.

7.1.2 Microbiological Production of Chemicals

Mobility control polymers. At the time of last year's report (see also ref. 4), we had concentrated our effort on glucan-producing biopolymers, primarily because of their superior potential in comparison with the xanthan gums usually projected for this application for production near the point of use. Field operation has a major advantage, in that it is not necessary for shipping economy to prepare a dry product. The alcohol addition process used for precipitation appears to account for about 40% of the cost of the polymer. In addition, redispersion of dry polymer for fluid to be injected is somewhat difficult.

During the past year, our work has been concentrated on phases that are particularly pertinent to in site production, although those phases may also be helpful in centralized operation. Glucan-producing organisms are relatively stable genetically. In addition, they produce acid, which brings the pH of the broth to low values (2 to 3) and discourages contaminating organisms. These characteristics suggest that continuous fermentation might be feasible. We have tested this possibility at bench level on a 10-liter scale. After a 2-d induction period, broth was withdrawn and nutrient added at a rate that corresponded to one-half-day residence time in the fermenter. Fermentation was maintained for nearly 3 months, with a polymer content of withdrawn broth of about 1% and a favorable yield of about 30% from the glucose carbon source.

If comparable results can be attained on a production scale, there are two significant implications. Continuous fermentation, being steady state, is easier to control than batch operation, which requires close monitoring of progress. Less skilled personnel would therefore be required in field operation. Further, batch cycles require about 3 d. The one-half-day residence time implies a factor-of-6 reduction in equipment volume, with perhaps a factor-of-2 reduction in capital costs.

Another major problem is the separation of polymer from unwanted broth constituents, particularly cell fragments and other substances that might plug oil-bearing formations. We have been attempting to adapt filtration techniques to this application.

This work is discussed in Sect. 7.4. Another possible source of plugging is incomplete dispersal of biopolymer aggregates. In the course of enzyme treatments to break down glucan polymer enough for studies of structure by NMR, it was noted that in the initial stages, clarification occurred with little apparent effect on viscosity. In further investigation, we have established significantly lower plugging, as evaluated by the rate of flux decline in passage through 1.2- μm filters (Fig. 7.7), as a function of time of enzyme treatment. Viscosities (Table 7.1) are not deleteriously affected; if anything, there is a small increase initially. We have identified enzymes that attack both xanthan and glucan polymers. This treatment, which may be useful either with dry polymers or in the processing of fermenter broth, is different from previously known enzyme processes to degrade cell fragments.

We have also looked into the possibility of carbon sources that might be cheaper than glucose. Contacts with the objectives of field production are possible.

Fig. 7.7. Plugging rates of 1.2- μm Acropor by Polytran solution as a function of time of enzyme treatment. Hours: 0, 0.2, 0.4, 0.6, 0.8, 1, 2, 4, 6, 8, 24.

Table 7.1 Viscosity of enzyme-treated polymer solution (500 mg/liter) with time: 1 enzyme treatment

Time (hr)	Shear (cP)	
	1.5	2.5
0	1620	602
2	1046	631
4	1039	641
6	1033	621
8	1082	634
24	1075	621

inexpensive or waste materials may not be available near oil fields, and unmetabolized feed may interfere with separating the polymer from the plugging substances. When these objections are not serious, however, several substrates look promising. Results with two are shown in Table 7.2. A 45% yield was obtained in one case with starch. Details may be found in ref. 5.

Disposal of the biomass would be an appreciable expense in field production, perhaps as much as 40¢ lb of polymer. Use of this waste as a feed supplement for cattle would be desirable. We are carrying out on cotton rats, *Sigmodon hispidus*, small-scale feeding tests of rat food supplemented with 10% biomass from glucose fermentation. The digestive process of this species is similar to ruminants. The rats have willingly eaten the mixture, somewhat preferentially to unsupplemented food,

and appear to be flourishing after 2 months of it, with weight gain at least matching that expected from a conventional diet.

Cosurfactants. If micella flooding should be implemented on a large scale, say 1 million barrels per day, production capacity for alcohols used as cosurfactants would probably have to be expanded; it is estimated that production of one incremental barrel of oil would require 4 to 10 lb. It therefore seems an appropriate time to reexamine methods of production. Fermentation once was the primary route for production of three- and four-carbon alcohols but has been largely displaced in this country by synthesis from petrochemical feedstocks. The reasons for the change were only partly economic, for example, the loss of the molasses supply from Cuba. We have begun to evaluate the use of waste carbohydrates as carbon sources and the use of alternatives to conventional batch fermentation.

The organisms tested were five industrial cultures of *Clostridia*, a class used for anaerobic production of alcohols by Weizmann and others before World War I. Small-scale batch fermentations were carried out with a number of carbohydrates that were typical of components of waste streams. In Table 7.3, results are presented for one of the more interesting of these, *Clostridium butylicum* NRRI B592. The content of ethanol, acetone, and butanol after cessation of gas production (at least 4 d) was assayed by gas chromatography.

This organism is one of the strains developed for the production of solvents from molasses between the world wars and, consequently, is adapted for high optimum concentrations of carbohydrates. This is reflected in the fact that total solvent production is highest in most cases for 10% feeds; the yield approached theoretical (38 to 40% for monosaccharides) for dextrin, sucrose, and fructose. With ribose and arabinose and with many other carbohydrates converted by some of the other strains, production was highest at lower feed concentrations. The NRRI B592 also has an unusual ability to ferment xylose and cellulose, which were difficult substrates for the others. With respect to the individual products, butanol and acetone concentrations were parallel, and butanol in general accounts for the largest share of the total solvent production. This organism has promise for use in fermentation of wood wastes, which contain xylan and cellobiose, and of dairy wastes, which contain lactose, as well as, perhaps, of starch-containing wastes. Results with this and the other strains are described in a forthcoming paper.

Table 7.2 Production of glucans

Organism	Time (d)	Polymer (g/liter)
a. From starch at 26°C (feed: 40 g/liter starch)		
ATCC 15263	4	10.29
ATCC 15265	4	4.2
ATCC 15196	4	13.57
NRRI 3129	5	8.15
NRRI 3006	5	18.20
b. From hydrolyzed sugar beet pulp at 26°C (feed: 50 g/liter pulp)		
ATCC 15263	4	2.21
ATCC 15265	4	2.02
ATCC 15196	4	2.16
NRRI 3129	5	0.93
NRRI 3006	5	8.14

Table 7.3. Production of solvents by NRRL B592

Carbohydrate (% w/v)	Ethanol (% w/v)			Acetone (% w/v)			Butanol (% w/v)			Total (% w/v)		
	2.5	5.0	10.0	2.5	5.0	10.0	2.5	5.0	10.0	2.5	5.0	10.0
Arabinose	trace	0.10	0.06	trace	0.20	0.30	trace	1.32	1.38	trace	1.62	1.74
Galactose	0.11	0.07	0.02	0.14	0.15	0.91	trace	0.23	0.12	0.26	0.13	0.15
Xylose	0.04	0.08	0.02	0.01	0.15	0.05	0.04	0.36	0.03	0.09	0.54	0.08
Xylan	0.05	0.04	0.04	0.01	0.02	0.36	0.10	0.26	2.19	0.16	0.31	2.50
Fructose	0.09	0.02	0.26	0.13	0.20	0.75	0.67	0.74	2.92	0.90	1.02	1.95
Glucose	0.15	0.18	0.11	0.17	0.28	0.52	0.88	1.16	1.23	1.20	1.62	1.98
Cellobiose	0.05	0.12	0.71	0.15	0.44	0.64	0.52	1.52	1.32	0.72	2.00	2.87
Lactose	0.06	0.13	0.34	0.10	0.11	0.69	0.60	0.47	1.81	0.76	0.72	2.89
Sucrose	0.08	0.07	0.22	0.16	0.13	0.82	0.95	0.73	2.66	1.07	0.98	1.75
Inulin	0.06	0.09	0.16	0.12	0.25	0.86	0.66	1.01	2.06	0.84	2.25	0.00
Celulose	0.11	0.07	0.08	0.02	0.02	0.02	0.12	0.05	0.14	0.25	0.15	0.00

Tests were also carried out with a fixed-film bioreactor configuration in which the organisms were grown on packing in a small column and a solution of the feed passed upflow past them. Yields were much lower, total solvent production from 5% sucrose by NRRL B592, for example, being only 0.33 % w/v, in comparison with 0.98, listed in Table 7.3. In addition, yield of the more valuable product, butanol, was relatively far less.

We have been attempting to ferment wood wastes, including weak-acid sulfite liquor, a condenser effluent, a thermomechanical effluent, and wood molasses. Weak-acid sulfite liquor looks the most promising in that the organisms are able to ferment dilutions of the normally produced concentration. However, some organism selection will be required for satisfactory butanol production. We are performing experiments to select strains appropriate for this use.

7.2 MISCIBILITIES OF AQUEOUS-HYDROCARBON SYSTEMS

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The micellar flood process for enhanced oil recovery involves very complex phenomena. Petroleum displacement is strongly dependent on the achievement of low interfacial tensions between aqueous and hydrocarbon phases. Occurrence of ultralow interfacial tensions, of the order of a millidyne, are in turn frequently correlated with certain aspects of phase behavior, for example, with appearance of a third, surfactant-rich, phase or with distribution coefficients of the surfactant between aqueous and hydrocarbon phases of one. The conditions under which such behavior occurs are likely to be highly specific: a narrow range of average hydrocarbon molecular weight, of salinity, of surfactant characteristics, of type and concentration of alcoholic cosurfactant addition, etc. To help understand some of the phenomena we have undertaken studies of some simpler systems in which micelles are not formed, for example, systems containing a hydrocarbon and an aqueous solution of a model surfactant. We have chosen benzene-sulfonates with short aliphatic side chains as the model surfactants because sulfonates are typical components of petroleum sulfonates commonly used in the micellar flood process. We hope by this approach to uncouple aspects of behavior arising from the chemical nature of the systems from behavior resulting from micelle formation.

1. Co-op student, University of Tennessee, Knoxville.
2. *Chem. Div. Annu. Prog. Rep. Mar. 31, 1977, ORNL-5297.*
3. W. H. Baldwin and G. W. Neal, "Colloidal Properties of Sodium Carboxylates," *Symposium on Chemistry of Oil Recovery, Anaheim, 1978*, American Chemical Society Symposium Series, American Chemical Society, Washington, D.C., in press.
4. W. I. Griffith and A. L. Compere, *Dev. Ind. Microbiol.* **19**, 609 (1978).
5. A. L. Compere and W. I. Griffith, *Dev. Ind. Microbiol.* **19**, 601 (1978).
6. A. L. Compere and W. I. Griffith, "Evaluation of Substrates for Butanol Production," to be published in *Dev. Ind. Microbiol.*

7.2.1 Solubility of Toluene in Aqueous Substituted Sodium Benzenesulfonates

The solubility of toluene in aqueous solutions of a number of sodium benzenesulfonates at 55°C as determined by gas chromatography is shown in Fig. 7.8. This temperature was chosen to allow measurements over a wider range of sulfonate concentration than is possible at room temperature. At low concentrations of the benzene and toluene sulfonates, there is a distinct salting-out of the toluene. At higher concentrations of these sulfonates, the effect is mostly salting-in. The extent of salting-in, especially with the more highly substituted benzenesulfonates, is substantial. With diisopropylbenzenesulfonate, nearly a mole of toluene per mole of the sulfonate in 2.5 M sulfonate. In all cases, salting-in increases with the number of carbons in the alkyl side chains. A paper describing these results has been submitted for publication.

Fig. 7.8. Solubility of toluene in aqueous solutions of various sodium benzenesulfonates (55°C).

7.2.2 Toluene in 'Aqueous Substituted' Sodium Benzoates

Many of our phase boundary studies in the enhanced oil recovery program have been carried out using various substituted sodium benzenesulfonates as the model surfactants. However, we are also investigating miscibility relationships in systems con-

taining substituted sodium benzoates as the model surfactant instead of sodium benzenesulfonates.

The solubility of toluene in aqueous solutions of a number of sodium benzoates as determined by gas chromatography at 55°C is shown in Table 7.4. At any given salt concentration, the solubility of the toluene increases with the number of alkyl carbons attached to the benzene ring of the carboxylate.

Table 7.4. The solubility of toluene in aqueous solutions of substituted sodium benzoates at 55°C.

Substituted sodium benzoate	Concentration of sodium benzoate (mol/kg H ₂ O)	Solubility of toluene (mol/kg H ₂ O)
Benzene	0.05	0.013
	0.07	0.015
	0.10	0.017
	0.15	0.021
	0.20	0.025
	0.25	0.030
2,4-Dimethylbenzoate	0.53	0.015
	0.77	0.022
	1.24	0.036
	1.48	0.048
	2.52	0.126
2,4,6-Trimethylbenzoate	0.84	0.038
	1.60	0.079
	2.17	0.163
p-t-Butylbenzoate	0.50	0.064
	0.96	0.203
	1.59	0.57
	2.17	1.14

Comparison of these results with those shown in Fig. 7.8 indicates that the solubility of toluene is somewhat higher in both aqueous sodium benzoate and sodium 2,4-dimethylbenzenecarboxylate solutions than in the corresponding sodium benzenesulfonate solutions at all concentrations of the salts. However, the solubility of toluene is about the same in either aqueous sodium 2,4,6-trimethylbenzenesulfonate or sodium 2,4,6-trimethylbenzenecarboxylate solutions at 55°C. A dramatic change occurs in the solubility relationships in these systems when four alkyl carbons are present on the benzene ring of the salt. The solubility of toluene is almost three times as great, at all concentrations of salt, in aqueous sodium p-t-butylbenzenecarboxylate than in sodium p-cymenesulfonate. In fact the solubility of the toluene is almost as high in the p-t-butylbenzenecarboxylate solutions (four alkyl carbons on the benzene ring) as in sodium 2,5-diisopropylbenzenesulfonate solutions with six alkyl carbons on the benzene ring of the salt.

Further miscibility studies using substituted sodium benzoates as the model surfactant are under way.

7.2.3 Hydrocarbon-*n*-Butanol-Aqueous Sodium Cymenesulfonate

We have discussed results with water, hydrocarbons, and protosurfactants; we now shall deal with systems with added alcohol. All classes of components typical of micellar floods are now represented, except inorganic salt. We deal here with the miscibilities of a number of hydrocarbons in the presence of a single alkylbenzenesulfonate.

Miscibility relationships have been studied in systems containing 1-butanol as the cosolvent, a 2.5 *m* aqueous solution of sodium *p*-cymenesulfonate (2-methyl, 5-isopropylbenzenesulfonate, the sulfonate taken to be at the one position) as the model surfactant, and a series of hydrocarbons, including both alkanes and alkylbenzenes. Some miscibility diagrams for alkanes are presented in Fig. 7.9, with data for no sulfonate in the aqueous phase (designated "H₂O") included for comparison. The region above the curves represents the compositions for which the systems are completely miscible, and the region below, two-phase systems. Sodium cymenesulfonate at 2.5 *m* makes *n*-butanol and water miscible. The miscibility curves for the various hydrocarbons are rather symmetrical, and the area representing complete miscibility decreases as the alkane molecular weight increases. Curves for alkyl-substituted aromatic hydrocarbons indicate similar behavior.

A comparison of alkanes with one another and with alkyl-substituted benzene is made in Fig. 7.10, in which the minimum amount of *n*-butanol required to produce miscibility for a 1:1 weight hydrocarbon:2.5 *m* aqueous sodium *p*-cymenesulfonate is plotted versus the number of alkyl carbons in the compound.

For the alkanes the amount of 1-butanol required increases from about 30% for hexane to 60% for pentadecane. For the alkylbenzenes the corresponding amounts of 1-butanol are about 22% for benzene (no alkyl carbons) to 45% for phenyldecane. The two points at four carbons on the side chains represent *p*-cymene (triangle) and *n*-butylbenzene (circle). It appears that the total number of alkyl carbon atoms in the side chains is more important than the distribution of the carbon atoms in the phase boundary relationships. It is of interest that hexylbenzene and hexane require about the same amount of *n*-butanol for miscibility but that, at greater alkyl

Fig. 7.9. Phase relationships of several hydrocarbon-*n*-butanol-2.5 *m* aqueous sodium *p*-cymenesulfonate systems (25°C).

Fig. 7.10. Minimum amount of *n*-butanol required to produce miscibility at 1:1 wt % alkane (alkylbenzene):2.5 *m* aqueous sodium *p*-cymenesulfonate).

chain length, the alkanes require less *n*-butanol for miscibility than benzene substituted with the same alkane.

7.2.4 Hydrocarbon-Butyl Carbitol-Aqueous Salicylate

Here we discuss miscibility relationships in systems containing an aqueous solution of sodium salicylate, *n*-butyl carbitol ($C_4H_9OCH_2CH_2OCH_2CH_2OH$), and a series of hydrocarbons that included both alkanes and alkylbenzene. The phase boundary curves obtained in these two series with 2.5 *m* sodium salicylate solution are shown in Figs. 7.11 and 7.12. The curves have been plotted on a water basis; i.e., the

Fig. 7.11. Phase boundary curves, 2.5 mol sodium salicylate per kilogram H_2O .

weight percentages in the figures represent the three components: hydrocarbon, *n*-butyl carbitol, and water, with 2.5 mol of sodium salicylate present per kilogram of water, rather than representing the percentage of the aqueous component as water plus sodium salicylate. Phase boundary diagrams were also obtained with aqueous 1.0 and 6.0 *m* solutions of sodium salicylate.

Values of the minimum weight fraction (water basis) of butyl carbitol necessary to produce miscibility in 1:1 weight mixtures of hydrocarbon and the aqueous solutions are shown in Table 7.5.

In the systems with benzene, toluene, 1-phenylethane, and *p*-xylene as the hydrocarbons, less alcohol is required to produce miscibility at all concentrations of sodium salicylate than in water. In the remaining systems, the presence of sodium salicylate in the aqueous phase has little effect on the minimum weight fraction of *n*-butyl carbitol necessary for miscibility. In most cases, slightly more cosurfactant seems to be required at the highest concentration of sodium salicylate.

7.2.5 Toluene-*n*-Butanol-Aqueous Substituted Benzenesulfonates

We reported last year (ref. 4, Fig. 5.6) some miscibility diagrams of this type of system, with concentrations of 2.5 *m* sodium benzenesulfonates substituted with up to four alkyl carbons. These illustrate the effect for a single hydrocarbon of changing the degree of alkyl substitution on the protosurfactant component. We have extended the comparison to six alkyl carbons. The area of miscibility continued to increase with increasing alkyl substitution, and the curves remained symmetrical. A comparison between compounds is presented in Fig. 7.13 in terms of the amount of alcohol required to produce miscibility at three different ratios of hydrocarbon-to-aqueous component. From toluene sulfonate to the highest alkyl substitution reported, 2,5-diisopropylbenzenesulfonate, *n*-butanol required decreases essentially linearly with the number of alkyl carbons. The distribution of the alkyl carbons on the ring seems to be of secondary importance.

Fig. 7.12. Phase boundary curves, 2.5 mol sodium salicylate per kilogram H₂O.Table 7.5. Minimum weight fractions of *n*-butyl carbitol necessary to produce miscibility in 1:1 wt % mixtures of hydrocarbon and aqueous solutions of sodium salicylate

Hydrocarbon	Sodium salicylate (mol/kg H ₂ O)			
	0	1.0	2.5	6.0
Benzene	0.557	0.380	0.319	0.319
Toluene	0.529	0.375	0.350	0.357
1- <i>o</i> -Ethane	0.493	0.400	0.382	0.400
<i>p</i> -Xylene	0.491	0.405	0.384	0.402
1- <i>o</i> -Butane	0.461	0.458	0.462	0.473
1- <i>o</i> -Hexane	0.518	0.522	0.529	0.544
Cyclohexane	0.527	0.532	0.531	0.557
1- <i>o</i> -Heptane	0.550	0.553	0.564	0.568
1- <i>o</i> -Octane	0.593	0.597	0.598	0.607
1- <i>o</i> -Nonane	0.638	0.639	0.640	0.641
1- <i>o</i> -Decane	0.659	0.661	0.663	0.665
<i>n</i> -Heptane	0.681	0.686	0.688	0.697
<i>n</i> -Nonane	0.734	0.741	0.734	0.748
<i>n</i> -Undecane	0.783	0.785	0.786	0.792
<i>n</i> -Tridecane	0.814	0.815	0.822	0.828
<i>n</i> -Pentadecane	0.845	0.843	0.844	0.852
<i>n</i> -Hexadecane	0.859	0.861	0.863	0.868

Fig. 7.13. Amount of *n*-butanol required to produce miscibility between 2.5 *m* aqueous solutions of sodium alkylbenzenesulfonates and toluene (25°C).

With 1 *m* sulfonate (Fig. 7.14), behavior becomes more complex. More alcohol is required for miscibility for a given sulfonate than at 2.5 *m*, as one might expect from the systems without alcohol (Sect. 7.2.1). However, although the curves are again fairly symmetrical up to three alkyls on the sulfonates, they

Fig. 7.14. Effect of substituents on phase relations in toluene-*n*-butanol-aqueous sulfonate systems (1.0 *m* sodium sulfonate, 25°C).

become highly asymmetric in the hydrocarbon-rich region at four and above. The reason for this pattern is not clear.

7.2.6 Toluene-Butyl Cellosolve-Aqueous Substituted Benzoates

Phase boundary relationships have been investigated in systems containing toluene, butyl cellosolve (2-butoxyethanol), and aqueous solutions of three different substituted sodium benzoates. The minimum amounts of butyl cellosolve necessary to produce miscibility in 1:1 weight mixtures of toluene and the aqueous sodium benzoate solutions as a function of salt concentration are shown in Table 7.6. At any given salt concentration, the amount of butyl cellosolve necessary to produce miscibility of the toluene and aqueous solution decreases as the number of alkyl carbons on the benzene ring of the salt increases. At both 1.0 and 2.0 *m*, however, the decrease is very slight between the sodium dimethylbenzoate and the sodium trimethylbenzoate.

Table 7.6. Minimum amounts of butyl cellosolve necessary to produce miscibility in 1:1 wt % mixtures of toluene and aqueous substituted sodium benzoate solutions

Salt	Concentration of salt (mol/kg H ₂ O)	Butyl cellosolve wt %
Sodium dimethylbenzoate	1.0	33.5
	2.0	28
Sodium trimethylbenzoate	1.0	33.0
	2.0	27
Sodium <i>p</i> - <i>t</i> -butylbenzoate	1.0	28
	2.0	22.5
	2.5	21

7.2.7 Toluene-Propanol-Aqueous Alkali-Metal or Alkaline-Earth Salts

Micellar-flood recipes usually contain inorganic salts, and in any case injected banks will mix with formation brines containing various ions. We have

not yet investigated model systems containing water and representatives of all classes of organic components plus salts, but last year we reported results on more limited systems. Some further observations involving salts are described here.

Phase boundary relationships have been investigated in a number of systems containing toluene, propanol (both 1-propanol and 2-propanol), and aqueous solutions of various inorganic salts. The inorganic salts include LiCl, MgCl₂, and CaCl₂; LiClO₄, NaClO₄, and Mg(ClO₄)₂; and NaI and NH₄SCN. Results obtained in the systems containing aqueous solutions of the chlorides and perchlorates will be mentioned first, followed by a discussion of the systems containing the NaI or NH₄SCN. Although some of these salts are not found in formations, the effect on miscibilities of ions having different salting-in or -out properties is of interest.

In the toluene-2-propanol aqueous perchlorate systems, the amount of 2-propanol required to produce miscibility is not much different for 0.5 *m* to 4.0 *m* solutions of lithium, magnesium, or calcium perchlorates. In all three systems the phase boundary diagrams are symmetrical, and about 50 wt % 2-propanol is required to produce miscibility in 1:1 weight mixtures of toluene and the aqueous solutions. With systems containing toluene, 2-propanol, and aqueous solutions of lithium or magnesium chlorides, on the other hand, salting-out occurs. In both cases increasing amounts of 2-propanol are required to produce miscibility as the salt concentration of the aqueous phase increases. About 68 wt % 2-propanol is required for 50:50 wt % mixtures of toluene and 2 *m* solutions of either lithium or magnesium chloride.

Comparisons of systems containing toluene, 1-propanol, and aqueous solutions of the various inorganic salts are shown in Fig. 7.15. All results are presented on a water basis; that is, in each case reference is made to the minimum amount of propanol necessary to produce miscibility at 1:1 weight ratio toluene:H₂O. These values have been taken from the complete phase boundary curves for each system.

In the system containing LiCl solutions, salting-out (here the term refers to the increase of alcohol required for miscibility) increases with concentration in the range measured, up to 6.0 *m*. In the system containing CaCl₂, salting-out also occurs at all concentrations of CaCl₂ but reaches a maximum near 2.0 *m*. With aqueous solutions of LiClO₄, Mg(ClO₄)₂, and Ca(ClO₄)₂, salting-in again occurs near 2.0 *m*;

Fig. 7.15. Amount of *n*-propanol required to attain miscibility between toluene and water at 1:1 wt ratio as a function of concentration of salts.

however, at NaClO₄ concentrations of 4.0 to 8.0 *m* salting-out occurs, the effect increasing with concentrations. Thus miscibility behavior in these latter systems contrasts with that mentioned above for the corresponding systems with 2-propanol as the cosolvent, whereas varying the concentration of the salt in the aqueous phase had practically no effect on miscibility.

In the case of the systems containing toluene, propanol, and aqueous solutions of sodium iodide or ammonium thiocyanate, measurements were made at salt concentrations of 0.5, 1.0, 2.0, and 4.0 *m*. It was found that, with 1-propanol as cosolvent, aqueous ammonium thiocyanate causes salting-in at all of these concentrations, but, with 2-propanol as cosolvent, salting-in occurs at the lower two concentrations, no change (computed with water) occurs at 2.0 *m*, and salting-out occurs at 4.0 *m*. Aqueous sodium iodide at all concentrations causes salting-in when 1-propanol is used as the cosolvent. The amount of salting-in increases to about 9 *m* sodium iodide and then levels off. With 2-propanol as the cosolvent, however, no change (compared to water) occurs at sodium iodide concentrations of 0.5 and 1.0, salting-in occurs at 2.0 *m*, and dramatic salting-out occurs at 4.0 *m*. Maximum salting-in seems to occur at about 2 *m* sodium iodide.

7.2.8 Discussion

Certain trends are apparent in these results. Alkyl-substituted sodium benzenesulfonates or carboxylates increase solubility of toluene in water, the effect

being greater with increasing sulfonate or carboxylate concentration and with an increasing number of alkyl carbons on the benzene ring. Carboxylates appear to be slightly more effective in promoting miscibility than are sulfonates. At least with low degrees of substitution, the solubilization seems primarily to depend on the number of alkyl carbons rather than on their distribution on the ring. Parallel trends hold with alcohol additions; that is, the amount of alcohol needed to effect miscibility of a hydrocarbon-aqueous system is usually less for a given concentration of sodium alkylbenzene-sulfonate or carboxylate for higher degrees of alkyl substitution on the sulfonate or carboxylate (the rule breaks down at lower concentration) and less for a given protosurfactant with increasing concentration of the sulfonate or carbonate. On the other hand, more alcohol is required for miscibility with a given protosurfactant when the molecular weight of alkane hydrocarbons is higher or when aromatic hydrocarbons are substituted with more alkyl carbons.

These solubilization trends occur under conditions for which micelle formation seems unlikely. The effects of inorganic salts are complicated, even in the systems, relatively simple in comparison with the micellar flood compositions studied so far. The patterns of salting-in and salting-out observed with water and a single organic component appear not to parallel closely patterns observed with water-hydrocarbon-alcohol systems, and isomeric alcohols can vary considerably in their effect on solubility for a given system.

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7.3 VISCOSITIES OF SOLUTIONS OF CETYLTRIMETHYLAMMONIUM BROMIDE-KBr-H₂O

D. H. Smith

Viscosity measurements have been used to study structural changes in micellar solutions of the system cetyltrimethylammonium bromide-KBr-H₂O (ref. 1).

The solutions studied contained up to 17 wt % cetyltrimethylammonium bromide (CTAB) at 0 wt % KBr and up to 30 wt % KBr at 0.03 wt % CTAB; inter-

mediate concentrations of surfactant and salt were also studied (Fig. 7.16). Measurements were made at 25 and 35 °C with a Brookfield viscometer. Four different shear rates were used, and viscosities as high as 40 cP were measured.

Fig. 7.16. Dependence of the viscosity on KBr concentration of various solutions of constant CTAR molality.

It is known from light-scattering² and other measurements³ that large viscosity increases of the type reported here result from the formation and growth of rod-like, polar-group-external micelles. The formation of rod-like micelles at high surfactant conditions (10–30 wt %) in salt-free solutions has been attributed to crowding among hydrated, spherical micelles at high micelle concentrations and their subsequent deformation, even though for CTAB water solutions this hypothesis made it necessary to postulate unusually thick layers of water of hydration for the micelles.⁴ The present measurements show that, with the addition of KBr, comparably large viscosities can occur when the CTAB concentration is as little as 1 wt % or less. Hence the sphere-rod transformation can no longer be attributed to intermicellar packing forces.

An empirical expression for the viscosity⁵ which contains the counter-ion concentration as well as the organic ion concentration⁶ has been given, and the sphere-rod transition has been interpreted in terms of intermolecular forces and the elastic-continuum theory of ordered liquids.

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7.4 SMALL-ANGLE X-RAY SCATTERING OF "INVERTED" MICELLAR SOLUTIONS OF CETYLTRIMETHYLAMMONIUM BROMIDE-H₂O-PENTANOL

D. H. Smith¹ R. W. Hendricks¹
J. S. Lin²

Scattering curves and their preliminary analysis have been reported¹ for the small-angle x-ray scattering (SAXS) of solutions of inverted micelles of the surfactant CTAB in the ternary system CTAB-H₂O-pentanol at $26 \pm 1^\circ\text{C}$. The data were collected with the ORNL 10-m SAXS camera at a specimen detector distance of 1.2 m and cover the angular range 5–60 milliradians. Advantages of this system are pinhole collimation and a two-dimensional position-sensitive detector. In all cases the scattering intensity was independent of azimuthal angles in the detection plane, showing that the samples were true, isotropic solutions.

For a series of solutions containing 1.05 g CTAB/g water and decreasing amounts of pentanol, a scattering peak was observed only when the pentanol concentration was less than $70 \pm 2\text{ wt } \%$, indicating that a critical micelle concentration (CMC) for inverted micelle formation occurs at this concentration. The half-width of the scattering peak and the inverse of the scattering angle at the peak maximum both increased linearly with decreasing pentanol concentration between the CMC and the phase boundary. These data show that the micelle size increases with increasing concentrations of water and surfactant at a constant water-to-surfactant ratio.

For a series of solutions containing 0.92 g CTAB/g pentanol, intense scattering was observed at all concentrations between the water-poor and water-rich phase boundaries. The half-width of the scattering peak was virtually constant from 16 to 47 wt % water but increased with decreasing water concentration below 16 wt % water. This behavior supports previous suggestions that the structure at very low water concentrations differs from that of the inverted micelles present at higher water concentrations. The inverse of the scattering angle at the peak maximum increased linearly with increasing water concentration, but the slope (0.49 mrad/wt % H₂O) between 9 and 38 wt % water was markedly different

from the slope (0.90 mrad/wt % H₂O) between 38 and 48 wt % water. In contrast to the peak width changes, this latter behavior does *not* reveal a structural change at very low water concentrations; but it does indicate that the structure in the salient, which extends toward the water-rich corner of the phase diagram, may differ from the inverted micelle structure present at intermediate water concentrations.

¹ Metals and Ceramics Division.

² D. H. Smith, R. W. Hendricks, and J. S. Lin, "Small-Angle X-Ray Scattering of 'Inverted' Micellar Solutions of Cetyltrimethylammonium Bromide-H₂O-Pentanol," presented at 52nd Annual Colloid and Surface Science Symposium, Knoxville, Tenn., June 1978.

7.5 CONCENTRATION AND TEMPERATURE DEPENDENCE OF THE COUNTERION SELF-DIFFUSION COEFFICIENT IN SURFACTANT SOLUTIONS

D. H. Smith

The concentration and temperature dependence of the counterion self-diffusion coefficient D_{w-} was measured for aqueous solutions of hexadecyltrimethylammonium bromide (CTAB) from below the critical micelle concentration (CMC, 0.036 wt %) to 17.3 wt % CTAB. The radiometric porous frit method was used. The concentration dependence of D_{w-} and of the activation energy for self-diffusion both apparently exhibited extrema near the CMC. However, above about 1% CTAB, D_{w-} was a linear function of the concentration, and this concentration dependence continued even at high surfactant concentrations at which the viscosity of the solution became very large. The data were analyzed in terms of a "two-site" model that had earlier been applied in the literature to the NMR linewidths of Br⁻ in CTAB solutions. It was shown that, within the model, the previously accepted interpretation of the linewidths was inconsistent with the bromide self-diffusion coefficient. This finding indicates that the second critical concentration in aqueous surfactant solutions marks a structural change in the counterion binding to the micelle, rather than a simple increase in the degree of counterion association as previously reported.

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8. Molten Salt Systems

8.1 MOLTEN CARBONATE FUEL CELL PROGRAM

8.1.1 Electrolysis and Relaxation in $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$

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In an operating molten alkali carbonate fuel cell, the electrode reactions may be represented as

or

Carbonate ion is thus the electroactive constituent in the melt, being produced at one electrode and consumed at the other. The net current can be represented in terms of the migration of Li^+ and K^+ relative to CO_3^{2-} so that a knowledge of the transport properties is important. If a sufficient difference exists between the electrical mobilities of the nonelectroactive constituents (Li^+ and K^+ ions), a variation in the ratio of these ions, that is, concentration gradients, might develop in the melt. The physical properties of the melt which are concentration dependent would change, and in an extreme case this phenomenon could lead to precipitation of Li_2CO_3 or K_2CO_3 (ref. 3). Computations have indicated the conditions under which such concentration gradients could occur. To test the computations as well as to obtain direct experimental measurements of changes occurring in the electrolyte and in the electrodes, an electrolysis apparatus was designed and constructed as shown in Fig. 8.1. The tiles containing LiKCO_3 in LiAlO_2 (~50 wt %) were disks about 0.2 cm thick and 2 cm in diameter.

Porous nickel disks were pressed against the tile faces by perforated stainless steel current-collector disks. The temperature at each electrode was monitored by the thermocouples as illustrated. The porous nickel disks were oxidized in situ at 873° K to catalytically active NiO (oxygen) electrodes by the operating gas mixture $\text{CO}_2\text{:O}_2$ (67-33 vol %). The use of identical electrodes and the same gas mixture for each electrode eliminated the need for wet seals. The potential changes resulting from current flow thus are measured relative to the very small bias potential between nearly identical electrodes rather than relative to a varying much larger potential difference resulting from the different electrode reactions of fuel and oxidant gases. Constant electrolysis current was supplied by a PAR potentiostat-galvanostat-coulometer operated in the galvanostatic mode. A series of electrolyses was carried out, varying the duration of electrolysis and the magnitude of the current. On termination of electrolysis at a fixed current for a fixed time (or specified number of coulombs), the open circuit potential difference between the electrodes was monitored with time.

Table 8.1 shows results obtained at a constant current density of 200 mA/cm when the electrolysis time varied from 5 to 100 min. The first column lists the difference in potential between the two electrodes referred to the equilibrium open circuit potential 30 s after cessation of electrolysis. This period of time is assumed, somewhat arbitrarily, to allow for double-layer relaxation to be completed. It may be seen that the values of ΔE increase steadily with duration of electrolysis up to 60 min and then seem to decrease slightly. The last column shows the time needed for the emf to relax to one-half the initial value. This relaxation time τ seems to be approximately constant, 10 min, except for cases where electrolysis was carried out longer than 60 min.

Table 8.2 shows data obtained at a constant electrolysis time but at various current densities. The left column lists the magnitude of the open circuit potential at cessation of a 60-min electrolysis, referred

Fig. 8.1. Electrolysis cell.

Table 8.1. Emf 30 s after cessation of electrolysis at 200 mA/cm² and time required $\tau_{1/2}$ to relax to half that value

ΔE_{30} (mV)	Electrolysis time (min)	$\tau_{1/2}$ (min)
4.2	5	8
6.0	10	10
6.5	15	10
8.5	20	9.8
9.4	30	10
9.6	40	11
9.4	50	10.2
10.3	60	10.1
9.0	70	15.0
7.5	100	20

Table 8.2. Emf after electrolysis for 60 min at differing current densities and relaxation time $\tau_{1/2}$ to relax to half that value

ΔE_0 (mV)	I (mA/cm ²)	$\tau_{1/2}$ (min)
5.0	28.6	10.1
5.5	57.1	9.9
5.1	85.7	9.8
6.9	114.3	9.9
8.1	142.9	9.6
8.7	171.4	10.0
10.3	200	10.1
11.3	228.6	10.0
12.7	257.1	10.0
10.7	285.4	9.8

again to the potential at equilibrium. The second column gives the nominal current density of each experiment, and in the right column the emf half-time values are listed correspondingly. Again, the emf increases with current density, and the time at which it reaches one-half its initial value is very near 10 min except for the last case described.

These data are illustrated in the experimental curves shown in Figs. 8.2 and 8.3.

A model for transport processes in molten salt fuel cells and batteries has been applied to the

computation and simulation of relaxation processes taking place in molten carbonate fuel cells. The results of the computation are illustrated by comparison between calculated curves and experimental points. A typical example is shown in Fig. 8.4 for a current density of $I = 200 \text{ mA/cm}^2$ and an electrolysis time of 20 min. The theoretical concentrations are calculated from a numerical solution of the diffusion-migration equation for electromigration and interdiffusion of the CO_3^{2-} and converted into the emf of the corresponding concentration cell. In

Fig. 8.2. Effect of current density on open potential difference between electrodes following electrolysis for 60 min. Current densities during electrolysis, mA/cm^2 : 28.6 (lowest curve), 51, 86, 114, 143, 171, 200, 229, 257, 286 (upper curve).

Fig. 8.3. Effect of electrolysis at fixed current density, 200 mA/cm^2 on open circuit potential difference after electrolysis.

Fig. 8.4. Comparison between calculated and experimental emf relaxation curves.

the computation, the interdiffusion coefficient was taken as $D = 3.5 \times 10^{-6} \text{ cm}^2/\text{s}$. This value of D probably is low for free electrolyte but is probably not far from the correct value in the porous matrix. The ratio of the mobilities of Li^+ and K^+ was taken as $U_{\text{Li}}:U_{\text{K}} = 1.45$. The left part of the curve shows the theoretical building up toward a steady-state concentration and emf. This rise and leveling off should correspond to the envelope of the curves of emf at cessation of electrolysis, experimental values of which are shown in Fig. 8.3 and Table 8.1. The slight downturn seen experimentally is not predicted by the model and may correspond to other electrode processes.

The predicted relaxation curve follows closely the experimental points for about 10 min, the time at which half the value of the initial potential difference

(referred to the open circuit potential) is reached. Thereafter the computed curve relaxes much faster than the experimental emf. Similar behavior is observed for data obtained at the other current densities and times. The mobility ratios required to reproduce the first 10 min of the experimental relaxation curves decrease as the current density increases but remain of a magnitude that is physically reasonable. Since the mobility ratios should not be functions of current density, this apparent variation may reflect composition dependence both of mobilities and of diffusion coefficients, convection, and other uncertainties in the model such as neglect of porosity of the electrodes and neglect of thermal effects at the electrodes. Fitting of the model to the relaxation data at very long times would require a much lower value of the interdiffusion coefficient, of

charge, but is thought to be responsible for the electrocatalytic activity of NiO fuel cells. Significant literature exists on the transport in the intercalated oxides to an oxidized state, and the transport of electrons and holes in the undoped oxides, but there is no published information on the transport of electrons and holes in the doped oxides. The purpose of this work is to study the transport of electrons and holes in the doped oxides.

Experiments are under way on single crystals of NiO having a (62 ± 3) mol % Li for various conditions differing oxidizing atmosphere, at an operating fuel cell. The extent of oxygen lithium penetration will be determined by techniques such as SEM and wavelength flame emission spectroscopy. In addition, single crystals were submerged in the precover gas of CO:O₂ (2:1) and held at 923°K for 100 h. Thermal analysis gave the crystals to contain 50 ppm lithium, or correspond to 0.06 mol % replacement Li. It is not known yet whether the uniformly distributed through the crystal on the surface. This concentration, if distributed, is insufficient to significantly electronic conductivity of NiO. Further experiments are under way under controlled oxidizing and temperature in an attempt to define substitution equilibrium.

$$\frac{1}{2}\text{O}_2 + \frac{1}{2}\text{Li}_2\text{CO}_3 + \text{NiO-Ni}^{2+}\text{O}^{2-}\text{Ni}^{2+}\text{O}^{2-} \rightarrow \text{NiO-Li}^{+}\text{ONi}^{2+}\text{O-NiO}$$

8.1.2 NiO Cathodes in $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$

H. R. Bronstein J. Braunstein

and ultimately to prepare such an electrode defined surface area to study cathodic kinetics in molten carbonates.

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8.1.3 Concentration Cells with Transference in $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$

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H. R. Bronstein J. Braunstein

Among the needed transport coefficients in molten carbonate fuel cell electrolyses are the transference numbers of the cations relative to the carbonate ion. These are in general determined by one of three methods: Hittorf (electrolysis method) type measurements, moving boundary measurements, or study of emf cells with transference. For molten salt mixtures at high concentrations for which a reversible electrode exists, the third method may be the most appropriate. It is being applied to molten carbonate mixtures using the cell indicated below.

It has been previously shown¹ that in a concentration cell with transference and two electrodes reversible to the common ion, such as (A), the emf is given by

$$E = -\frac{1}{2F} \int_{\mu_1}^{\mu_2} (t_+ - 1) \frac{d\mu}{\mu} \quad (1)$$

where y is the equivalent fraction of the Li_2CO_3 in the melt. The estimation of the transference numbers from the change of the emf with the Li_2CO_3 fraction requires a knowledge of the change in chemical potential with melt composition. This composition dependence is being calculated from the phase diagram² and heat-of-mixing data³ for the system $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$ by a new method. It may be seen from Eq. (1) that only the derivative is needed, not μ itself nor the standard chemical potential μ° ; these latter quantities are irrelevant, and, unless the data are closely spaced and accurate, serious errors may result

from extrapolation inherent in evaluating an integration constant. For systems with sparse data, errors arising from integration and subsequent differentiation can be avoided by evaluating the derivatives (numerically or graphically) directly from the data. With the partial molar enthalpy of mixing $\bar{H}$ (ref. 3), the isothermal derivative $[(\partial \mu / \partial X)_T]_T$ at a fixed temperature T may be obtained from the liquidus temperature T' by means of Eq. (2), written for the case where neither solid solutions nor heat capacity terms are significant:

$$\begin{aligned} [(\partial \mu / \partial X)_T]_T &= -T \Delta T' + \bar{H}' dT' / dX \\ &= -dT' / dX [(T - T') + \bar{H}'] \quad (2) \end{aligned}$$

This approach, besides not requiring the evaluation of integration constants, is also insensitive to uncertainties in the melting points of the pure components and simplifies application of the Gibbs-Duhem equation.

Even without accurate activity coefficients, however, the sign of $(t_+ - 1)$ and hence the more mobile ion may be obtained directly from the sign of the experimental cell. An apparatus has been constructed to measure the emf of the concentration cell (A) over a range of compositions. Melt of one composition is contained in an alumina crucible. Melt of the second composition is contained in a closed-end alumina tube immersed in the melt in the crucible. The liquid junction between the two melts is established by a small hole in the inner tube and a fitted sleeve.

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8.2 TRANSPORT AND THERMODYNAMICS

8.2.1 Electrochemical Measurements on Model Systems Simulating Molten Salt Batteries

D. E. Heatherly C. E. Vallet

This study has as its aim an experimental test of predictions of the component separation in Li-KCl-LiCl-S batteries and other electrochemical systems. Measurements of composition changes

resulting from electrolysis of silver nitrate-alkali nitrate melts between silver electrodes have been completed for $\text{AgNO}_3\text{-KNO}_3$ mixtures, and initiated for $\text{AgNO}_3\text{-NaNO}_3$ mixtures. The ion flows during electrolysis between silver electrodes in these nitrate melts are analogous to the flows in an Li-S battery with molten KCl-LiCl as the electrolyte. The measurements of the composition changes in $\text{NaNO}_3\text{-AgNO}_3$ mixtures provide a more accurate test of the model because the composition dependence of the interdiffusion coefficient, the transference number, and the activity coefficient have been measured independently in this system.

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Fig. 8.5. Electrolysis cell with the electrolyte contained in a quartz frit. A: outer quartz tubing; B: coarse quartz frit sealed at the end of A; C: outer quartz tubing; D: aluminum block; 1, 2: silver electrodes for electrolysis; and 3: silver nitrate electrolyte.

Electrochemical measurements. The composition changes at both electrodes during electrolysis are obtained from emf measurements during short current interruptions or at the end of electrolyses of differing duration. In a further test of the model, the emf is recorded during relaxation on open circuit following electrolyses of differing duration. The measured emfs are compared with those calculated from the model for diffusional relaxation (back to the uniform initial composition) from the composition gradient established by electrolysis.

The electrolysis cell, shown in Fig. 8.5, consists of two silver disks (area 0.5 cm^2) pressed against the two faces of a coarse quartz frit ($0.35\text{--}0.5 \text{ cm}$ thick) impregnated with the melt. The assembly is analogous to that in batteries in which the molten salt is contained in a powder matrix. Typical values of the observed composition changes during electrolysis at 0.15 A/cm^2 in $0.2 \text{ AgNO}_3\text{-}0.8 \text{ KNO}_3$ at 350°C are shown in Table 8.3 together with the predicted values from the transport model. The predicted values agree within a few percent with the measured values. Figure 8.6 shows experimental emf relaxations in $0.2 \text{ AgNO}_3\text{-}0.8 \text{ NaNO}_3$ mixtures at 300°C following electrolyses of various times at 0.150 A/cm^2 . Striking agreement is observed for the entire relaxation curves.

Table 8.3. Experimentally measured compositions at electrodes resulting from electrolysis and compositions calculated with the transport model.

Electrolysis time, hr	Experimentally measured composition		Calculated composition	
	Mol % Ag	Mol % K	Mol % Ag	Mol % K
0	0.20	0.80	0.20	0.80
1	0.18	0.82	0.18	0.82
2	0.16	0.84	0.16	0.84

The electrolysis was carried out at 0.150 A/cm^2 in $0.2 \text{ AgNO}_3\text{-}0.8 \text{ KNO}_3$ at 350°C .

Chemical analysis of composition profiles. Composition profiles from electrolysis have been determined by chemical analysis of both silver and potassium in thin slices of frozen electrolytes of various initial compositions. The results from both analyses, reported in Fig. 8.7, show a clear trend of increasing Ag:K ratio from cathode to anode. In all cases the standard deviation of fit of a linear dependence on distance is smaller than the standard deviation about an assumed constant value. The differences between the calculated composition at the cathode and at the anode from the linear regression

Fig. 8.6. Relaxation of polarization e.m.f. and of composition following electrolysis of 0.2 AgNO₃, 0.8 NaNO₃ at 300°C.

Fig. 8.7. Least-squares fit of a linear dependence on distance to compositions from silver analysis (O) and from potassium analysis (●) during 90 s at 0.15 A cm⁻², 0.2 AgNO₃, 0.8 KNO₃ electrolyzed during 40 s at 0.15 A cm⁻², 0.5 AgNO₃, 0.5 KNO₃ electrolyzed.

are larger than twice the standard deviations of fit of the linear expression.

The electrochemical and analytical results both confirm the direction and magnitude of the composition changes at the two electrodes predicted from our model.

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8.2.2 Simulation of Linear Sweep Voltammetry with Composition Dependent Transport Coefficients¹

C. E. Vallet and J. Braustein

Composition dependence of transport coefficients may have significant effects on voltammetry in mixed molten salt electrolytes. Flux equations and their numerical solution by finite difference methods, applied previously to chronopotentiometry of major constituents in binary molten salt mixtures, have been modified to simulate linear sweep voltammograms in ionic and network-forming binary mixtures.

The calculation has been applied to mixtures of high concentration of the electroactive constituent in which the transference number is composition dependent and different from zero. Composition dependence of the diffusion coefficient, which can be strong in mixtures with a network-forming component, is included.

The calculations are used to simulate the cases of reduction of lithium in LiCl-KCl mixtures (ionic mixture) and oxidation of beryllium in LiF-BeF₂ (network-forming) mixtures or aluminum in chloroaluminates. Cathodic voltammograms have been calculated with sweep rates from 0.24 V/min to

3.0 V min in LiCl-KCl mixtures [with compositions from 0.05 mol fraction of LiCl to 0.2 mol fraction of LiCl (i.e., 5.9×10^{-2} mol LiCl cm⁻³). The diffusion coefficient is taken constant and equal to 1×10^{-5} cm² s⁻¹. The calculations have been made for the cases of transference number of potassium relative to chloride, $t_K = 1$ and $t_K = X_K$. The case $t_K = 1$ implies no migration of the electroactive constituent, lithium, and corresponds to voltammetry with a supporting electrolyte. The transference number equal to the mole fraction gives a good approximation to the composition dependence of transference numbers in ionic binary melts. Figure 8.8 shows the variations of the peak height with the concentration for melts with

Fig. 8.8. Deviation from the Randles-Sevcik equation: concentration, transference number.

$t_K = 1$ (lower curve) and for melts with $t_K = X_K$ (upper curve). The Randles-Sevcik line gives the height of the peak in very dilute solution and with $t_K = 0$. High concentration and migration (with $t_K = X_K$) lead to higher peaks. Figure 8.9 shows, at one concentration, the effect of concentration and transference on the portion of the peak. With $t_K = X_K$ the peaks occur at

Fig. 8.9. Peak potential and scan rate: concentration, transference number.

less cathodic potentials and the portion of the peak depends on the scan rate. Figure 8.10 gives simulated anodic voltammograms. Curve 1a is obtained with a constant diffusion coefficient and a composition-dependent transference number shown in the insert; it simulates the oxidation of aluminum in a chloro-aluminate melt. Comparison of 1a and 1b shows that the varying transference number gives a wider and higher peak than the peak calculated without migration. Curves 2a and 3a are calculated with composition-dependent transference number and diffusion coefficient. They simulate the oxidation of beryllium in an LiF-BeF₂ mixture. The peaks are wider than the peak obtained with zero transference number and a constant D (curve 1b). Their height depends on the composition at which the inter-diffusion coefficient begins to decrease.

Fig. 8.10. Anodic voltammograms with variable diffusion coefficient and transference number (network melt).

The results obtained show that the Randles-Sevcik equation is not directly applicable to the case of composition-dependent transference numbers. Our numerical method provides a means for the analysis of the entire voltammogram in concentrated mixed electrolytes.

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8.2.3 Steady-State Solutions of the Migration Diffusion Equations for Molten Salt Batteries and Fuel Cells

C. E. Vallet J. Braunstein

Steady-state composition profiles in mixed molten salt electrochemical devices. I. Lithium/sulfur battery analogs. During charge or discharge of batteries with binary molten salt mixtures as the electrolyte, composition gradients are produced by the electrode reactions and modified by the differences in mobilities of the electroactive and

nonelectroactive ions. The effects of current density, electrode separation, and initial composition of the electrolyte are predicted by an analytical solution of the flux equations derived with transport properties similar to those of LiCl-KCl mixtures. Numerical solution of the flux equations predicts the composition profiles in lithium sulfur battery analogs with LiCl-KCl mixtures of differing compositions. Either complete depletion of the electroactive constituent at one electrode or precipitation of a solid phase at the electrodes could result from the predicted composition gradients. Changes in electrolyte composition at the electrodes may also affect β -phase formation at the sulfur electrode during discharge.

Steady-state composition profiles in mixed molten salt electrochemical devices. II. Molten carbonate fuel cell analogs. Composition changes in a CO-CO₂-Li₂CO₃-K₂CO₃-O₂-CO₂ fuel cell operated at high current density can result from electrical mobility differences of the two cations, neither of which is electroactive. The steady-state composition profile between the electrodes may be calculated analytically from the diffusion-migration flux equations.

Generalized parametric plots have been developed to predict compositions and phases at the electrode surfaces at different times as functions of the operating variables and physical properties that constitute the parameter: current density, electrode separation, temperature, ion mobility ratio, molar volume, and diffusion coefficient. Figure 8.11 is a plot of the development of the composition change at an electrode surface in terms of the parameter $P = bQ = (b/z) (FD)$, where b is the coefficient, related to the mobility ratio, in the expression for the transference number of lithium ion relative to carbonate ion $t_L = (1 + b)X_L - bX_C$, I is the current density, V the average equivalent volume of the molten salt mixture, z the electrode separation, D the interdiffusion coefficient, and F the Faraday.

Liquidus compositions at several temperatures between 550 and 800°C are indicated. Solid K₂CO₃ could precipitate for values of current density and electrode separation giving a P value corresponding to a composition lying below a liquidus composition indicated by temperature on the left. The initial time dependence (slope) of concentration is proportional to $bVI/\sqrt{D}$, and the final steady-state composition depends only on $P = bQ$. Compositions for other values of the physical properties, for example, b , V , and D , can therefore be read from the parametric plot in Fig. 8.11. Table 8.4 gives examples of rescaling

Fig. 8.11. Parametric curves for predicting compositions and phases at the electrode surfaces at different times.

Table 8.4. Examples of reworking of the current density lines I_0 and of the electrode separation curves Ξ for changes in the inherent properties of a 0.5 melt.

Reference line slope line with initial concn	Change in the properties of the melt	Revised potential values Ξ
1	1	1
2	2	2
3	3	3
4	4	4
5	5	5
6	6	6
7	7	7
8	8	8
9	9	9
10	10	10
11	11	11
12	12	12
13	13	13
14	14	14
15	15	15
16	16	16
17	17	17
18	18	18
19	19	19
20	20	20
21	21	21
22	22	22
23	23	23
24	24	24
25	25	25
26	26	26
27	27	27
28	28	28
29	29	29
30	30	30
31	31	31
32	32	32
33	33	33
34	34	34
35	35	35
36	36	36
37	37	37
38	38	38
39	39	39
40	40	40
41	41	41
42	42	42
43	43	43
44	44	44
45	45	45
46	46	46
47	47	47
48	48	48
49	49	49
50	50	50
51	51	51
52	52	52
53	53	53
54	54	54
55	55	55
56	56	56
57	57	57
58	58	58
59	59	59
60	60	60
61	61	61
62	62	62
63	63	63
64	64	64
65	65	65
66	66	66
67	67	67
68	68	68
69	69	69
70	70	70
71	71	71
72	72	72
73	73	73
74	74	74
75	75	75
76	76	76
77	77	77
78	78	78
79	79	79
80	80	80
81	81	81
82	82	82
83	83	83
84	84	84
85	85	85
86	86	86
87	87	87
88	88	88
89	89	89
90	90	90
91	91	91
92	92	92
93	93	93
94	94	94
95	95	95
96	96	96
97	97	97
98	98	98
99	99	99
100	100	100

$\Xi_0 = 0.40$, $\Xi_1 = 0.45$, $\Xi_2 = 0.50$, $\Xi_3 = 0.55$, $\Xi_4 = 0.60$, $\Xi_5 = 0.65$, $\Xi_6 = 0.70$, $\Xi_7 = 0.75$, $\Xi_8 = 0.80$, $\Xi_9 = 0.85$, $\Xi_{10} = 0.90$, $\Xi_{11} = 0.95$, $\Xi_{12} = 1.00$, $\Xi_{13} = 1.05$, $\Xi_{14} = 1.10$, $\Xi_{15} = 1.15$, $\Xi_{16} = 1.20$, $\Xi_{17} = 1.25$, $\Xi_{18} = 1.30$, $\Xi_{19} = 1.35$, $\Xi_{20} = 1.40$, $\Xi_{21} = 1.45$, $\Xi_{22} = 1.50$, $\Xi_{23} = 1.55$, $\Xi_{24} = 1.60$, $\Xi_{25} = 1.65$, $\Xi_{26} = 1.70$, $\Xi_{27} = 1.75$, $\Xi_{28} = 1.80$, $\Xi_{29} = 1.85$, $\Xi_{30} = 1.90$, $\Xi_{31} = 1.95$, $\Xi_{32} = 2.00$, $\Xi_{33} = 2.05$, $\Xi_{34} = 2.10$, $\Xi_{35} = 2.15$, $\Xi_{36} = 2.20$, $\Xi_{37} = 2.25$, $\Xi_{38} = 2.30$, $\Xi_{39} = 2.35$, $\Xi_{40} = 2.40$, $\Xi_{41} = 2.45$, $\Xi_{42} = 2.50$, $\Xi_{43} = 2.55$, $\Xi_{44} = 2.60$, $\Xi_{45} = 2.65$, $\Xi_{46} = 2.70$, $\Xi_{47} = 2.75$, $\Xi_{48} = 2.80$, $\Xi_{49} = 2.85$, $\Xi_{50} = 2.90$, $\Xi_{51} = 2.95$, $\Xi_{52} = 3.00$, $\Xi_{53} = 3.05$, $\Xi_{54} = 3.10$, $\Xi_{55} = 3.15$, $\Xi_{56} = 3.20$, $\Xi_{57} = 3.25$, $\Xi_{58} = 3.30$, $\Xi_{59} = 3.35$, $\Xi_{60} = 3.40$, $\Xi_{61} = 3.45$, $\Xi_{62} = 3.50$, $\Xi_{63} = 3.55$, $\Xi_{64} = 3.60$, $\Xi_{65} = 3.65$, $\Xi_{66} = 3.70$, $\Xi_{67} = 3.75$, $\Xi_{68} = 3.80$, $\Xi_{69} = 3.85$, $\Xi_{70} = 3.90$, $\Xi_{71} = 3.95$, $\Xi_{72} = 4.00$, $\Xi_{73} = 4.05$, $\Xi_{74} = 4.10$, $\Xi_{75} = 4.15$, $\Xi_{76} = 4.20$, $\Xi_{77} = 4.25$, $\Xi_{78} = 4.30$, $\Xi_{79} = 4.35$, $\Xi_{80} = 4.40$, $\Xi_{81} = 4.45$, $\Xi_{82} = 4.50$, $\Xi_{83} = 4.55$, $\Xi_{84} = 4.60$, $\Xi_{85} = 4.65$, $\Xi_{86} = 4.70$, $\Xi_{87} = 4.75$, $\Xi_{88} = 4.80$, $\Xi_{89} = 4.85$, $\Xi_{90} = 4.90$, $\Xi_{91} = 4.95$, $\Xi_{92} = 5.00$, $\Xi_{93} = 5.05$, $\Xi_{94} = 5.10$, $\Xi_{95} = 5.15$, $\Xi_{96} = 5.20$, $\Xi_{97} = 5.25$, $\Xi_{98} = 5.30$, $\Xi_{99} = 5.35$, $\Xi_{100} = 5.40$.

of the current density lines I and of the electrode separation curves Ξ for changes in the inherent properties of a 0.5 mol fraction melt. Composition changes at both electrodes result in a polarization emf between anode and cathode. The effects of the transport parameters in the binary mixture (transference number, interdiffusion coefficient) and of the

Fig. 8.12. Effect of transport and thermodynamic parameters on the time dependence of the emf (open circuit) of anode relative to cathode during electrolysis and subsequent relaxation. (a) no activity coefficient correction, $D = 1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, $t = 1.5, 2.0$; dashed line is calculated with transference number given by $t = 2.82 A_1 - 1.82 A_2$; (b) activity coefficient given by Eq. (17), $D = 1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, $t = 1.5, 2.0$; (c) no activity coefficient correction, $D = 20 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, $t = 2$; (d) same D and t as (c) but with activity coefficient correction.

activity coefficient on the predicted polarization potential difference between the electrodes during an electrolysis followed by a relaxation on open circuit are illustrated in Fig. 8.12. These results suggested an empirical method for estimating the interdiffusion coefficient and the transference number in a binary electrolyte in which direct measurements may be more difficult.

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9. Environmental Chemistry

9.1 KINETIC MODEL FOR PREDICTING THE COMPOSITION OF CHLORINATED ESTUARINE OR SEAWATER DISCHARGED FROM POWER PLANT COOLING SYSTEMS

M. H. Lietzke¹ W. R. Haag²

A kinetic model for predicting the composition of chlorinated water discharged from power plants using fresh water for cooling has been described previously.² The model was verified³ using data supplied by the Quad Cities Nuclear Plant located on the Mississippi River. This model has now been extended to be applicable to power plants located on estuaries or on the seacoast where saline water is used for cooling purposes.

Seawater contains about 65 ppm bromide ion. When chlorine is added to seawater to prevent biofouling in power plant cooling systems, bromine is liberated. Since this reaction proceeds at a finite rate, there is a competition between the bromine (or hypobromous acid) and the added chlorine (or hypochlorous acid) for reaction with any amine species present in the water. Hence not only chloramines but also bromamines will be formed, with the relative concentrations of each a function of pH, temperature, and salinity of the water. Both the chloramines and bromamines are toxic to marine life. However, both types of species are unstable with respect to hydrolysis and other mechanisms that contribute to their destruction.

The model as formulated takes into account the forward and reverse rates of chemical reactions leading to the formation and disappearance of monochloramine, dichloramine, organic chloramine (modeled by methylchloramine), hypobromous acid, dibromamine, and tribromamine. (Under the conditions obtaining in seawater the formation of trichloramine and monobromamine may be neglected.) Provision is also made for the irreversible uptake of chlorine or bromine in satisfying the halogen demand of the water. Ionic strength dependence of all equilibrium and dissociation constants is incorporated into the model to make it

applicable to estuarine water as well as to seawater.

Not all the necessary rate constants for the chemical reactions have been experimentally determined; in lieu of measured values, reasonable guessed-at values have been used to test the model. The eight simultaneous differential equations are solved using a variable time-step, fourth-order Runge-Kutta method. Calculated values of the various chemical species as a function of time appear to be in qualitative agreement with expectation.

Further quantification of the model awaits experimental determination of the missing rate constants. Analytical data from an operating power plant on the seacoast will be necessary for verification. A proposal has been submitted to the Nuclear Regulatory Commission seeking funds to have the necessary analyses performed.

1. Graduate student, Chemistry Department, University of Tennessee, Knoxville.

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3. M. H. Lietzke, *A Validation of the Kinetic Model for Predicting the Composition of Chlorinated Water Discharged from Power Plant Cooling Systems*, ORNL NUREG-32 (December 1977).

9.2 EFFECTS OF WATER ON SALT REPOSITORIES

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The behavior of water in salt repositories for nuclear wastes under various thermal and pressure gradients is important in assessing the integrity of the storage facility. Water from migration of brine inclusions and from aquifers could gain access during the initial operational period, during the period of consolidation of backfilled salt, and conceivably during the long-term storage thereafter. An experimental program is under way with the objective of gaining information sufficient to predict credibly the

consequences of any plausible form of water ingress to the repository.

A test apparatus was constructed for studying the consolidation of beds of granulated salt. Saturated NaCl brine was passed through small cylindrical salt beds (10 cm long $\times$ 1.3 cm diam) in a negative temperature gradient ($\sim 5^\circ\text{C}/\text{cm}$). At low pressure drops (< 0.02 atm), nearly all voids were filled by deposition. A model assuming Poiseuille flow through a mixture of capillary and crevice flow channels fits the data at low pressure drop quite well. In Fig. 9.1 experimental points are shown together with a smooth curve derived from the model. The number and diameter of the capillaries and the thickness and

Fig. 9.1. Experimental points and smooth curve from model for flow through salt bed under $5^\circ\text{C}/\text{cm}$ negative temperature gradient.

integrated width of the crevices were parameters adjusted by a least-squares program. At higher pressure drops (> 1 bar) plugging occurred after only a fraction of the available void space was filled. To deal with these results, a more versatile model, including other effects such as conductive and convective heat flow, salt compaction, salt recrystallization, and elasticity, will be necessary.

Measurement of water loss from unstressed cylindrical halite cores (15 cm diam $\times$ 7 cm long) subjected to an axial thermal gradient ($7^\circ\text{C}/\text{cm}$) at an average temperature of $\sim 125^\circ\text{C}$ indicated that most of the water originally present was lost over a period of a few months. Loss from the hot (lower) face was only slightly greater than from the cold face, contrary to expectations if transport were only by movement of completely filled brine inclusions through salt crystals. Pending confirmation with blank experiments, this result suggests that movement along salt grain boundaries may be an important transport mechanism.

A microscope stage assembly has been fabricated for the direct observation of (1) the movement of brine inclusions formed in polycrystalline salt and halite specimens and (2) the compaction and consolidation rate of salt-brine mixtures subjected to mechanical pressures of up to 60 bars and temperature gradients of up to $25^\circ\text{C}/\text{cm}$ (Fig. 9.2). A halite block $1/4 \times 1/4 \times 1$ in. long or a brine-salt mixture is confined in a rectangular quartz enclosure. Windows in the stainless steel case holding the quartz cell permit viewing by transmitted light up to magnification of 100X. The rectangular pressurizing piston is

Fig. 9.2. Microscopic stage assembly for the study of brine slurries and halite specimens under pressure and temperature gradient.

provided with an internal heater, a thermocouple well, and a porous tantalum surface frit and weep hole to permit water discharge. A commercially available pressurized plunger contacts the piston rod and provides a controlled force on the salt specimen. The opposite, cold end of the apparatus is maintained at a preset temperature with cooling water.

Preliminary compaction tests on free standing salt beds subjected only to gravity showed a linear

relationship between the logarithm of the void fraction and the logarithm of the time. In contrast, data obtained with our microscope stage apparatus for an isothermal sample subjected to mechanical pressures up to 215 psig showed an increasing slope with the logarithm of time. Volume fraction, solids increased from about 0.56 to 0.62 during the 90-h test period.

10. Nuclear Chemistry

10.1 MASS ASYMMETRY AND TOTAL KINETIC ENERGY RELEASE IN THE SPONTANEOUS FISSION OF $^{258}\text{105}$

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We report here results from the spontaneous fission of 34.1 ± 4.6 -s $^{258}\text{105}$, the second heaviest known nuclide. The total kinetic energy (TKE) predicted by Schmitt and Mosel⁶ is about 250 MeV for near-symmetric mass splits, whereas the (TKE) expected from fission systematics is about 200 MeV. In our experiments the recoiling $^{258}\text{105}$ nuclei, obtained from the reaction $^{209}\text{Bi}(\alpha, n)^{258}\text{105}$, were deposited onto 40- $\mu\text{g}/\text{cm}^2$ carbon foils, using a helium jet technique. In a given cycle, the target was bombarded for 80 s; the collection foil was then rotated between two surface-barrier detectors (detectors 1 and 2) and counted for 80 s. During the following cycle, the same foil was counted by a second pair of detectors (detectors 3 and 4). Correlated energies of fission-fragment pairs were measured with both sets of detectors, and corresponding masses and total kinetic energies were deduced. No corrections for neutron emission were made.

No events with anomalously high TKE were observed, contrary to the theoretical expectations. The mass distribution from the fission of $^{258}\text{105}$ is very probably asymmetric and similar to distributions obtained from all spontaneously fissioning systems with the exception of ^{258}Fm and ^{259}Fm .

10.2 CALCULATION OF SPONTANEOUS FISSION PROPERTIES OF VERY HEAVY NUCLEI: $98 \leq Z \leq 106$ AND $150 \leq N \leq 164$

M. G. Mustafa¹ R. L. Ferguson²

Experiments on spontaneous and low-energy neutron-induced fission of fermium isotopes have shown that between ^{256}Fm and ^{258}Fm a transition from asymmetry to symmetry occurs in the mass distributions. This behavior in fermium was explained theoretically as being due to the energetically preferred formation of fragment nuclei in the region of the doubly magic ^{126}Sn nucleus. It was expected that the isotopes of other heavy elements with mass number greater than 258 would likewise fission symmetrically. However, the mass distribution of $^{258}\text{105}$ was recently found to be asymmetric.

To understand the fission of such very heavy elements, we have calculated the minimum potential energy surfaces (PES) for several nuclei in this region. The calculations utilize the asymmetric two-center shell model and are described in detail in ref. 3. When the PES for a neck radius $D < 4\text{ fm}$ indicated minima corresponding to an asymmetry parameter $\lambda > 1$, it was inferred that the fissioning system preferred asymmetric mass division. When a minimum was calculated for $\lambda \approx 1$, the system was considered to prefer symmetric division.

Results of these calculations are compared with experimental data in Fig. 10.1. The filled circles correspond to the even-even nuclei that our calculations indicate to be at the transition from asymmetric to symmetric mass division, and the lines connecting the points divide the $A-Z$ plane into corresponding regions of mass symmetry on the right. The open points (squares for even-even nuclei and circles for odd nuclei) indicate measurements. In all cases there is qualitative agreement between our calculations and the experimental results. Only ^{258}Fm and ^{259}Fm are observed to fission with an appreciable symmetric component. The striking feature of the calculation is the pronounced dip in the transition region to lower neutron numbers for

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5. A more complete account of this work appeared in *Phys. Rev. Lett.* **39**, 1246 (1977).

6. H. W. Schmitt and I. Mosel, *Nucl. Phys. A* **186**, 1 (1972).

Fig. 10.1. Calculated points (filled circles) of transition from mass asymmetry to symmetry for even-even nuclei, connected by lines to define regions in the $N-Z$ plane; open points (○) for even-even nuclei, (●) for odd nuclei indicate existence of experimentally near transitions. SF stands for spontaneous fission, NF for fission of the compound nucleus formed by low-energy neutron induced reactions.

fermium nuclei. Obviously, it would be of interest to study experimentally some other system predicted to lie to the right of the transition region, but such studies have so far proven to be impossible. Finally, it should be noted that the new result for 105 is well accounted for by the calculation.

1. Lawrence Livermore Laboratory, Livermore, Calif.

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10.3 ENERGY LOSSES FOR ^{84}Kr IONS IN NICKEL, ALUMINUM, AND TITANIUM

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Recently published measurements² of the slowing down of energetic heavy ions in matter have indicated serious discrepancies between experimental and calculated stopping powers for ions such as argon and krypton. Because we have been investigating the behavior of compound nuclei formed in reactions with ^{40}Ar and ^{84}Kr (Sect. 10.4), we have determined the energy losses of ^{84}Kr in nickel, aluminum, and titanium foils used to degrade the beam's energy.

The measurements were performed with a beam of 615-MeV ^{84}Kr at the Lawrence Berkeley Laboratory SuperHILAC. A time-of-flight (TOF) system³ was used to measure the traversal time of the beam over an accurately known distance; thus the beam velocity and energy were determined. Once the energy of the beam was known, individual absorber foils were placed in the beam in front of the TOF system, and the resultant energy losses were measured. A set of energy measurements was concurrently made with a surface barrier Si(Au) detector placed directly in the attenuated beam behind the TOF system. The energy scale for the solid-state detector (SSD) was calibrated against the TOF value for the initial beam energy of 615 MeV. Then, as each foil was placed in the beam, energy-loss values were independently measured with the TOF and SSD systems.

In Fig. 10.2 are plotted the absorber foil thicknesses ΔR vs the observed energies E for both the TOF and SSD measurements. It is seen that the two different measurement techniques agree very well, with a maximum spread in measured values for a given absorber of <6 MeV or <1%.

Figure 10.2 also shows the ΔR vs E values obtained from different energy-loss calculations: from Northcliffe and Schilling,⁴ from Steward,⁵ and from Brown and Moak.⁶ It should be noted that the Brown

Fig. 10.2. Thickness of absorbers ΔR plotted vs the energy of the degraded ^{84}Kr beam E . Absorbers were foils of nickel, titanium, and aluminum. Measurements were done with time-of-flight and solid-state detector systems. Calculated values are taken from P. G. Steward (St.), University of California Report No. UCRL-18127 (1976); J. G. Northcliffe and A. I. Schilling (NS), *Nucl. Data A* **7**, 233 (1970); and M. J. Brown and C. D. Moak (BM), *Phys. Rev. B* **6**, 90 (1972), with values calculated by a program developed by C. D. Moak and W. L. Milner.

Table 10.1. Comparison of measured and calculated energy losses for 615 MeV ^{84}Kr

Foil	Thickness (mg/cm ²)	$\Delta E(M)^a$ (MeV)	Northcliffe and Schilling		Steward ⁴		Brown and Moak ^d	
			$\Delta E(C)^b$ (MeV)	F ^c	$\Delta E(C)^b$ (MeV)	F ^c	$\Delta E(C)^b$ (MeV)	F ^c
Ni	0.70	20.3 ± 1.5	15.6	0.23	19.0	0.66		
	0.75	22.0	16.5	0.25	20.7	-0.06		
	1.17	31.8 ± 0.1	26.7	0.16	32.6	-0.03		
	1.36	38.4 ± 2.6	31.9	0.17	39.3	0.02		
	1.64	46.0 ± 0.4	38.1	0.17	45.6	0.00		
	2.00	50.2 ± 0.8	39.3	0.17	47.6	-0.03		
	2.50	74.5 ± 2.4	58.1	0.22	70.5	0.05		
	2.60	73.0 ± 1.7	60.6	0.17	73.1	0.00		
	3.13	85.8 ± 0.6	73.0	0.15	88.4	-0.03	86.4	0.01
	3.30	97.5 ± 0.4	79.7	0.18	95.9	0.02	94.5	0.03
	3.68	107.8 ± 0.8	86.5	0.20	104.2	0.03	102.5	0.05
	3.34	123.7 ± 0.6	102.4	0.17	122.9	0.01	120.2	0.03
	4.56	126.2 ± 1.0	107.2	0.15	128.9	-0.02	126.2	0.00
	5.46	155.9 ± 1.3	128.8	0.17	155.1	0.01	152.1	0.02
Al	1.21	42.3 ± 0.1	33.5	0.21	39.7	0.06		
	2.22	78.1 ± 0.5	62.4	0.20	74.7	0.04	72.4	0.07
Ti	3.11	92.0 ± 0.9	70.0	0.24	89.2	0.03		
	3.17	97.6 ± 1.3	83.9	0.14	97.1	0.01		

^a $\Delta E(M)$ = measured energy loss. Errors are standard deviations of replicate measurements.^b $\Delta E(C)$ = calculated energy loss.^c $F = [\Delta E(M) - \Delta E(C)] / \Delta E(M)$.^dWhen not listed, values from Brown and Moak are very similar to those from Steward.^eThis titanium foil was placed behind a 5.76-mg/cm² nickel foil and bombarded with 615-MeV ions. The data indicate an energy loss of 158 MeV in the nickel foil, with the remaining energy loss ascribed to 157-MeV ions passing through the titanium.

and Moak curves were obtained by extrapolation, to 7.3 MeV/amu, of an analytic function that had been derived by fitting stopping power data for uranium, iodine, and bromine ions with energies ≤ 1 MeV/amu. Two conclusions are readily apparent from the figure: (1) there is a significant difference between the Northcliffe-Schilling values and those obtained from Steward and from Brown and Moak and (2) the values of Steward and of Brown and Moak are in close agreement with our measurements.

Table 10.1 presents the measured energy losses, which are averages of the replicate values obtained by both the TOF and SSD systems. Comparison is made with the calculated values, and fractional deviations are shown relative to the measured energy losses. It is seen that the Northcliffe and Schilling values for ^{84}Kr are 15–25% smaller than the measurements, whereas the Steward and Brown and Moak values vary from 3% above to 7% below the measured values.

It is expected that energy-loss measurements such as these for very heavy ions will be of practical use in nuclear physics experiments and will also serve in choosing between different theoretical approaches to the problem of the slowing down of energetic ions in matter.

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7. Values were calculated with a program developed by C. D. Moak and W. I. Milner.

10.4 ARE THERE DIFFERENCES IN COMPOUND NUCLEI FORMED WITH ^{40}Ar AND ^{84}Kr PROJECTILES?

R. L. Hahn H. Gauvin
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Several years ago shortly after usable beams of ^{84}Kr first became available, a series of experiments was done at the ALICE accelerator in Orsay to compare the decay of erbium compound nuclei, ^{153}Er and ^{152}Er , formed in two different ways, in reactions of ^{40}Ar with ^{116}Sn and ^{118}Sn and of ^{84}Kr with ^{74}Ge and ^{76}Ge . The results of these experiments, in which the α -emitting radioactive products were collected with a gas-jet system, were unusual: the thresholds and peaks of the $(^{84}\text{Kr}, xn)$ reactions were systematically shifted by ~ 15 MeV to higher excitation energies, compared to the corresponding $(^{40}\text{Ar}, xn)$ reactions, for $x = 3$ to 6. To interpret these differences between the argon and krypton induced reactions, it was necessary to invoke some special mechanism for the krypton reaction, such as the pre-equilibrium emission of neutrons or the existence of angular-momentum effects that would reduce the probability of compound nucleus formation at low ℓ values (the ℓ -window effect).

Since that initial paper,² we have continued, at Orsay and at the SuperHILAC at Lawrence Berkeley Laboratory, our investigations of the comparison of ^{40}Ar and ^{84}Kr reactions leading to the same compound nucleus: the ^{153}Er system has been re-investigated to check the initial results, and ^{208}Po , a heavier system in which fission is significant, has been studied.

It should be noted that, in ref. 4 and in some of our later experiments, the energy values corresponding to the measured cross sections were not measured directly: absorber foils served to degrade the beam energy, and the Northcliffe-Schilling range-energy tabulation³ was used to calculate the energy of the beam on target. However, it has been found recently, as noted in Sect. 10.3 for time-of-flight measurements with ^{84}Kr at Berkeley and for proton recoil experiments⁴ at Orsay with ^{40}Ar and ^{84}Kr that the Northcliffe-Schilling values differ appreciably from measured energy losses. Accordingly, all of our data have been reanalyzed and tied directly to experiments in which we measured the energy of the beam after it had passed through the absorber foils.

Figures 10.3, 10.4, and 10.5 show our excitation function data plotted against the redetermined

Fig. 10.3. Relative excitation functions for $^{84}\text{Kr}(^{74}\text{Ge}, 5n)$ - $^{153,152}\text{Er}$ plotted vs laboratory energy. Open points were measured at Orsay; closed points, at Berkeley.

Fig. 10.4. Relative excitation functions plotted vs excitation energy for the production of ^{153}Er and ^{152}Er , compared for ^{40}Ar and ^{84}Kr induced reactions.

energy scales. Figure 10.3 shows the $^{84}\text{Kr}(^{74}\text{Ge}, xn)$ reactions leading to ^{153}Er and ^{152}Er plotted vs laboratory energy. The open points were determined at Orsay; the closed points, at Berkeley. It is seen that there is good agreement between the results obtained at the two laboratories, both in the shapes of the excitation functions and in the independently determined energy scales. Similar conclusions apply to the

Fig. 10.5. Excitation functions for the reactions $^{160}\text{Dy} + (^{40}\text{Ar}, xn) ^{200}\text{Po}$ and $^{160}\text{Dy} + (^{160}\text{Dy}, xn) ^{200}\text{Po}$.

$^{118}\text{Sn} + (^{40}\text{Ar}, xn)$ data taken at both laboratories. In Fig. 10.4, the $(^{40}\text{Ar}, xn)$ and $(^{160}\text{Dy}, xn)$ excitation functions are compared for ^{118}Er and ^{138}Er ; data from both accelerators appear in the figure. We see that, contrary to the earlier results,⁴ there are no significant differences in reaction thresholds and peak cross sections between the data obtained with the argon and krypton beams for the emission of 5 and 6 neutrons. These results are consistent with recent measurements⁵ in the erbium region of evaporation

residue cross-sections and γ -ray multiplicity, which no evidence was found for the existence of a window.

The excitation functions for neutrons from ^{200}Po compound nuclei formed from $^{160}\text{Dy} + (^{40}\text{Ar}, xn)$ and $^{160}\text{Dy} + (^{160}\text{Dy}, xn)$ are shown in Fig. 10.5. Again, the energy scales are from direct measurements, and again no differences occur in the thresholds and peak cross sections corresponding to $5n$ and $6n$ channels.

We conclude from these studies that the excitation functions for neutrons from heavy-ion induced reactions are very similar to those from fission reactions, and that the excitation functions for neutrons from heavy-ion induced reactions are very similar to those from fission reactions.

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10.5 MEASUREMENT OF THE ENERGY DIVISION VS MASS IN HIGHLY DAMPED REACTIONS

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Deep inelastic collisions between heavy ions are characterized by lifetimes comparable to disintegration processes and by kinetic energies similar to those of (equilibrium) fission reactions. It is known how many other reaction properties are equilibrated during the very short interaction. However, we have been able to determine from experiment how the internal excitation (intrinsic plus deformation) divides between fragments in deep inelastic collisions.

Our experiment consisted of simultaneous measurement of mass, nuclear charge, and kinetic

for products of 440-MeV and 760-MeV ^{86}Kr bombardments of ^{210}Sn . From these data we deduced the average mass (A_f) for each fragment charge Z_f in the deep inelastic product region for both bombarding energies.

These results are shown in the lower portion of Fig. 10.6 as the difference between (A_f) and the mass that the product with given Z_f would have if it had the

Fig. 10.6. Lower portion: The triangles represent the deduced average fragment masses (A_f) for the corresponding fragment nuclear charge Z_f , normalized as indicated by the formula given on the ordinate. Upper portion: The circles represent the difference between the partition of the additional 160 MeV of excitation energy brought in by the higher bombarding energy (assuming division proportional to mass) and the amount removed by the neutron evaporation implied by the lower portion of the figure. Zero on the ordinate means that one can exactly explain the separation between the two sets of triangles by assuming a division of excitation energy that is proportional to fragment mass.

same mass-to-charge ratio as the compound nucleus (^{210}Sn). The displacement between the (A_f)-vs- Z_f curves for the two bombarding energies is related to the difference in partition of the 160-MeV increase in total excitation energy brought in at the higher bombarding energy. The displacement varies from about 5 neutrons at $Z_f = 27$ to 7 neutrons at $Z_f = 50$. Qualitatively, this supports the equilibrium hypothesis that the excitation divides proportionally with mass.

For several Z_f 's a quantitative comparison was made of the differences in excitation energies by taking the sum of the neutron binding energies B between the average masses of the 440-MeV and 760-MeV points plus twice the estimated temperature T for each neutron. These results are plotted vs Z_f in the upper portion of Fig. 10.6, where the ordinate is the excitation energy difference, as estimated above, minus the excitation energy a fragment would have if the total excitation energy difference ΔE were partitioned according to average fragment mass. As can be seen, the points cluster about zero ordinate, in quantitative support of our conclusion that excitation energy divides proportionally to mass and therefore is also an equilibrated quantity in these deep inelastic collisions.

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10.6 AMBIGUITIES IN THE INFERENCE OF PRECOMPOUND EMISSION FROM EXCITATION FUNCTION ANALYSIS

M. Blann, R. L. Ferguson

Many heavy-ion experiments have been performed in which final-product yields and/or γ -ray multiplicities for particular products have been measured. In some cases there has been an attempt to infer the average kinetic energy of emitted neutrons from these data and to assume that high kinetic energies imply precompound neutron emission. We have performed a Weisskopf-type statistical model calculation¹ for the neutron-rich nuclide ^{137}Cd at excitation energies of 30 to 180 MeV to illustrate that, under the conditions of some of these experiments, pure statistical decay can appear to yield neutrons of quite high kinetic energies.

The results of our calculation are summarized in Table 10.2. The first column gives the compound nucleus excitation energy. The second column shows the energy per neutron required to form the $3n$ product, ignoring all other channels. Column three gives the average energy per neutron leading to all $3n$ products, and column four gives the average energy to remove the last neutron in the $3n$ channel, where charged-particle channels are ignored. Columns five and six show analogous results when all channels are considered (charged particle as well as neutron), as

Table 10.2. Summary of neutron emission energies for ^{137}Cs resulting from equilibrium evaporation

Compound nuclear excitation (MeV)	3 σ Channel (MeV neutron)	1 σ Channel (MeV neutron)	Last σ channel (MeV neutron)	All channels (MeV neutron)	Last σ , all channels (MeV neutron)
30		10		10	
40	11	11	14	11	14
50	16	11	13	11	13
60	20	12	19	12	14
70	23	13	24	12	16
80	26	14	52	13	19
120	40			14	
130				14	21
140				14	23
150				15	24
160	53			15	
170				16	
180	60			16	25

would be sampled if one measured total neutron multiplicity but ignored charged-particle emission in apportioning energy removed.

As can be seen from the table, quite high apparent kinetic energies can result from purely statistical decay under all these conditions. These results follow from prejudicial gating due to ignoring charged-particle emission, and the error is present even if only the σ channels are measured and analyzed. We feel, therefore, that conclusions as to non-statistical behavior of emitted particles based on such inferential analyses should be made with caution.

at a known time after its production. A delay of a few microseconds allowed time for collection of the 3×10^6 electrons created by the slowing down of the 80-MeV Cs^{55+} fragment; then a pulsed laser was fired along each particle track to remove one electron from each cesium atom by the saturated two-step resonance ionization process. These electrons were then drifted into a gas proportional counter and detected individually to measure the probability that a neutral cesium atom would be found at the end of the fission particle track. The apparatus used in our experiments is shown schematically in Fig. 10.7.

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10.7 SELECTIVE LASER ONE-ATOM DETECTION OF NEUTRAL PROMPT FISSION FRAGMENTS¹

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The technique of saturated resonance ionization spectroscopy,⁴ applicable to the detection of single atoms, has been used to search for atoms that are created from the neutralization of heavy ions as they lose their energy in a gas. When ^{137}Cs decays by binary fission, Cs^{55+} ions are formed about 14% of the time (in the heavy mass peak). These ions were injected into a gas at a low rate such that the cesium neutral atom could be searched for individually and

Fig. 10.7. Schematic of apparatus used to detect a single atom formed in spontaneous fission. A signal generated in the surface-barrier detector indicates the occurrence of a single fission of ^{137}Cs . After the initial ionization has been swept onto the collector plate, a tunable laser pulse is used to photoionize the selected single atom. The liberated photoelectron then drifts into a proportional counter and is detected as a single event.

Our results show that a cesium neutral species is formed about 12% of the time, and thus nearly all Cs^+ ions become Cs when the ions are thermalized in P-10 (90% Ar plus 10% CH_4) counting gas.

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10.8 LASER-INDUCED NUCLEAR POLARIZATION: APPLICATION TO THE STUDY OF SPONTANEOUS FISSION ISOMERS

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The techniques of optical pumping can be used to produce large population imbalances among the sublevels of atomic ground states and, through the hyperfine interaction, can be used to produce an orientation of nuclei. Since the first experimental observation of ground-state atomic polarization by Brossel, Kastler, and Winter¹ in 1952, optical pumping has been used to great advantage in hyperfine structure studies for a variety of atomic systems, as outlined in the excellent review article by Happer.² More recently, short-lived radionuclides have been studied using an optical pumping method where the optical resonance is monitored by the observation of anisotropic γ rays or β particles emitted in the subsequent nuclear decay.³ These optical hyperfine experiments can give information about nuclear spins and nuclear magnetic and quadrupole moments and can lead to a measurement of the nuclear deformation by a determination of the optical isotope or isomer shift.^{4,5} However, approximately 10^4 atoms per experiment are needed to perform these optical pumping experiments, using conventional spectral lamp sources.

We are developing and implementing a laser-based optical pumping technique that we call LINUP (Laser Induced Nuclear Polarization) to overcome the light intensity limitations of conventional sources and thus apply the method to very short-lived nuclei produced in heavy ion reactions. Similar suggestions for optical-pumping orientation experiments with

lasers have also been made.⁶ Our first application of the technique is a study of the 1-ms ^{241}Am spontaneous-fission isomer that is produced in the $^{235}\text{U}(1.5n)$ reaction at ORIC. Americium is an ideal optical pumping candidate because it has an approximately spherically symmetric atomic ground state (7S_3), which should minimize the loss of orientation due to atomic collisions. The ^{241}Am recoils from the $^{235}\text{U}(1.5n)$ reaction are stopped in an inert buffer gas (He, Ne, or Ar) within the volume of an intersecting circularly polarized laser beam tuned to one of the $5f\ 7s^2 \rightarrow 5f\ 7s7p$ transitions in americium. The technique of depopulation optical pumping, in the absence of an external magnetic field, is used; and, if the optical resonance conditions are satisfied, order is transferred from the laser beam to the atomic system. In the case of the absorption of right circularly polarized light ($\Delta m_l = +1$) the nuclear system will eventually be oriented such that $m_l = I = K$, that is, along the laser beam propagation axis, in the absence of mitigating relaxation effects and for nonzero nuclear spin. For the ^{241}Am fission isomer, the optical resonance condition is monitored by the observation of the anisotropic fission fragments detected in position-sensitive surface barrier detectors placed above and below the laser beam.

A determination of the ^{241}Am optical isomer shift and thus a determination of the nuclear deformation, which is expected to be very large for fission isomers, is the objective of our first experiments. We use an argon-ion, laser-pumped, tunable-CW dye laser system with a bandwidth of $\sim 0.5\ \text{\AA}$ to induce the $f\ 7s\ (^7S_3) \rightarrow f\ 7s7p\ (^7P_3)$ transition at $\sim 6405\ \text{\AA}$ in americium. This bandwidth is sufficiently broad to cover the manifold of hyperfine states associated with these levels. Preliminary developmental experiments are currently being performed.

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10.9 QUADRUPOLE AND HEXADECAPOLE DEFORMATIONS IN THE ACTINIDE NUCLEI

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In an earlier communication, we presented information on $E2$ and $E4$ transition moments deduced from Coulomb excitation of the ground-state rotational bands in the even- Z actinide nuclei ($230 \leq Z \leq 248$) with ^4He ions. Model-dependent deformation parameters β_2 and β_4 were extracted from the measured $E2$ and $E4$ transition moments for distribution of nuclear charge represented by two-parameter deformed Fermi distributions and by a deformed homogeneous distribution. The functional form of the two-parameter Fermi distribution does not include a parameter to vary the central charge density to account for the Coulomb field effect. Because of Coulomb repulsion, the central proton density is depressed in the nuclear interior. As a result of the increased proton density in the nuclear surface region, the charge $E4$ moments are larger than those of the potential moments. Thus one should take this Coulomb effect into account in the extraction of β_2 and β_4 from the measured $E2$ and $E4$ moments.

We have extracted model-dependent deformation parameters β_2 and β_4 from measured $E2$ and $E4$ transition moments for a distribution of nuclear charge represented by a three-parameter deformed Fermi distribution with parabolic center depressions. For the thorium and uranium nuclei, this shape of the charge distribution reduces the extracted values of β_2 by 5–10% and β_4 by 10–15% from the values obtained with the two-parameter deformed Fermi distribution.

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10.10 HIGH-SPIN STATES IN ^{164}Yb

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The "backbending" phenomenon in which a low-lying rotational band encounters a higher lying band with an appreciably larger moment of inertia is a rather common occurrence. Beyond the backbend,

one expects the yrast sequence to cross additional bands built on other excited nucleon structures and hence to produce additional backbends. To this point, only one such second-band-crossing in the yrast sequence has been observed.

In an effort to determine the properties of very high spin states in ^{164}Yb and especially to search for a second band crossing and to study this phenomenon, we have carried out the reaction $^{140}\text{Nd}(^{24}\text{Ne}, 6n)^{164}\text{Yb}$ at ORIC. To enhance the desired reaction channel, a multiplicity filter consisting of an array of 14 NaI detectors was used in coincidence with three Ge(Li) detectors. The Ge(Li) detectors were located near 180° and 0° with respect to the beam direction so as to reduce the Doppler broadening effects on the γ rays. Thin targets ($<1 \text{ mg cm}^{-2}$) of ^{140}Nd were used to allow the excited nuclei to recoil into vacuum where they could decay while in flight.

A large amount of coincidence data (76 magnetic tapes) was collected. Analysis of this data has led to the assignment of states up to 28 in the yrast sequence as seen in the standard backbending plot shown in Fig. 10.8. Although this is the second highest population of discrete states measured in a compound-nucleus reaction leading to an even nucleus, there is no evidence for an additional backbend. However, at spin 28, we see that the amount of inertia I is once again increasing, and thus there may be a reasonable probability for seeing a second backbend within two or three more states.

Fig. 10.8. Backbending plot of ^{164}Yb . I is the moment of inertia and ω is the rotational frequency of the nucleus.

We are planning additional measurements with ^{40}Ar projectiles that will carry more angular momentum into the compound system and thus enhance the possibility for our seeing these higher discrete states.

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10.11 CONTRASTING BEHAVIOR OF $h_{11/2}$ AND $i_{13/2}$ BANDS IN ^{185}Au

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There are legitimate questions about the exact role that the $h_{11/2}$ proton plays in backbending of rotational bands in even-even deformed and transitional nuclei in the $150 < A < 190$ region. The consensus now seems to be that in most cases the Coriolis rotation alignment¹ of a high- j /low- Ω pair of particles causes the abrupt increase in I , the moment of inertia, and often a corresponding decrease in ω , the rotational frequency. The usual test to determine which Nilsson orbitals contribute most to even-even backbending is to search for the absence of backbending in the rotational bands in adjacent odd- A nuclei where the odd nucleon occupies one of these critical orbitals. Such blocking experiments have been performed on several rare-earth nuclei (e.g., ref. 5) and led to the conclusion that $i_{13/2}$ neutrons are primarily responsible for backbending in that region.

In contrast to the solidarity of experimental evidence, indicating $i_{13/2}$ neutron alignment in the rare earth region, is the conflicting information on the cause of backbending in the prolate W-Os-Pt region (note that the heavier platinum isotopes are oblate; the change from oblate to prolate shapes occurs between ^{194}Pt and ^{196}Pt) (ref. 6). A variety of rotational bands in odd- A nuclei in this region have been observed (^{183}Os , ^{185}Re , ^{187}Ir , ^{189}Au). The excitation of the extra nucleon into these various orbitals has been found only sometimes to block core backbending, leading to no clear consensus about which particles align most easily in this region. The difficulty in drawing definite conclusions from these

experiments is due to the difficulty in comparing the even-even nucleus with the effective even-even core in odd- A nuclei when the Fermi surface is slightly different and where the extra nucleon may have a sizeable effect on the core deformation and thus on the whole alignment mechanism. For example, our earlier blocking experiments on ^{171}Yb proved rather conclusively that the $i_{13/2}$ neutron dominates even- A ytterbium backbending. In contrast, Foin and Barneoud⁷ observed a nonbackbending [541] band in ^{171}Lu , seemingly leading one to the conclusion that $h_{11/2}$ protons also contribute to ytterbium backbending. However, theoretical calculations of Faessler et al.⁸ predict the dominance of the $i_{13/2}$ neutrons and attribute the absence of backbending in the $h_{11/2}$ proton band to deformation effects resulting from the steeply sloping [541] orbital.

We present here the results of a rigorous blocking experiment in ^{185}Au where the subtle, but significant, deformation effects of the extra proton should be nearly identical in each band, enabling us to reach definite conclusions about the cause of the gentle backbending in ^{185}Pt (ref. 12). Levels in ^{185}Au have been populated by the $^{181}\text{Lu}(^{4}\text{He}, 0.6n\gamma)$ reaction at 113 MeV and the $^{181}\text{Tm}(^{4}\text{He}, 4n\gamma)$ reaction at 98 and 103 MeV. At the Oak Ridge Isochronous Cyclotron, we performed the excitation function and γ - γ - t coincidence measurements on thin targets and γ -ray angular distribution measurements on thick targets. In addition, an in-beam conversion-electron experiment was performed at the Texas A. & M. University Cyclotron. Without going into all of the experimental evidence and supporting arguments, we will simply state that, from these measurements and with the aid of preliminary data on the decay of ^{185}Hg studied at the UNISOR facility at Oak Ridge, we have constructed two decoupled bands (Fig. 10.9) and have assigned these to $h_{11/2}$ and $i_{13/2}$ proton orbitals.

The normal backbending plots for these two bands and for the ^{185}Pt core are shown in Fig. 10.10. While the ^{185}Pt nucleus does not severely backbend as do ^{183}Os (ref. 7), there is an obvious increase in I at $I \approx 12$. The $h_{11/2}$ band deviates from this pattern, but the $i_{13/2}$ band follows the core backbending very closely. This different behavior provides important evidence concerning the dominating high- j orbitals in the backbending process in ^{185}Pt .

Since the $i_{13/2}$ band backbends and the $h_{11/2}$ band does not (Fig. 10.10), even though they both arise from downsloping Nilsson orbitals, we conclude that it is the alignment of a pair of $h_{11/2}$ protons which gives

Fig. 10.9. Level scheme, ^{197}Au . Gamma-ray intensities in parentheses are corrected for angular anisotropies. The $1^+ \rightarrow 0^+$ transition is unobserved, hence all level energies are given with respect to the 0^+ level. The intensity for the 212.34 keV transition is uncertain due to the double nature of this peak. Angular distribution measurements indicate that all transitions are either of $E2$ character except for those of 292 and 308 keV (likely $E1$ of pure $1^+ \rightarrow 0^+$ and $1^+ \rightarrow 1^+$ and $2^+ \rightarrow 1^+$ transitions).

Fig. 10.10. Backbending curves for the ^{197}Pt core [energies obtained from S. Beshai et al., *Z. Phys. A* 277, 351 (1976)] and the $1^+_{[541]}$ and $1^+_{[660]}$ bands in ^{197}Au . The variables plotted are extracted from the level energies and spins (after subtracting $1/2$ or $3/2$ for ^{197}Au) using equations listed in S. Andre et al., *Phys. Rev. Lett.* 38, 327 (1977).

rise to the increase in the moment of inertia in ^{197}Pt . The 79th proton in ^{197}Au excited to the $1^+_{[541]}$ orbital blocks the alignment of a pair of $h_{1/2}$ protons from the core and thus prevents backbending. The presence of this odd proton in the $1^+_{[660]}$ orbital does not block alignment, and so backbending occurs. Thus we have provided the first strong evidence for the dominant role of $h_{1/2}$ protons to the backbending process in this region.

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10.12. MULTIPLE BAND CROSSINGS IN ^{164}Er

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From the amassing experimental evidence, it is now generally concluded that the backbending phenomenon is caused by the intersection of the ground-state rotational band, with a second rotational band possessing an appreciably larger moment of inertia (e.g., Stephens¹ and Lee et al.). In the rotation-alignment model,² the structure of this band corresponds to two quasiparticles, whose angular momenta are aligned with the rotating core. Further, this model³ predicts a series of rather similar rotation-aligned bands commonly called superbands.

The structure of the superbands can be probed by studying their interactions with the ground and the β -

and γ -vibrational bands. Thus far, only the interaction of the lowest (yrast) superband with the ground and β bands has been observed. However, the γ band would appear to be a better probe of the superbands since here one can study the interactions with both even- and odd-spin states. The present measurements of ^{164}Er give the first evidence for higher superbands and also the first example of intersections between the γ band and these superbands.

A beam of 69.6-MeV ^{16}O ions from the Oak Ridge Isochronous Cyclotron was used to bombard a 2.4-mg cm^{-2} metallic neodymium foil enriched to 96% in mass 150. Both γ -ray singles and γ - γ time coincidence data (total of 3.5×10^6 coincidence events) were stored simultaneously in the experiment at a γ -ray resolution of 2.3 keV for 1.33 MeV. The resulting level scheme for the positive-parity states is shown in Fig. 10.11. This figure shows the ground state rotational band up to spin 22 $^+$, the yrast sequence up to 24 $^+$, and both the odd- and even-spin members of the γ -vibrational band up to 21 $^+$. Negative parity bands were found but are not shown in Fig. 10.11.

Fig. 10.11. Level scheme of ^{164}Er showing the ground band, the yrast superband, and the γ -vibrational band populated in the reaction $^{16}\text{O}(^{150}\text{Nd})^{164}\text{Er}$. Shown on each transition are the energy and, in parentheses, the relative intensity. Uncertainties range from less than 10% for the intensities of the stronger transitions up to 30–40% for some of the very weak ones.

The plot of the experimental excitation energies vs I [Fig. 10.12(a)] clearly shows several intersecting rotational bands. To understand these results, a calculation was made using typical parameters to illustrate the general features predicted for ^{164}Er by the rotation-alignment model.²² Both zero- and two-quasineutron configurations within the complete $i_{13/2}$ orbit were included. The excitation energies from these calculations are shown in Fig. 10.12(b). The γ band is shown for illustration but was not explicitly included in the calculations. The correspondence between experiment and theory is indeed striking.

Fig. 10.12. Plot of the level excitation energies for various bands in ^{164}Er from (a) experiment and (b) the rotation-alignment model. The solid circles correspond to even-spin states and the open circles to odd-spin states.

The interaction between the intersecting bands is most clearly illustrated, using the back bending plot of the data shown in Fig. 10.13. From the present data and previous work,²³ it is found that near the intersection of the ground-state band and lowest yrast superband both the level energies and γ -ray branching ratios indicate the interaction matrix elements to be about 45–50 keV between these bands.

If a 45-keV interaction is used, then the unperturbed ground-band energies lie on a smooth extension of the lines up through the 18 $^+$ state and the yrast even- I superband energies likewise vary

Fig. 10.13. Plot of $2 \cdot h^2$ vs $(\hbar\omega)^2$ for members of the ground band, γ -vibrational band, and superbands in ^{164}Er . The open circles on the ground and yrast-even superbands are corrections for a 45-keV interaction matrix element. Open circles on the γ band result from a 25-keV shift in the 10^+ energy. The circles represent even-spin and the squares odd-spin states.

smoothly as shown by the open circles in the left half of Fig. 10.13. However, the 20^+ and 22^+ members of the ground band are affected very little by this interaction. Interestingly, if we extrapolate the yrast-even superband as shown by the dashed line in Fig. 10.12(a) and assume an interaction matrix element of 45 keV, then the upward kink in the ground band for the 20^+ and 22^+ states is largely removed.

On the right-hand side of Fig. 10.13 we show a plot for the transitions in the γ -vibrational band. We have made a 25-keV shift in the 10^+ level energy, which produced equal but opposite shifts in the $10^+ \rightarrow 8^+$ and $12^+ \rightarrow 10^+$ transition energies. Such an energy shift is expected due to a crossing of the γ band and the lowest (yrast) superband, provided there is an interaction matrix element of about 45 keV. The odd-spin state energies in the γ band are smooth in this spin region without such a shift, providing the first direct evidence that the odd-spin states in the yrast superband lie considerably higher than the even-spin states. Backbends of both the even- and odd-spin members of the γ band are apparent around spins 13 and 14.

A marked reversal in the odd-even staggering occurs through the backbend region in the γ band. The direction of this staggering is that the odd-spin states lie high relative to the even-spin ones below the backbend, and low after the backbend. This reversal in the staggering is the strongest evidence that these

higher superbands indeed correspond to the higher $i = 7$ bands coupled to the ground band.

In summary, we have found additional even-spin and odd-spin superbands lying above the well-known superband that produces the backbend for the yrast states. We have observed the intersection of the γ band with all three superbands, and this provides evidence that all of these superbands consist of two quasineutron $i = 7$ bands coupled to the quasiparticle vacuum (ground state).

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10.13 LIFETIME MEASUREMENTS IN ^{164}Er

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The nucleus ^{164}Er is one of the few stable nuclei that shows the backbending effect. Therefore, in this case it is possible to study this phenomenon by means of Coulomb excitation. With heavy ions such as ^{136}Xe , one is able to excite the levels in the backbending region with appreciable cross section. The large recoil velocity ($v/c \approx 0.08$) imparted by the xenon projectiles makes the Doppler-broadened-line shape a sensitive method for studying the short lifetimes characteristic of the high spin states excited here.

A beam of 620-MeV ^{136}Xe from the Lawrence Berkeley Laboratory SuperHILAC was used to bombard a thick ($\sim 30 \text{ mg cm}^{-2}$) ^{164}Er target. The deexcitation γ rays following the Coulomb excitation were detected in a 50-cm 2 Ge(Li) detector placed

at 0° with respect to the beam. The γ rays emitted during the slowing down of the recoiling nucleus in the target are Doppler shifted. Thus from the shape of the γ -ray line and the slowing-down time, the lifetime of the state can be determined.

The line shapes were analyzed by computer program. This program takes the recoil velocity and the angular distribution of the target nucleus together with the stopping power and calculates the expected line shape for a given lifetime. The angular distribution and the excitation function of the Coulomb excitation process were calculated using the program of Winther and de Boer. All the $E2$ and $E4$ matrix elements were included. The values of these matrix elements were derived from $B(E2, 0^+ \rightarrow 2^+)$ and $B(E4, 0^+ \rightarrow 4^+)$ using the rotational model. Note that the derived lifetimes are not sensitive to the values of the matrix elements (a 10% change in the matrix element produces negligible change in the angular distribution).

The electronic stopping powers, taken from the table of Northcliffe and Schilling,⁷ were corrected at low energies for the medium dependences using the table of Ziegler and Chu.⁸ We used nuclear stopping powers taken from the theory of Lindhard et. al.¹⁰

Lifetimes are obtained from a least-squares fit of the calculated line shapes to the experimental data. The uncertainties include the statistical error of the data and the uncertainties of the stopping power. The state with highest spin is analyzed first. Hence, the γ ray feeding the next lower state is properly accounted for by using the experimentally determined lifetime.

Figure 10.14 shows the fit to the 8^+ , 10^+ , and 12^+ states. The comparisons with the rigid rotor values based on the measured $B(E2, 0^+ \rightarrow 2^+)$ value¹¹ are shown in Table 10.3. These measured lifetimes agree with the rotational model predictions within about 15%. Further, they agree with the early measurement of the γ -ray yields¹² as well as with the predictions of the rotational alignment model of backbending.

Fig. 10.14. Doppler-broadened line shapes for high-spin states in ^{164}Er . The points are the experimental data, and the solid lines are the calculated fits from the program DOPCO by W. T. Milner, Physics Division.

Table 10.3. Lifetimes of states in ^{164}Er

J	τ_{exp} (psec)	τ_{rot} (psec)	$\tau_{\text{exp}}/\tau_{\text{rot}}$
8	3.69 (0.18)	3.88	0.95 (0.05)
10	1.46 (0.09)	1.51	0.97 (0.06)
12	0.8 (0.06)	0.76	1.05 (0.08)

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10.14 RECOIL-DISTANCE MEASUREMENT OF LIFETIMES OF ROTATIONAL STATES IN ¹⁶⁴Dy

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N. C. Singhal ²	M. W. Guidry ²

Recently we completed our study⁶ of lifetimes of rotational states in ¹⁶⁴Dy. For the measurements, a 1.0-mg/cm² foil enriched to 98.4% in ¹⁶⁴Dy was bombarded with 152.6-MeV ⁴⁰Ar ions from ORIC. An 18% efficient germanium detector for measuring the γ rays was located at 0° relative to the beam direction. The Doppler-shift recoil-distance apparatus used has been described elsewhere.⁷

Data were collected for nine target-stopper distances over the range 25–670 μm appropriate for the 6–4 and faster transitions and for three longer distances up to 6352 μm suitable for the 4–2 transition. A plot of these data is shown in Fig. 10.15.

Fig. 10.15. Plot of the unshifted fraction U ($U+S$) as a function of target-stopper distance for the $4 \rightarrow 2$, $6 \rightarrow 4$, $8 \rightarrow 6$, and $10 \rightarrow 8$ transitions in ^{164}Dy . Excitation was produced by a 152.6 MeV ^{40}Ar beam, and the average recoil velocity corresponded to $v = 0.03226$ for excitation of the 6^+ state. Three large distance points for the $4 \rightarrow 2$ transition are not plotted. The lines represent least-squares fits to the data.

Our best values for the mean lives and corresponding $B(E2)$ ratios are given in Table 10.4. Quoted uncertainties include contributions from uncertainties in peak areas and in a series of corrections (see ref. 7), which must be applied to the data.

In our earlier Coulomb excitation yield measurements⁸ as well as in those by Oehlberg et al.,⁹ there was an indication that the $B(E2; 6-4)$ was about 15% below the value predicted by the rotational model. However, we interpret our present results to be indicative of agreement with rotational theory for all states measured. It is true that the ratios in column 6 of Table 10.4 tend to be slightly less than unity, but

Table 1-4. Mean flows and RAE D values for 194 D.

$J - I$	$\frac{M_{\text{H}}(J - I)}{10^4}$	$\frac{L}{L_{\odot}}$	σ	$\frac{M_{\text{H}}(J - I)}{10^4} \frac{1}{\cos i}$	$\frac{M_{\text{H}}(J - I)}{10^4} \frac{1}{\sin i}$
2 - 0				1.116 ± 0.048	1.0
3 - 2	236.0 ± 15	168.44	0.026	1.879 ± 0.075	0.92 ± 0.05
4 - 3	105.0 ± 10	149.00	0.023	1.220 ± 0.048	0.77 ± 0.03
5 - 4	105.0 ± 10	142.15	0.022	1.294 ± 0.107	0.68 ± 0.06
				± 0.05	± 0.25
10 - 9	57.0 ± 0.7	41.16	0.025	1.12	0.01
				± 0.11	0.05
				± 0.1	1.0
22 - 19	1.6 ± 0.6	444.0	0.10	1.0	0.05
				± 0.1	0.1

*Reference to any company or product does not imply endorsement or approval.

* Reported expenditures include a 20% contribution from the principal affiliates.

¹ Directed graphs of four measurements. See J. D. Koster and R. P. Schuchman, *Phys. Rev. Lett.* **101**, 200401 (2008); K. A. Jan, J. A. Hader, L. Y. Lee, L. M. Sander, and L. R. Saito, *Phys. Rev. Lett.* **29**, 1010 (1972); H. F. W. Beekman, B. Winkler, W. E. Love, and D. Petráš, *Phys. Lett.* **49B**, 323 (1974); and A. H. Stein and J. Greenberg, *Phys. Rev. D* **10**, 263 (1974).

we feel that it would be necessary to reduce the experimental uncertainties by a factor of 2 in order to expose reliably any deviations from theory. Time-consuming alignment attenuation measurements for high-spin states may be mandatory for achievement of the desired accuracy from recoil-distance measurements.

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10.15 LIFETIMES OF GROUND-BAND STATES IN ^{192}Pt AND ^{194}Pt AND APPLICATION OF THE ROTATION-ALIGNMENT MODEL

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Recently we carried out lifetime measurements on members of the ground bands in ^{192}Pt and ^{194}Pt . There were two primary reasons for these measurements. In the first place we were interested in understanding some of the strong irregularities observed^{6,7} in the rotational-like band structure of the even $^{184-194}\text{Pt}$ isotopes. A pronounced compression of the energy spacing between the 10⁺ and 12⁺ states is observed, and the level spacing pattern above spin 2⁺ in ^{190}Pt and ^{192}Pt resembles that of the low-spin states. Furthermore a $B(E2; 12^+ \rightarrow 10^+)$ value of $(0.33 \pm 0.06) e^2 b^2$ has been deduced from the measured^{8,9} half-life of the 12⁺ level in ^{192}Pt , and this value is only about 50% of the rotational limit based on an average of the ^{192}Pt $B(E2; 2^+ \rightarrow 0^+)$ measurements. The above observations have been interpreted^{6,10} within the rotation-alignment (RA) model,¹¹ and the anomalies are reproduced if an oblate deformation is assumed for the nucleus together with alignment of two $i_{11/2}$ neutrons. A measurement of the lifetimes of the states up to 12⁺ should add some clarity to the picture. A second reason for this study involved more than a factor-of-2 discrepancy between the previously measured¹¹ half-life value of the 4⁺ state in ^{192}Pt and that predicted by either the RA or the pure rotational models.

Lifetime measurements were carried out by the Doppler-shift recoil-distance method. The states were Coulomb excited by a beam of 149-MeV ^{40}Ar ions from ORIC. The target was a 3.1-mg/cm² metallic platinum foil enriched to 57.3% in ^{192}Pt and 26.1% in ^{194}Pt . The average recoil velocity imparted to the platinum ions when the ^{40}Ar -backscattered ions were detected in coincidence with an annular silicon detector was $v/c = 0.0249 \pm 0.0004$. Details of the experimental method and data analysis techniques can be found in refs. 12-13.

Due to the low Coulomb excitation cross section with ^{40}Ar ions, we were able to get good data for only three states in ^{192}Pt and two states in ^{194}Pt . A summary of the results and comparisons with previous measurements are given in Table 10.5.

As pointed out in our recent paper,¹⁴ both the RA and pure rotational models give essentially the same

Table 10.5. $B(E2)$ and $T_{1/2}$ values for ^{192}Pt and ^{194}Pt .

Isotope	State	$B(E2)$ (e ² b ²)	$T_{1/2}$ (ps)
^{192}Pt	4 ⁺	0.33 ± 0.06	1.2 ± 0.2
	8 ⁺	0.33 ± 0.06	1.2 ± 0.2
	12 ⁺	0.33 ± 0.06	1.2 ± 0.2
^{194}Pt	4 ⁺	0.33 ± 0.06	1.2 ± 0.2
	8 ⁺	0.33 ± 0.06	1.2 ± 0.2

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10.16 COULOMB EXCITATION OF VIBRATIONAL NUCLEI WITH HEAVY IONS

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Recently the rotational motion of many well-deformed rare-earth^{4,5} and actinide⁶ nuclei has been studied with Coulomb excitation, using heavy ions such as ¹³⁶Xe. Transitional nuclei such as osmium and platinum have also been studied with the same method. However, our knowledge of the vibrational nuclei is limited to the low-lying states. In an effort to understand the high-spin behavior of these nuclei and to document their collective nature, we began Coulomb excitation studies on the most collective vibrational nuclei around the mass 100 region.

The experiments were carried out with 121- and 130-MeV ⁴⁰Ar beams from ORIC. Metallic foils of ¹¹⁰Pd, ¹¹⁴Pd, and ¹¹⁶Cd with thicknesses of about 1.5 mg/cm² were used as targets. The back-scattered ⁴⁰Ar projectiles were detected in a solid-state annular detector, which extended from 155° to 175°. Gamma rays were detected in two Ge(Li) detectors in coincidence with the back-scattered ⁴⁰Ar. These two detectors, located at 0° and 55° with respect to the beam, were also placed in coincidence with each other to aid in establishing the order of transitions in the level scheme.

Since the energy of a back-scattered particle is mainly dependent on the target depth at which the interaction occurs, it is possible to select γ rays in coincidence with argon ions of different energy ranges. Hence, we can obtain an excitation function that provides information on the spin of the levels. Figure 10.16 shows a spectrum from 121-MeV ⁴⁰Ar on ¹¹⁰Pd. Gamma rays from levels in the ground-state band with spins of up to 6⁺ are observed. A 2⁺ and a 4⁺ state in a second band are also observed. An interesting feature of the spectrum is that it does not resemble the spectrum of an ideal vibrator. For an ideal vibrator, the γ rays between the various phonon

Fig. 10.16. Gamma-ray spectrum in coincidence with the back-scattered beam from the Coulomb excitation of ¹¹⁰Pd by 121-MeV ⁴⁰Ar.

states have the same energy. Actually, the spectrum is very similar to a rotational sequence where the transition energies increase with spin in a rather regular fashion.

In addition to the level energies, the Coulomb excitation cross section can provide a better insight of the collective properties. We have compared the experimental γ -ray yields with the predictions of several models. The Coulomb excitation yields were calculated using the program of Winther and de Boer. For the input of the program, we used the experimental level energies and several sets of theoretical matrix elements. The values of the matrix elements were normalized to the known values⁷ of $\langle 0 || m(E2) || 2 \rangle$.

Figure 10.17 shows the comparisons between the experimental and calculated results. Both the vibrational model and the Boson-expansion model calculations give good agreement for the ground-state band. However, there are large differences for the second 4⁺ and the second 0⁺ states. The experimental yields are much lower than the calculations. This may indicate the loss of the collectivity in the side band and the concentration of the collectivity into the ground-state band. Combined with the observed quasi-rotational energy level spacings, these results may be the first indication that these "vibrational" nuclei change to rotational behavior at rather low spin.

Fig. 10.17. Relative γ -ray yield from Coulomb excitation of ^{110}Pd by 121-MeV ^{40}Ar . The points are the experimental data, the solid lines are the values calculated with the vibrational model, and the dashed lines are the results from a Boson expansion calculation.

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10.17 SURFACE STRUCTURE OF DEFORMED NUCLEI

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Heavy-ion projectiles at energies near the Coulomb barrier can excite deformed rare-earth and actinide nuclei sufficiently to exhibit Coulomb

nuclear interference (CNI) effects. For such heavy systems, the short deBroglie wavelength allows radial localization, and the transfer of multiple rotational quanta permits angular localization around the nuclear surface. Recently refinements to the classical limit S-matrix (CLSM) scattering theory have made tractable the analysis of inelastic excitation of rotational nuclei to high-spin states.^{4,5}

In some early experiments performed at the Berkeley SuperHILAC and the Oak Ridge Isochronous Cyclotron, we studied the systems $^{84}\text{Kr} + ^{232}\text{Th}$, $^{40}\text{Ar} + ^{238}\text{U}$, and $^{16}\text{O} + ^{162}\text{Ly}$. We analyzed the data according to the CLSM theory and found support for the basic features of the theory and the first experimental evidence for CNI in the excitation of high-spin states by very heavy projectiles. In an attempt to make some quantitative measures of the surface structures of these nuclei, we tried to fit the data for each system with a standard complex deformed Woods-Saxon potential with six adjustable parameters. We were successful for some states, but we were unable to meet the criterion that all spin states be fitted simultaneously by the same potential (Fig. 10.18). These results suggest possible inadequacies in standard parameterizations of the deformed nuclear potential.

In the last few months, we have devised a method whereby equipotential contours of the interaction potential are determined without introducing particular models for the potential. In addition, it should be possible to probe both charge and mass parameters in the same experiment. We have completed two experiments at ORIC in which the systems studied were $^{40}\text{Ar} + (^{154}\text{Gd}, ^{160}\text{Gd}, ^{162}\text{Dy}, ^{164}\text{Dy})$. However, at this time the analysis of the data is not yet complete.

In the future, we plan to continue a systematic probe of the rotational rare-earth and actinide nuclei. Furthermore, we hope to perform cross-bombardment experiments on the same targets to facilitate the unfolding of the interaction potentials. Such characteristic surface potentials should prove instructive to the study of collective excitations of nuclei.

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Fig. 10.18. Excitation functions in the CNI region. The solid line is a calculation for pure Coulomb excitation. Data for Kr-232 from I. Y. Lee et al., *Phys. Rev. C* **12**, 483 (1975). The approximate energy uncertainty is indicated by the horizontal bars at the bottom. Dashed and dash-dotted lines are calculations using a nuclear potential as described in M. W. Guidry et al., *Nucl. Phys.* **A274**, 1 (1976). The potential parameters are taken from J. R. Birkehead et al., *Phys. Rev. C* **13**, 133 (1976) (dashed) and R. Vandenbosch, T. D. and M. Webb, in *Symposium on Classical and Quantum Mechanical Aspects of Heavy-Ion Collisions*, Heidelberg, 1974, W. L. Huls, Springer, Berlin, 1975 (dash-dotted) and correspond to potentials III and II, respectively, in M. W. Guidry et al., *Nucl. Phys.* **B83** (1976).

10.18 VALENCY CONTRIBUTION TO NEUTRON CAPTURE IN ^{235}S

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Peaks in the s -wave neutron strength vs mass curve in the region of $A = 50$ and 150 (regions beyond the closed neutron shells) corresponding to the filling of $3s$ and $4s$ neutron orbitals are well established. In fact, the curve structure can be matched in some detail with optical model calculations. A similar feature for the $3p$ region is apparent at $A = 95$ in the p -wave neutron strength function curve. However, the scarcity of data for p -wave resonances in other mass regions has not led to as well defined structure

as in the s -wave case. Evidence has been presented by Allen and Musgrove¹ that shell model single contributions (i.e., single neutron transition) to neutron resonance capture become significant may even dominate in the mass regions at and near the neutron closed shells and correlate well with the neutron strength function peaks. In favor of such valence neutron contributions can be cited various initial and final state correlation made to demonstrate the effect.

Mass 33 lies in the $2p$ region and may be used to show enhanced valence contributions for resonance capture. We have calculated this contribution (I_{ν}) to s , p , and d resonances in the $^{235}\text{S} + n$ system and compared them with

ed values of $\Gamma_{\gamma}^{\text{obs}}$ for a number of resonances neutron capture. The partial gamma width for a transition "A" to a final state "B" in valency capture, using electromagnetic dipole deexcitation, can be written as

$$\Gamma_{\gamma}^{\text{obs}} = k(Z/A)^2 a_{\gamma}^2 E_{\gamma}^3 S_{\gamma} \gamma_{\gamma}^2 I_{\text{pg}} M_{\gamma}^2 \quad (1)$$

where $k = [(16\pi)/9] [(m_e c^2)^2 (hc)^4] a_{\gamma}^2$ = channel width, E_{γ} = the energy of the primary gamma, S_{γ} = the spectroscopic factor for resonance A. The term $I_{\text{pg}} = \int u_p(r) u_f(r) dr$ is the overlap integral between initial and final states and has been tabulated by Lynn. The term

$$M_{\gamma}^2 = [(\langle f | U_{\gamma} | i \rangle)^2 / (2J_i + 1)]$$

represents the angular part of the transition matrix and can be expressed in terms of the angular momenta and spins of the target and neutron initial and final states.

The capture gamma spectrum for ^{32}S has been studied,^{1,2} and the level scheme is well established.³ By summing the calculated partial widths to all final states, we have estimated the valency capture in some 27 resonances. Only four s-wave resonances have been identified in ^{32}S up to a neutron energy of 1100 keV. We have measured only an upper limit of Γ_{γ} for the 1064.7-keV level, but the remaining resonances yield an average value of the calculated valency contribution, $\Gamma_{\gamma}^{\text{calc}} / \Gamma_{\gamma}^{\text{obs}} = 0.07$ (Table 10.6). This low value is consistent with the valley in the s-wave neutron strength vs the A curve near mass 30. There are eight resonances that have been unambiguously identified as $d_{5/2}$ for which we calculate an average $\Gamma_{\gamma}^{\text{calc}} / \Gamma_{\gamma}^{\text{obs}} = 0.25$. This value is significantly greater than that for s-waves but is still a minor component of Γ_{γ} . Six $p_{1/2}$ and nine $p_{3/2}$ resonances have been clearly identified and show a relatively large valency component; $\Gamma_{\gamma}^{\text{calc}} / \Gamma_{\gamma}^{\text{obs}} = 0.63$ for $p_{1/2}$ and $\Gamma_{\gamma}^{\text{calc}} / \Gamma_{\gamma}^{\text{obs}} = 0.76$ for $p_{3/2}$ resonances. This large valency component is consistent with the suggested strong single particle character of the ($^{32}\text{S} + n$) system. It is also of interest to note that ^{32}Si has been reported^{4,5} to show similarly a large valency component.

Table 10.6. Calculated valency contribution to resonance neutron capture in ^{32}S

E_n (keV)	$10^{-4} \gamma_{\gamma}^2$ (eV)	$\Gamma_{\gamma}^{\text{obs}}$ (eV)	$\Gamma_{\gamma}^{\text{calc}}$ (eV)	$\Gamma_{\gamma}^{\text{calc}} / \Gamma_{\gamma}^{\text{obs}}$
s-1/2				
102.8	2.68	7.0	0.48	0.069
377.5	0.74	2.18	0.15	0.071
695.9	0.82	3.0	0.21	0.069
1064.7	0.017	<3.0	0.03	<0.01
				av = 0.070
d-5/2				
462.7	1.78	0.44	0.14	0.33
586.8	6.25	0.93	0.52	0.56
649.2	1.58	0.93	0.14	0.15
675.3	7.79	0.40	0.066	0.16
818.6	1.11	0.37	0.10	0.28
919.7	3.94	1.67	0.38	0.23
957.1	1.46	0.67	0.14	0.21
1055.2	1.45	1.6	0.15	0.094
				av = 0.25
p-1/2				
30.4	0.92	1.01	0.55	0.55
202.6	2.88	0.90	1.62	2.02
272.1	1.06	4.07	0.68	0.17
724.7	0.90	1.0	0.67	0.67
776.3	0.038	1.4	0.086	0.06
984.9	1.14	3.0	0.90	0.30
				av = 0.63
p-3/2				
97.5	0.30	0.29	0.19	0.66
112.2	1.22	0.37	0.75	2.02
288.4	0.67	1.82	0.42	0.23
412.3	0.027	0.90	0.017	0.02
740.8	0.22	0.30	0.17	0.55
778.5	0.26	0.30	0.63	2.10
1007.7	0.079	0.60	0.086	0.14
1047.5	0.43	0.5	0.48	1.0
1091.3	0.052	0.50	0.055	0.11
				av = 0.76

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10.19 NEUTRON CAPTURE CROSS SECTION OF MANGANESE

J. B. Garg¹, R. L. Macklin²,
J. Halperin

Neutron capture cross-section measurements of Mn have been carried out at the ORELA time-of-flight facility over the energy interval 2.6 to 600 keV. These measurements were carried out with the total energy detector at the 40-m flight path, which has been previously described.³ The total capture width Γ_c has been evaluated for 143 resonances (up to ~110 keV) from the measured capture areas and from published neutron widths.⁴ The resonance parameter analysis was carried out in terms of the single-level Breit Wigner formula, using the method of least squares. Account was taken of instrumental resolution, Doppler broadening, and resonance self-protection. The asymmetric shape of the detector response was fitted to a Gaussian function with an exponential tail. For broad resonances, it was necessary to include multiple scattering as well as the prompt neutron sensitivity.

The s-wave resonances have been largely identified from the transmission experiments by their characteristic asymmetric shape. The remaining resonances have been assumed to be p-wave except for a small number assigned as d-wave because of their exceptionally small p-wave reduced widths (less than 10^{-4} eV).

The average level spacing has been measured for s-wave resonances as $\bar{D}_{s,0} = 2.33(25)$ keV and for p-wave resonances as $\bar{D}_{p,1} = 1.07(8)$ keV. Their ratio is in good agreement with the expected value of $2\ell + 1 = 2$.

The neutron strength functions, defined as

$$S_\ell = [1/(2\ell + 1)](\Sigma g \Gamma_\ell^2) (\Delta E)^{-1},$$

have been evaluated here for p-wave resonances and a lower limit established for d-wave resonances. Γ_ℓ^2

reduced neutron width for t-wave resonances, $g =$ statistical weight factor, and $\Delta E =$ energy range spanned. For a value of the nuclear radius, $R = 4.5$ fm, we find $S_1 = 0.35(4) \times 10^{-4}$ eV⁻¹, which is consistent with values obtained for other neighboring nuclei. We also report $S_2 > 1.0 \times 10^{-4}$ eV⁻¹ based on the small sampling of d-wave resonances assigned in this study.

The average radiative widths for 46 s-wave and 28 p-wave levels have been measured as $(\bar{\Gamma}_\gamma)_s = 0.75(15)$ eV and $(\bar{\Gamma}_\gamma)_p = 0.40(10)$ eV. The difference would appear to be significant, although the p-wave average is for only 1.3 of the resonances in the energy range due to experimental difficulties.

The correlation between the reduced neutron widths and the total radiative widths has been investigated for s-wave resonances. A correlation coefficient $\rho = 0.64(14)$ has been measured. The probability that so high a correlation coefficient could result from a random distribution of these parameters is 0.001, which indicates a highly significant correlation and implies a nonstatistical interpretation such as doorway states or valency capture.

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10.20 SEARCH FOR SUPERHEAVY ELEMENTS IN NATURAL SAMPLES BY NEUTRON MULTIPLICITY COUNTING

10.20.1 Superheavy Element Search in Bismuthinite, Bi₂S₃

B. H. Ketelle¹, R. W. Stoughton²,
E. L. Fireman³

Recently, Flerov and collaborators^{1,2,3} presented evidence for the presence of a superheavy element (SHE) in the carbonaceous chondrites Allende, Saratov, and Efremovka and in hot spring water from the Cheleken Peninsula. Their positive results are so small that it is exceedingly difficult to substantiate their claim by repeating their measurements on similar materials. The SHE concentrations in the carbonaceous meteorites (3×10^{-10} to 3×10^{-11}

g/g) required the detection of a few multiple neutron events in several months from many kilograms of meteoritic material. The work of Flerov et al.,¹ although difficult to verify, encourages additional searches for materials with higher SHE abundances. Their work, in fact, stimulated our study of bismuthinite.

If a long-lived SHE exists as a result of nucleosynthesis, it should be present not only in meteorites but also in terrestrial materials at some concentration level. In fact, Flerov¹ claimed a higher concentration, 2×10^{-10} g/g, of a superheavy, multiple-neutron emitter in minerals from the hot spring water of the Cheleken Peninsula than in the meteorites. Zvara et al.² investigated the chemical properties of the multiple-neutron emitter in Flerov's samples and found it to be more volatile than lead and to form a sulfide that is insoluble in dilute acids and alkalis. It had the properties expected for an element with atomic number 112, 113, 114, or 115. Such elements are the homologs of Hg, Tl, Pb, and Bi. Flerov's carbonaceous chondrite results give the following SHE:cosmic abundance ratios: SHE:Hg, $\sim 3 \times 10^{-10}$; SHE:Tl, $\sim 2 \times 10^{-10}$; SHE:Pb, $\sim 3 \times 10^{-10}$; and SHE:Bi, $\sim 1 \times 10^{-10}$.

If the SHE followed its homolog, Hg, Pb, or Bi, through its geochemical evolution into the sulfide minerals, galena and cinnabar would contain superheavy concentrations of approximately 3×10^{-10} g/g, and bismuthinite would have a superheavy concentration of approximately 10^{-10} g/g.

Bismuth samples have been measured with neutron counters previously,³ but in each case results have been negative or inconclusive due to high background rates or uranium contamination.

Prior to the present study, careful tuning of the improved multiplicity counter⁴ reduced the empty counter background. The uranium content of our samples was low and quantitatively evaluated. The sample contained 30 ppm of uranium. The bismuthinite samples weighed a total of 595 g and were counted for 15.46 live days.

The observations, corrections, and conclusions are summarized in Table 10.7. The column titled "Total background" is the sum of observed counts with the counter empty plus those due to the uranium spontaneous fission and those due to cosmic-ray interactions with the bismuth. The errors shown are single standard deviations of the counting only. Since the net counts are zero within statistics, upper limits of counts for each multiplicity were taken as twice the standard deviation σ . The detection probability $P(N)$ at each average value of the emitted neutron multiplicity $\bar{v}$ was calculated from the instrument efficiency of 47%. The numbers of superheavy element atoms at $\bar{v}$ of 3 and 6 are shown under the assumption that the SHE has a half-life of 10^7 years.

If the atomic weight of SHE is assumed to be 300, the maximum concentrations of the SHE in the bismuthinite are 5.6×10^{-10} g/g bismuth, if $\bar{v} = 3$, and 1.4×10^{-10} g/g bismuth, if $\bar{v} = 6$.

According to Flerov et al.,¹ the average number of neutrons from SHE fissions that they have detected is between 3 and 6. From their carbonaceous chondrite data, the cosmic abundance ratio of SHE:Bi is $\sim 10^{-10}$ g/g; this ratio is approximately four orders of magnitude larger than the ratio we measure in bismuthinite. The superheavy element, if it exists, did not follow bismuth during its geochemical evolution into our bismuthinite samples.

Table 10.7. Neutron count data for bismuthinite, background corrections, and analysis

Neutron multiplicity	Bismuthinite (counts/day)	Total background (counts/day)	Net (counts/day)	2σ (CV) (day ⁻¹)	$\bar{v} = 3$		$\bar{v} = 6$	
					$P(N)$	No. SHE (atoms)	$P(N)$	No. SHE (atoms)
1	8220 $\pm$ 23							
2	19.7 $\pm$ 1.1	19.98 $\pm$ 1.1	0.3 $\pm$ 1.6	3.2	0.292	5.8×10^{12}	0.255	2.1×10^{12}
3	1.6 $\pm$ 0.3	3.06 $\pm$ 0.4	1.4 $\pm$ 0.5	1.0	0.116	4.5×10^{12}	0.273	1.9×10^{12}
4	0.26 $\pm$ 0.13	0.64 $\pm$ 0.2	0.4 $\pm$ 0.2	0.4	0.0245	8.6×10^{12}	0.186	1.1×10^{12}

10.20.2 Superheavy Element Search in Other Natural Samples

R. W. Stoughton J. Halperin
B. H. Ketelle O. E. Myers
G. D. O'Kelley J. Maly
D. R. Walz

In our previous annual report, we presented neutron multiplicities on monazites from Australia; Georgia; United States; Malaysia; South Africa; and Madagascar. The two samples containing monazites from Madagascar were the first ones counted, and the corrections used at that time were not the final ones used. Hence the results on the Madagascar monazites in our previous report have now been superseded. The changes in some of our numbers do not change our former conclusions: we found no positive evidence for SHE in any of the monazite samples.

We have also wondered about possible biological concentrations of SHE in nature. Folsom, Wong, and Hodge¹³ while at the Scripps Institution of Oceanography, La Jolla, California, reported concentration of ^{210}Po in the caecal masses of Albacore tuna by factors of some two million compared to the surrounding seawater. Presumably any ekapolonium ($Z = 116$) would, and possibly some other elements might, also concentrate in such caecas. We contacted members of the Van Camp Sea Food Company, Division of Ralston Purina Company, San Diego, California. They sent us ten standard tuna cans of yellowfin tuna caecas and ten of the albacore tuna caecas. These caecas had been canned, sealed, and then heated for sterilization; this procedure should have precluded the loss of any volatile substances. The yellowfin caecas showed no neutron multiplicities above background. We are still counting the albacore caecas, and we now have more caecas from the Monterey, California, area.

Wolke¹⁴ has suggested that caecas of marine fauna, especially near regions of coastal monazite sands, might be collected and wet-ashed, then converted to a hydrochloric acid solution and circulated over such metal foils as Ag, Ni, Bi, Pt, or Pd to remove any element 116. He suggested that the foil could then be used as a target for proton-induced x-ray spectroscopy. If a SHE exists in the caecas and has chemical properties similar to polonium, he suggested it could be concentrated by a factor of 10^{12} with respect to the caecas or 10^{14} with respect to the surrounding seawater. We are uncertain why these limits have been set on the concentration factors, since it isn't clear what sets a limit. It would seem that

the greater the amount of caecas the lower the limit of SHE that could be detected. If it is assumed that the wet-ashing process does not volatilize (or could be made not to volatilize) any SHE present and if sufficient caecas could be made available, a much lower limit (many orders of magnitude) can be set than we will be able to detect. We suggest that, if such a procedure is ever carried out, neutron multiplicities gated on fission fragments be counted to get both fragment energies and multiplicities. These two combined measurements should give definitive proof of the presence of any SHE.

Sea kelp is known to concentrate a number of elements, including iodine. We were able to get some kelp from the kelp beds off San Clemente Island, Southern California. Although we had a couple of kilograms of kelp, it was very bulky. We preferred to count it in a mode with 10-cm sample cavity diameter (single neutron efficiency $\epsilon = 0.47$) rather than a mode with 24-cm cavity ($\epsilon = 0.30$), since the measurement would be more sensitive with the higher efficiency if $\bar{r}$ were ≥ 6 . Accordingly, we packed 0.4 kg of kelp tightly into a bag and counted it in the smaller cavity. The results were negative.

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10.21 GAMMA-RAY STUDIES ON THE GEOCHEMISTRY OF ACHONDRITIC METEORITES

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Gamma-ray spectrometry is a useful method for assay of radionuclide concentrations in geological samples. Because gamma rays are very penetrating, gamma radioactivity of samples ranging from a few grams to several kilograms can be determined after appropriate calibration. Gamma-ray analysis is an excellent method for obtaining average concentrations in large samples nondestructively. Such measurements often may prove to be useful when large samples contain small-scale inhomogeneities,

so that high-sensitivity analyses of small fragments can lead to large sampling errors.

We are continuing to apply our high-sensitivity, low-background gamma-ray spectrometer to measurements of low levels of radioactivity in geological and environmental samples. A description of the gamma-ray spectrometer and the methods of calibration and data analysis have been published.¹ We are investigating a series of achondritic meteorites because of recent interest in petrogenetic models, which suggest that the parent bodies of the several groups of achondritic meteorites, though distinct, are related.

Analyses of nine meteorite samples are shown in Table 10.8. Duplicate samples of the widely studied Pasamonte and Stannern eucrites were measured, and our results show that the concentrations of K, Th, and U are rather uniform for different stones from the same meteorite fall.

The first eight specimens listed in Table 10.8 are eucrites, and the last entry, Nakhla, is the representative member of the nakhlite group of igneous meteorites. The range of concentrations of K, Th, and U in eucrites is about 280-620 ppm, 330-660 ppb, and 90-200 ppb respectively. These values suggest somewhat more uniformity in primordial radioactive content than is usually assumed from trace-

Table 10.8. Results of analysis of some achondritic meteorites by nondestructive gamma-ray spectrometry
Calibration for assay of K, Th, and U assumed terrestrial isotopic abundances and equilibrium of thorium and uranium decay series

Meteorite, specimen No.	Source ^a	Weight (g)	Density (g/cm ³)	K (ppm)	Th (ppb)	U (ppb)	²⁶ Al (dpm/ke)	Th/U	K/U
Pasamonte, 2284 (19K)	USNM	126	2.46 ± 0.04	346 ± 19	361 ± 18	90.5 ± 8.2	82.7 ± 1.8	3.99 ± 0.41	3823 ± 405
Pasamonte, 2284 (19.0)	USNM	135	2.51 ± 0.12	364 ± 15	466 ± 16	124 ± 8	90.3 ± 1.6	3.76 ± 0.27	2935 ± 225
Stannern, 3080	USNM	162	2.58 ± 0.06	614 ± 26	647 ± 11	162 ± 5	99.0 ± 1.1	3.99 ± 0.14	3790 ± 199
Stannern, 3244	USNM	136	2.65 ± 0.10	5 ± 24	663 ± 15	190 ± 9	93.8 ± 1.3	3.49 ± 0.18	3253 ± 199
Nuevo Laredo, 1783	USNM	128	2.58 ± 0.10	411 ± 10	530 ± 9	138 ± 5	80.8 ± 0.7	3.84 ± 0.15	2978 ± 130
Sioux County, 896	USNM	130	2.58 ± 0.06	278 ± 27	338 ± 13	89.1 ± 7.6	97.0 ± 1.1	3.79 ± 0.35	3120 ± 403
Juvinas, 439	USNM	98	2.68 ± 0.04	347 ± 21	365 ± 14	109 ± 8	98.7 ± 1.1	3.35 ± 0.28	3183 ± 303
Haraiya, 637.1	ASU	34	^b	308 ± 54	335 ± 19	99.3 ± 8.9	85.0 ± 1.3	3.37 ± 0.36	3102 ± 611
Nakhla, 426	USNM	118	2.90 ± 0.01	1150 ± 20	246 ± 10	54.4 ± 5.7	83.4 ± 0.8	4.52 ± 0.51	21140 ± 2245

^aUSNM = U. S. National Museum, Washington, D. C. (Dr. Roy S. Clarke, Jr.); ASU = Arizona State University, Tempe, Ariz. (Dr. Carleton B. Moore).

^bBulk density of this specimen was not determined due to its extreme friability.

element data obtained by other methods having larger analytical errors.

Concentration ratios K:U, which are characteristic of the early chemical fractionation in a planetary body, ranged from about 3000-4000 for the samples studied. This narrow range of values for K:U and the potassium concentration range of 280-620 ppm both lie within the spread of values measured for the Apollo 15 and 17 lunar basalts,⁷ which reinforces the view that the parent body of the eucrites was subjected to an early igneous history similar to that of the moon.

Concentrations of ²⁶Al produced by cosmic-ray-induced spallation are shown in Table 10.8. Where comparisons are possible, these concentrations compare favorably with those of other work. An

analysis is in progress relating these data to the irradiation history of the meteorites in space.

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II. Chemical Physics

II.1 STRUCTURAL CHEMISTRY

II.1.1 The Crystal and Molecular Structure of *tris-o*-Bipyridyl Ruthenium(II) Hexafluorophosphate

H. A. Levy¹ D. S. Jones²

Interest in this complex of ruthenium(II) arises in connection with systematic studies at UNC-Charlotte for the development of photocatalysts. Schematically, a molecule X is photoexcited to an excited species X^* , which subsequently reacts with the material of interest. An example of great current interest is the solar photosplitting of water to yield hydrogen by photoreduction or oxygen by photo-oxidation, the product depending on the nature of the catalyst. Complexes of ruthenium have shown promise as catalysts in this regard. The properties of the excited species, including lifetime, barrier to electron transfer, and self-exchange rate constant, are critical to achieving the desired catalytic behavior; and the ability to predict such properties and ultimately to design a molecule that will have optimal properties is highly desirable. Application of current theoretical methods to this purpose requires detailed knowledge of the structures to be expected in prototypes of the complexes, including accurate interatomic distances. As a start in acquiring these structural data, the structure of the complex *tris-o*-bipyridyl ruthenium(II) hexafluorophosphate $Ru(C_{10}H_8N_6)(PF_6)_2$ was undertaken at ORNL.

X-ray data from a single crystal yielded the structure of the complex cation shown in Fig. 11.1. The point-symmetry is D_{3h} , with the bidentate bipyridyl ligands arranged in propeller fashion around ruthenium. The six ruthenium-nitrogen linkages occupy the corners of a nearly regular octahedron with a ruthenium-to-nitrogen distance of 2.06 Å. The fluorophosphate ion has the form of a distorted octahedron of symmetry C_{3v} with three $P-F$ distances of 1.57 Å and three others of 1.54 Å.

Fig. 11.1. The structure of the complex cation *tris-o*-bipyridyl ruthenium(II) ($2+$) from x-ray diffraction of the hexafluorophosphate salt. The symmetry is D_{3h} , and the view is along the threefold axis. Ellipsoids give the 50% probability surface for thermal displacements.

This ion displays evidence of large-amplitude librational motion.

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II.1.2 The Molecular and Crystal Structure of the Compound $Co(acacen)(pyridine)_3PF_6$, $CoC_{22}N_4O_2H_{21}PF_6$

D. S. Jones¹ H. A. Levy

Studies at UNC-Charlotte of chemical systems giving promise as photocatalytic materials were

briefly described in a previous section of this report. Mixed complexes containing both ruthenium and cobalt appear to offer desirable properties, and basic geometric data characteristic of binding to cobalt is needed for understanding and prediction of properties. The present study was undertaken as a start on acquiring these data.

The compound is the hexafluorophosphate salt of the complex ion of Co^{3+} with two molecules of pyridine and one of the tetradentate ligand *acacen*, the dienolate of the condensation product of two molecules of acetylacetone with ethylenediamine. The structural formula is

X-ray diffraction measurements yielded a structure containing the complex cation illustrated in Fig. 11.2. The ion has no special crystallographic symmetry but approximates that of point group C_{2v} . The linkages to cobalt occupy the vertices of a distorted octahedron with two nitrogen atoms from pyridine molecules along a polar axis and with two oxygen

Fig. 11.2. The structure of the complex ion $\text{Co}(\text{acacen})(\text{pyridine})_2^+$ in the hexafluorophosphate salt crystal. The atoms are represented by circles of arbitrary radius. Those atoms that are unlabeled are carbon atoms; the hydrogen atoms are omitted. This drawing is based on preliminary values of the structural parameters.

atoms and two nitrogen atoms from the tetradentate ligand around the waist. An unusual aspect is the mutually perpendicular conformation of the two pyridine rings.

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3. D. P. Rillema, University of North Carolina at Charlotte, personal communication.

11.1.3 The Oak Ridge Crystallographic Imaging and Graphics System

C. K. Johnson

Computer graphic systems have been used advantageously by crystallographers for nearly 20 years. One of the earliest successful demonstrations of this approach was provided by Busing¹ in 1960, using an IBM-704 computer and an on-line cathode ray tube display device. Batch computing is often used to provide crystallographic illustrations with programs such as ORTEP,² which was written at Oak Ridge in 1965. Unfortunately, the batch-computing approach is poorly suited to the production of illustrations, and the time required to make the illustrations for a structure paper often approaches or exceeds that required to solve and refine the structure. Time-sharing computing over a telephone line also is inadequate because of the large volume of graphic control information that must be transmitted to the remote graphics terminal. Dedicated mini- and microcomputers directly coupled to the graphics device seem to offer the only viable solution to the problem.

The newly acquired ORCIG (Oak Ridge Crystallographic Imaging and Graphics) system has a Data General S 130 Eclipse minicomputer with 128K 16-bit words of memory, a writable control store, and a 10-megabyte disk. This computer is coupled to a Genisco GCT-3000 raster graphic display system, which has a programmable graphics processor, two 1024 × 1024 bit-plane frame buffers with independent zoom-scroll controls, a hardware vector character generator, and a joystick-controlled cursor. This configuration of equipment is quite different from that normally employed by crystallographers using interactive graphics in that most of the previous display devices are based on the stroke graphics oscilloscope principle, whereas the present device utilizes the video scan principle of a television set. The figure or picture to be displayed is represented

digitally in the 1024×1024 random access bit-map frame buffer, and the video sweep scans through this million-point memory 30 times a second, mapping each point onto the display screen. A raster-graphics device cannot change figures as rapidly as a stroke-based device, but it can support a much more complex drawing without the flicker problem that plagues the stroke-based systems.

The raster-graphics technique provides image processing capability as well as graphics capability. Image processing is concerned with continuous representations, while graphics is concerned with line drawings. The basic elements in the two techniques are the line segment in graphics and the pixel (picture element) in a digitally represented image. A number of image processing possibilities in crystallography are based on Patterson and electron density map manipulation functions. One of the applications we have in mind is the use of independently scrolled bit planes to superimpose sections of three-dimensional Patterson functions, producing minimum-function displays for the solution of crystal structures.

Other graphics projects currently under way include the development of an interactive version of ORTEP² and an interactive version of the critical-point analysis program ORCRIT, which is used to aid in the interpretation of complicated density-function maps.

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2. C. K. Johnson, ORTEP II, A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations, ORNL-5138 (3d rev. of ORNL-3794) (March 1970).

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11.1.4 Diffraction Studies of Ion-Water Interactions¹

A. H. Narten R. Triolo

The bulk thermodynamic and transport properties of aqueous electrolyte solutions are determined by ion-ion and ion-water interactions. Properties that are predominantly determined by ion-water interactions include transfer coefficients (ΔG , ΔH , ΔS), partial molal coefficients (volume, heat capacity, etc.), and intrinsic solute coefficients (diffusion, friction, conductivity, etc.). A traditional approach has been to compare these solvation data with the predictions of models in which the ion is treated as a

macroscopic body and the solvent as a medium characterized by macroscopic properties. Deviations of solvation coefficients from these simple model predictions are then attributed to the formation of solvation complexes.

It has now become clear that it is both necessary and feasible to probe these interactions directly at the molecular level. 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. The spatial correlations between a monatomic ion (I) and its surrounding water molecules can be described by two atom-pair distribution functions, namely, $g_{IO}(r)$ and $g_{ID}(r)$. The functions $g_{IO}(r)$ and $g_{ID}(r)$ measure the probability density for finding an oxygen atom and a hydrogen atom, respectively, at r when an ion is at the origin. Hence, the function $g_{IO}(r)$ describes the positional and $g_{ID}(r)$ the orientational correlations between an ion and its surrounding water molecules. These distribution functions are related by liquid-state theory to the intermolecular forces on the one hand and by statistical mechanics to measurable thermodynamic properties on the other.

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. However, the interpretation of a single diffraction pattern is always difficult, often ambiguous, and never unique. This ambiguity of interpretation is greatly reduced if a solution is studied with both x rays and neutrons, and a few such studies (LiCl, HCl) have been reported. The only currently feasible way of uniquely determining the correlations between water molecules and monatomic ions in solution is to vary the scattering factor of the ion; a simple difference measurement then yields the ion-water correlations.

Neutrons are scattered by atomic nuclei, and the neutron scattering factor depends on the isotopic state of the nucleus. There is no large systematic variation of the neutron scattering factors with the atomic number Z ; hence neutrons are an excellent probe for the location of light atoms such as hydrogen. Using neutron diffraction, one measures the diffraction patterns from two ionic solutions that are identical in all respects except the isotopic state of one of the ions. The algebraic difference between the two scattering cross sections is then directly related to a weighted sum of the distribution functions $g_{IO}(r)$ and $g_{ID}(r)$ for ion-oxygen and ion-deuterium interac-

tions. These results can be uniquely interpreted in terms of distances and coordination numbers; unique separation of the two distribution functions $g_{\text{H}}(r)$ and $g_{\text{O}}(r)$ is, however, not possible. The neutron difference method has been applied to NiCl_2 , NaCl , CaCl_2 , and RbCl solutions in D_2O .

X-ray scattering arises from electron-photon interactions. Unlike neutrons, x rays have strong resonances with every atom at energies of the electron binding energies. Synchrotron sources emit intense photon fluxes from the visible into the hard x-ray region. This provides for the selection of a particular energy (wavelength) to enhance or decrease the x-ray scattering factor of any element. Since water molecules are "seen" by x rays as single scattering centers, information about ion-hydrogen interactions cannot be obtained by this method. However, a difference experiment with x rays yields directly the function $g_{\text{H}}(r)$ rather than the weighted sum of the functions $g_{\text{H}}(r)$ and $g_{\text{O}}(r)$ accessible from neutron diffraction. Furthermore, the enormous intensity available from synchrotron sources permits the study of ion-water interactions at very low ionic concentrations. The x-ray difference method is currently being applied to ionic solutions, but results have not yet been reported.

Difference experiments require a high degree of accuracy and are feasible only at high flux reactors and synchrotron x-ray sources. This fact requires a change in attitude of the experimenter who will have to carry out the measurements in the regional, user-dedicated facilities, which are becoming available in increasing numbers.

† Extended abstract of paper to be published in *Proc. Appl. Chem.* 1975.

11.1.5 Structural Analysis of a Compound Synthesized in the Coal Chemistry Project

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B. M. Benjamin

The compound 2,6-di-*tert*-butyl-1,4-methylphenol was used as a model system to study the course of oxidation of hindered phenols in coal. Several compounds were isolated from the oxidation mixture. This report deals with the structure determination and stereochemical properties of one of those products, 2,6-di-*tert*-butyl-1,4-benzoquinone. The orange crystals used in this experiment were prepared from 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde,

using a procedure similar to that of Yohe.¹ A 25-g sample of the aldehyde was placed into a solution of 60 g NaOH in 1 liter H_2O and heated at 90 °C with stirring for 4 d, with a constant flow of O_2 bubbled through the reaction mixture. The crude product was washed from the condenser with ether and recrystallized from hexane.

Crystals of 2,6-di-*tert*-butyl-1,4-benzoquinone ($\text{C}_{12}\text{H}_{16}\text{O}_2$, M.W. = 220.32) display the symmetry of the monoclinic space group $P2_1/a$ with cell dimensions, $a = 12.315(8)$, $b = 10.623(4)$, $c = 10.281(7)$, and $\beta = 97.285(9)^\circ$, at $19 \pm 1^\circ\text{C}$. The experimentally determined density is 1.09 g cm^{-3} , the calculated density is 1.10 g cm^{-3} , and the volume of the unit cell equal to $1333.9 \text{ \AA}^3$. Intensity data were collected for the 2369 unique reflections in the sphere $2\theta \leq 50^\circ$, using the Oak Ridge computer-controlled diffractometer and $\text{Mo K}\alpha$ radiation. The structure was solved, using direct methods and refined with a full-matrix least-squares routine to a final $R(F)$ of 0.073. The molecular packing in the crystal consists of "pseudodimer" formations with an interplanar separation of 3.51 Å. Although the molecule does not lie on any crystallographic symmetry element, the non-crystallographic stereochemical symmetry is very close to 2 mm, as shown by the bond distances and angles given in Fig. 11.3. The averaged bond distances before and after correction for thermal motion (described below) are given in Table 11.1.

Thermal motion drawings indicated that some torsional oscillation occurs in the tertiary butyl groups even though the steric interaction of the two tertiary butyl groups prevents large amplitude internal torsional oscillation. A segmented body thermal motion model was used, and the rms amplitudes of torsional oscillation were found to be 7.3° for C(2), C(7) and 5.3° for C(6), C(11). The rigid body libration of the parent segment gave principal rms values of 5.2°, 3.1°, and 2.1°, with the largest amplitude along the approximate twofold axis of molecular symmetry.

The molecular packing shown in Fig. 11.4 illustrates the dimeric nature of the molecular interactions. The bulky *tert*-butyl groups force the overlapping molecular rings of the dimer to be shifted from direct superposition.

† ORNL Summer Research Participation Program, Brookhaven State College, Brookhaven, Pa.

1. G. R. Yohe, *J. Org. Chem.* 21, 1156 (1956).

2. C. K. Johnson, pp. 151-154, *Topics in X-ray Crystallography: Generalized Treatment of the Problem*, M. J. G. Oxford Press, London, 1970.

Fig. 11.3. Bond distances and angles in 2,6-di-*tert*-butyl-1,4-benzoquinone. The range of standard deviations for the bonds is 0.0025–0.0042 Å and for the angles 0.2–0.3°. Several bond angles were omitted from the drawing for the sake of clarity; they are C(10)–C(7)–C(2), 109.9°; C(8)–C(7)–C(9), 107.7°; C(14)–C(11)–C(6), 110.1°; and C(12)–C(11)–C(13), 107.2°.

Table 11.1. Bond lengths before and after correction for segmented-body motion

	Uncorrected (Å)	Corrected (Å)
C–O	1.218	1.246
C–CH	1.464	1.469
C–C ^{tr}	1.504	1.508
C–C	1.332	1.340
C–C(CH ₃) ₂	1.528	1.534
C–CH ₃	1.533	1.549
C–H	0.98	
C–H	0.99	

The symbol T designates tertiary butyl, i.e., C(CH₃)₃.

Fig. 11.4. Stereo drawing of the contents of a unit cell with *a* axis horizontal and *b* axis vertical.

11.1.6 The Gas Phase Conformation of *o*-Terphenyl as Inferred from Crystal Structure Analysis and Potential Energy Calculations

W. R. Busing G. M. Brown

The aromatic hydrocarbon *o*-terphenyl (Fig. 11.5) is an interesting example of an overcrowded molecule. The partial double-bond character of the links 1-1' and 2'-1" will tend to make the molecule planar, but a planar arrangement is not possible because of the close contacts between atoms of the substituent rings.

Early electron diffraction studies of the molecule in the gas phase are inconclusive but tend to favor models in which the end rings are rotated at least 75° out of the plane of the central one.

Recently the crystal structure of *o*-terphenyl has been precisely determined at ORNL by neutron diffraction. The molecular conformation observed in the crystal (Fig. 11.5) has the two-substituent rings rotated 42.1° and 62.1° in the same sense from the planar arrangement. The lack of symmetry of the molecule probably reflects the lack of symmetry of its crystal environment, but it could conceivably be a property of the isolated molecule.

The equilibrium conformation of a molecule can be calculated, either in the gas phase or in the crystal, if an expression for the potential energy of the system

is known in terms of its geometry. Such a potential would include terms for the attraction and repulsion of nonbonded atom pairs and other terms that are functions of intramolecular variables such as bond angles and torsion angles.

A flexible molecule can be modeled with various degrees of complexity. We have chosen to represent *o*-terphenyl as five segments: the three rings and the two links between them. The geometry of each ring including its hydrogen atoms is held constant, as is the length of each link. Each link is permitted to pivot about its connection to the central ring with two degrees of freedom, and each substituent ring can pivot on the end of its link with three degrees of freedom. The conformation of the molecule thus depends on the values of ten variables. The model for this molecule in the crystal has nine additional variables: the six that describe its overall rotational and translational positioning and the three lengths that define the orthorhombic unit cell.

We have used an atom-atom potential function derived by Williams¹⁴ to represent both inter- and intramolecular nonbonded interactions. This potential, often called an exp-6-1 potential, includes an exponential repulsion term, an inverse sixth-power van der Waals attraction, and the Coulomb interaction between fractional charges assigned to the atoms of the C-H groups. Two nonbonded potentials with slightly different constants¹⁴ were tested by showing that they reproduce the observed crystal structure quite accurately, provided that the internal molecular conformation is held rigid. For each potential the energy was minimized by adjusting the lattice parameters and the overall molecular translation and rotation. In both cases the lattice parameters changed by less than 3%, the molecular rotation was approximately 2°, and the net translation was 0.06 Å. These small changes give us confidence that the nonbonded potentials are realistic.

The nonbonded potential is assumed to apply to pairs of atoms in different segments of the same molecule, provided that these atoms are not geminal (i.e., are not bonded to the same atom). In addition, we assume an internal potential with three more constants: (1) a ring-ring torsion potential of the form $k(1 - \cos^2 \phi)$ is derived from each torsion angle ϕ about a link. Examples of such angles are 2'-1'-6' and 3'-2'-1"-2". This term in the potential tends to push these ring-ring torsion angles toward 0° or 180°. (2) A similar potential is assumed for torsion angles such as 1-1'-6'-5' or 1'-1'-2-3. These terms tend to keep the links in the planes of the

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Fig. 11.5. The molecular structure of *o*-terphenyl in the crystal as determined by neutron diffraction. The numbered atoms are carbon, and the remaining ones are hydrogen.

rings to which they are attached. (3) A quadratic term in angles at the ring-link pivots tends to equalize pairs of angles such as $\angle 1-1-2$ and $\angle 1-1-6$. The three constants of this internal potential were adjusted by the method of least squares so that, in the crystal with the observed structure, the derivatives of the calculated energy with respect to the ten internal variables would approach zero. This potential, including the nonbonded contributions, was then tested by minimizing the energy of the crystal with respect to these ten internal degrees of freedom. The changes in bond angles and torsion angles which accompany this relaxation are all less than 1.5° . Again, the fact that the calculated structure nearly reproduces the observed one lends credence to our derived potential.

Finally, we minimize the energy of the isolated five-segment molecule, using the derived internal potential and the nonbonded terms. For this purpose the model was idealized by averaging chemically equivalent distances and angles and forcing each ring to be planar. The resulting conformation has twofold symmetry, with each substituent ring turned 47° in the same sense around the link. Many of the angles have values near those observed in the crystal. The torsion angle $\angle 1-1'-2'-1''$, which measures the bend of the links from the plane of the central ring, has increased from 5° in the crystal to 10° in the gas phase. Presumably this increase could result from the removal of the neighboring molecules, which exert a compressive effect in the crystal, but final judgement on the reliability of this model awaits further analysis.

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11.1.7 A Search for Disorder in Crystalline Coronene by Reanalysis of Published X-Ray Data

W. R. Busing W. E. Thiessen

The crystal structure of the highly symmetric aromatic hydrocarbon coronene (Fig. 11.6) was determined some time ago by Fawcett and Trotter¹ using x-ray diffraction techniques. Recently Boyd, Fyle, and Wright² have calculated the energy required to rotate a single molecule about its pseudo-

Fig. 11.6. Coronene, $C_{24}H_{12}$. The solid lines represent the structural formula with a carbon atom at each junction and hydrogen atom on the periphery. The dashed lines show how a 30° rotation results in nearly the same hydrogen positions with drastically displaced carbon atoms.

sixfold axis, assuming that its neighbors in the crystal remain unperturbed. They used an atom-atom potential of the exp-6 form with parameters recommended by Williams.³ They noted that the model with one molecule rotated 30° is nearly as stable as the ordered crystal. Figure 11.6 shows that this can be attributed to the approximate 12-fold symmetry of the hydrogen atoms that dominate the calculated energy. The authors predicted that there should be a significant fraction of molecules in the metastable orientation at ambient temperatures; after correcting an error in their work, we computed this fraction to be 0.034.

Because Fawcett and Trotter had not considered the possibility of such a disorder and because they had not reported making a final difference Fourier synthesis, we undertook to search for it by making a new least-squares refinement based on their published values of 1139 x-ray diffraction data. We assumed a rigid planar molecule with 6 *mmm* symmetry positioned on a crystallographic center of inversion. The thermal motion was assumed to consist of rigid-body anisotropic translation and libration. The parameters adjusted were three molecular rotations, six coordinates of the four independent atoms in the model, and six trans-

lational and six librational thermal motion parameters. Adjustment of these 21 variables yielded a better agreement than that reported in the original work, with a conventional R of 12.6% compared with the previous 15.7%.

We then introduced a second molecule superimposed on the first and rotated 30° with respect to it. The least-squares refinement of the above 21 parameters was continued with the addition of a single fractional occupancy factor for the rotated molecule. At convergence this factor was 0.004 ± 0.003 , and the R factor had not changed.

We conclude that the fraction of disordered molecules indicated by x-ray diffraction at room temperature is probably at least an order of magnitude less than that predicted from potential energy calculations. This result may raise some doubts about the validity of the exp-6 atom-atom potentials as a description of the force field in this aromatic crystal.

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11.1.8 Crystal and Molecular Structure of an Unusual Organoactinide Complex $[\text{Th}[(\text{CH}_3)_5\text{C}_5]\text{H}(\mu\text{-H})_2\text{C}_6\text{H}_5\text{CH}_3]$ from Neutron-Diffraction Data¹

B. W. Broach² J. M. Manriquez³
A. J. Schultz⁴ P. J. Fagan⁵
J. M. Williams⁶ T. J. Marks⁷
G. M. Brown⁸

In exploratory research in actinide organometallic chemistry aimed partly at developing practical catalysts, especially for hydrogenation reactions, Manriquez et al.¹ have recently prepared the first organoactinide hydrides, compounds of thorium and uranium with pentamethylcyclopentadienyl ligands. From the mode of preparation, elemental analyses, molecular weight determinations, and infrared and NMR spectroscopy, these new compounds were inferred to be complexes with two hydride bridges between two actinide atoms, for which the molecular formula $[\text{M}[(\text{CH}_3)_5\text{C}_5]\text{H}(\mu\text{-H})_2]$ can be written. The definitive structural characterization of such a hydride requires single-crystal neutron-diffraction

analysis, so that the hydrogen atoms can be precisely located in spite of the presence of the very heavy actinide atoms. Such characterization is important because the uranium compound is known to active hydrogen exchange in molecules such as benzene and toluene. In an interlaboratory cooperative project we have done the neutron structure analysis of a thorium compound (more stable than the uranium compound) and demonstrated that the crystal structure is indeed the one expected from the occurrence of the analysis, which used no information about the compound except the supposed empirical formula of the dinuclear complex molecule. We discovered the presence of one molecule per unit cell, one solvation per complex molecule, as indicated by the formula given in the title above.

Figure 11.7 shows the geometry of the complex in which each thorium atom is bonded to two pentamethylcyclopentadienyl rings, to one nonbridging hydrogen atom, and to two bridging hydrogen atoms (one from the two thorium atoms). The separation between the two thorium atoms is $4.007(8)$ Å, considerably longer than the 3.59 Å observed in thorium metal and suggesting that any Th-Th interaction in a molecule is weak. The mean Th-H(bridging) and Th-H(nonbridging) bond lengths are $2.27(3)$ and $2.03(1)$ Å respectively. The mean Th-C(ring distance) is $2.83(1)$ Å. The mean angle (ring centroid)-Th-(ring centroid) is $130(1)^\circ$.

Fig. 11.7. Perspective view of the $[\text{Th}[(\text{CH}_3)_5\text{C}_5]\text{H}(\mu\text{-H})_2]$ dimer as determined by single-crystal neutron-diffraction analysis. The hydrogen atoms on the four pentamethylcyclopentadienyl ligands are omitted. The atoms are represented by their ellipsoid of 50% probability (spheres for the carbon atoms, which were given isotropic temperature factors).

The crystals of the solvated complex

are monoclinic (space group $P2_1/c$) with four formula units per cell. The cell constants, determined by neutron diffractometry, are: $a = 27.983(8) \text{ \AA}$, $b = 9.967(4) \text{ \AA}$, $c = 17.364(3) \text{ \AA}$, $\beta = 103.09(1)^\circ$. The solution for the structure was obtained easily with the direct-method program *MULTAN*. The present discrepancy index $R(F)$ is 0.194 for the 3127 data with $F \geq \sigma(F)$ and $(\sin \theta) / \lambda \leq 0.565 \text{ \AA}^{-1}$, after least-square refinement with anisotropic thermal parameters for the thorium and the hydride hydrogen atoms and isotropic thermal parameters for all other atoms. The relatively high $R(F)$ value reflects the inadequacy of the isotropic thermal parameters for treating the motions of the carbon atoms, which are known to be highly anisotropic in *pentahaptocyclopentadienyl* complexes. For further refinement the pentamethylcyclopentadienyl groups will probably have to be treated as rigid.

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11.19 α -D-Glucose: Further Refinement Based on Neutron-Diffraction Data

G. M. Brown H. A. Levy

Thirteen years ago we reported atomic coordinates and selected derivative structural parameters for α -D-glucose (Fig. 11.8) from a fairly precise refinement, based on neutron-diffraction data, of the structure of McDonald and Beavers. The data used in the 1965 work appear to be of high quality by present standards; but there are considerable extinction effects, and the least-squares procedure did not include the adjustment of extinction parameters that is commonplace in refinements today. Instead we had attempted to minimize the effects of extinction by the somewhat unsatisfactory method of giving zero weights to the 37 observations of $|F|$ corresponding to the highest observed intensities. Because of the biochemical importance of α -D-glucose, we have now completed the refinement, using our original data and applying anisotropic extinction corrections.² To match the quality of the refinement, we have also redetermined the cell parameters precisely.

Attempts to refine all six of the type I anisotropic extinction parameters Z' of Coppens and Hamilton³ led to a nonpositive-definite quadratic form. However, adjustment of only the three Z' axial parameters was successful, leading on convergence to the following measures of goodness of fit for the 1584 reflections included: $R(F) = 0.048$, $R(F^2) = 0.045$, $R_w(F^2) = 0.063$, $s = 1.053$. The improvement over the previous values (0.099, 0.061, 0.077, and 1.260 respectively) is striking. There are slight decreases in the estimated standard errors of the parameters.

Fig. 11.8. Stereoscopic view of the molecule of α -D-glucose from further refinement based on the neutron data of 1965. Atoms are represented by their ellipsoids of 50% probability.

The rms coordinate difference and the rms thermal parameter U difference between the new parameters and the 1965 parameters are 0.0006 Å and 0.0005 Å; the corresponding rms $\Delta\sigma$ values are 0.26 and 0.53. No apparent atom position shifted more than 0.0024 Å.

We have used the segmented-body model of Johnson⁵ as incorporated in the program *ORSB4* to analyze the thermal parameters. Bond lengths and valence angles were corrected by combining as appropriate the corrections for segmented-body motion and for riding motion.⁶ The additive corrections for the C-C and C-O lengths range from +0.003 to +0.010 Å; those for the C-H and O-H bonds range from 0.004 to 0.027 Å.

Precise translations were determined for α -D-glucose (orthorhombic, $P2_12_12_1$) as follows: $a = 10.3662(9)$, $b = 14.8506(16)$, $c = 4.9753$ Å, at 21–23°C, based on $\lambda(\text{Cu } K\alpha_1) = 1.54051$ Å. The precision and accuracy of these parameters eliminates uncertainty in cell translations as a source of error in the derived bond lengths and angles.

The structural data from our 1965 publication¹ on α -D-glucose have been used in many discussions in the chemical and crystallographic literature on carbohydrate molecular and crystal structures. The new data, which will be reported elsewhere, are not sufficiently different to furnish any new structural inferences or to require modification of any old ones; consequently, we shall not present more details here. We emphasize, however, that the structure of α -D-glucose is now known more accurately and precisely than before.

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11.1.10 Structure Elucidation of 1,5'-Bidecaboran(14)yl, a New Borane from γ Irradiation of Decaborane(14)

G. M. Brown¹ J. W. Pinson²
L. L. Ingram, Jr.³

The work reported here¹ exemplifies the nearly unique power of modern single-crystal diffraction

analysis in elucidation of chemical structure. The structure of a new borane of formula $\text{B}_{10}\text{H}_{12}$ from gamma-ray radiolysis¹ of solid decaborane(14) (ref. 2) has been determined from x-ray data from a minute crystal specimen without use of chemical information other than the empirical formula.

Eight isomers of formula $\text{B}_{10}\text{H}_{12}$ (determined by mass spectroscopy) were isolated, along with other boranes, by high-performance liquid chromatography. It seemed probable, but not certain, that each isomer was made up of two of the various moieties B_5H_6 , theoretically producible by abstraction of a single hydrogen atom from the $\text{B}_{10}\text{H}_{14}$ molecule. The isomer whose structure is described here (mp 115–115°C) is the most abundant one, accounting for 70% of the total irradiation product. Its infrared spectrum suggested molecular asymmetry.

Only two single crystals large enough to be useful were available. These crystals were colorless, cloudy, and of poor quality, grown by evaporation of a cyclohexane solution. Of the two crystals, the larger one (~50 μg) was used in determining the cell parameters precisely and in recording intensity data. The crystal's symmetry is that of the monoclinic space group $P2_1/n$. The cell parameters are: $a = 7.235(1)$ Å, $b = 15.453(4)$ Å, $c = 14.895(3)$, $\beta = 91.42(2)^\circ$. There are four formula units $\text{B}_{10}\text{H}_{12}$ per cell. The set of reflection data was comprised of the F_o and $\sigma(F_o)$ values for the 2663 independent $\text{Cu } K\alpha$ reflections to the limit 125° in 2θ .

The solution for the structure, the approximate location of all 20 boron atoms, was obtained by use of Long's multiresolution direct-method program.⁴ All 26 hydrogen atoms were subsequently located, and the structure was refined with anisotropic thermal parameters for all atoms. For the 2229 data used in the final least-squares cycles, the usual discrepancy index $R(F)$ is 0.059.

Since the structure and the compound itself were previously unknown, the structural aspect of prime chemical interest is the atom connectivity, the molecular topology. As shown in the drawing of Fig. 11.9, two decaboran(14)yl groups of formula $\text{B}_{10}\text{H}_{11}$ are connected to each other by a two-center B-B bond, from atom B1 in the unprimed group to atom B'5 in the primed group. The compound is therefore named 1,5'-bidecaboran(14)yl, in accordance with IUPAC conventions.

Particular interest attaches to the two-center intergroup bond B1-B'5, which has (including a +0.002-Å correction for rigid-body thermal motion) the length 1.698(3) Å, at the lower end of the normal

Fig. 11.9. Stereoscopic view of the 1,5'-bidecaboran(14)yl molecule, showing the atomic thermal ellipsoids of 10% probability. Only the boron atoms are numbered, and the boron skeleton is emphasized by the black stick bonds connecting the boron atoms.

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Fig. 11.10. Stereoscopic view showing the packing of molecules in the 1,5'-bidecaboran(14)yl crystal. Boron atoms are represented by their ellipsoids of 10% probability; hydrogen atoms are not shown.

B-B distance range. This is the first precise (presumably accurate) metrical datum for a two-center B-B bond, a type known or inferred to exist in only four other boranes. The only other datum is the value 1.74 ± 0.06 Å given by Grimes et al.⁵ from a two-dimensional x-ray structure analysis of 1,1'-(B-H)₂, a decaborane(16) isomer.

Other interatomic distances and the valence angles in B-H₂ are very close to the corresponding distances and angles in B-H₃ (ref. 6). Most of the larger perturbations are for distances and angles involving the linking atoms B1 and B5'.

The packing of the molecules is shown in Fig. 11.10. There are no unusually close contacts between molecules. The closest contacts for the three

kinds of atom pairs are: B...B, 3.908 Å; B...H, 3.077 Å; H...H, 2.38 Å (all uncorrected).

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atom C(5), which is across the ring from the C(2)–C(3) double bond, is 0.474(3) Å from the best least-squares plane through the other four-ring atoms, none of which is more than 0.025(1) Å from the plane. Some of the bond lengths and angles displayed in Fig. 11.11 are rather far from normal values, suggesting considerable strain in the molecule. The notably long C(4)–C(5) bond length, 1.574(2) Å, and large angles O(4)–C(4)–C(5) and C(11)–C(5)–C(4), 116.5(1)° and 117.0(1)°,

respectively, are consistent with the fact that the conformation about the bond C(4)–C(5) is only $\sim 26.5^\circ$ from the eclipsed conformation, which implies considerable repulsion, especially between the hydroxyl group on C(4) and the bulky *tert*-butyl group on C(5). Specifically, torsion angle O(4)–C(4)–C(5)–C(11) is $25.2(2)^\circ$. It is not clear why the bond C(5)–C(11) should also be abnormally long to the same degree as bond C(4)–C(5).

The molecular packing and hydrogen bonding are shown in Fig. 11.12. Each molecule is linked by a very weak hydrogen bond (one-half of a bifurcated bond) from its O(5) hydroxyl to the O(4) hydroxyl oxygen of the translation-equivalent molecule in the adjacent cell along *c*, resulting in H-bonded molecular chains along *c*. The other branch of the bifurcated bond is intramolecular, between the O(5) hydroxyl and the carbonyl oxygen O(1). Each of the H-bonded chains is further connected by O(4)–H(4)–O(5) H-bonds to the equivalent chain related to it by a screw axis 2_1 parallel to *c*. The result is a system of ribbons two molecules wide, held together internally by H-bonds, the ribbons being packed in herringbone fashion with no H-bonds between them.

Crystals of the compound are orthorhombic (space group *Pha*2₁) with $a = 21.171(3)$, $b = 10.415(2)$, $c = 6.359(1)$, $Z = 4$. The structure solution and re-

finement made use of 1314 F_o data (Cu $K\alpha$ radiation) obtained by standard experimental procedures and data processing. Absorption corrections were applied. Least-squares refinement led to a final discrepancy index $R(F)$ of 0.029 and an index $R(F^2)$ of 0.042. All hydrogen atoms were located approximately.

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11.1.12 Stereochemical Course of an Intramolecular Photochemical Cycloaddition Reaction¹

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W. E. Thiessen

It has been recently established¹ that irradiation of **2** and **3** produced the "ene" type products **4** and **5** respectively (Fig. 11.13). It seemed of interest to investigate the photochemistry of **1** since cycloaddition was observed in a closely related case. Accordingly, a dilute cyclohexane solution of **1** was irradiated with a Hanovia 450 W medium-pressure lamp through Pyrex for 2 h, and the major product showed spectral characteristics and chemical transformations consistent with a cycloaddition product of the anticipated azabicyclo[2.1.1]hexane type. Since this product was nicely crystalline, it seemed most expeditious to determine its structure and stereochemistry unambiguously via x-ray crystal-structure analysis.

Fig. 11.12. Stereoscopic drawing showing the molecular packing and hydrogen bonding in crystalline (4*R*,5*S*)-2,5-di-*tert*-butyl-4,5-dihydroxy-4-methylcyclopent-2-en-1-one. Only the hydroxyl hydrogen atoms are shown (as small spheres); the other atoms are represented by their ellipsoids of 20% probability. The single-line bonds indicate the H...O hydrogen bond interactions. The direction **a** is along the vertical from bottom to top, **b** is horizontal from left to right. The cell outline shown is centered at the point (0, 0, 0).

Fig. 11.13. Reactants and products in photochemical reactions.

Crystal Data (from single-crystal diffractometry; niobium filtered Mo K α , $\lambda = 0.70926$ Å at $20 \pm 1^\circ\text{C}$): $a = 20.815(8)$, $b = 10.875(2)$, $c = 6.625(1)$ Å; $P2_12_12_1$; $Z = 4$; $d = 1.218$, and $d = 1.19$ g cm $^{-3}$ by flotation in NaBr solutions; $F(100) = 600$.

Integrated intensities of 1540 unique reflections were measured by $\theta/2\theta$ scans for $2\theta \leq 50^\circ$. The structure was solved using the MULTAN program¹ from normalized structure factors calculated by the ORESTES program, assuming an anisotropic thermal-motion model. Least-squares refinement was carried out in two blocks with nonhydrogen atoms anisotropic and hydrogens isotropic. At convergence, the conventional $R(F)$ for the 1423 observations for which $I > 3\sigma(I)$ was 0.033. No significant features were found in a final difference map.

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Fig. 11.14. The photochemical cycloaddition product from irradiation of compound 1 (Fig. 11.13).

A perspective view of the cycloaddition product is displayed in Fig. 11.14. Both cyclohexane rings are able to assume the minimally strained chair conformation despite the fact that the unsubstituted one is *trans* fused to the cyclobutane ring. The cyclobutane ring is highly puckered, reflecting the strain introduced by linkage of the $-\text{CH}_2\text{N}(\text{Ac})-$ group to C1 and C7. The angle between the C2-C7-C8 and C8-C1-C2 plane normals is 51.5° .

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11.1.13 Diffraction Patterns and Models of Liquid Hydrocarbons and Alcohols

A. H. Narten E. Johnson
S. I. Sandler

In the past, we have used x-ray diffraction data on simple molecular fluids to broaden our understanding of the liquid state and, together with Monte Carlo computer simulations, to test molecular interaction potential models and statistical mechanical theories.^{1,2} As a first step in an extensive study of liquid alkanes and alcohols, we here report results for liquid neopentane (which we will refer to as CMe $_4$) and tertiary butyl alcohol (CMe $_3$.OH). Both of these liquids consist of globular molecules, the structure of which is known; hence the main focus of our work has been the determination of the intermolecular rather than the intramolecular structure.

The intermolecular correlations in a heteroatomic molecular fluid can be described by site-site distribution functions $g_{\alpha\gamma}(r)$. The sites α , γ may but need not coincide with the nuclear positions in a molecule. When sites α and γ designate atomic positions, $g_{\alpha\gamma}(r)$ is referred to as an atom-atom distribution function.³ The quantity accessible from diffraction experiments is the distinct structure function, defined as

$$H_d(k) = \left[\sum_{\alpha, \gamma} f_{\alpha}(k) f_{\gamma}(k) \rho \hat{h}_{\alpha\gamma}(k) \right] / \left[\sum_{\alpha} f_{\alpha}(k) \right]^2 \quad (1)$$

with $\hat{h}_{\alpha\gamma}(k)$ being the Fourier transform of the site-site correlation function $h_{\alpha\gamma}(r) \equiv g_{\alpha\gamma}(r) - 1$, ρ the molecular number density, $f_{\alpha}(k)$ the scattering factor for site α , m the number of scattering sites per molecule, and k the momentum transfer coordinate. For the work reported here, the methyl and hydroxyl groups were treated as single scattering (and force) sites. Fourier inversion of the function

$H(k)$ derived from experiment yields a radial distribution function

$$G(r) = 1 + (2\pi\rho r)^{-1} \int_0^\infty k H(k) \sin(kr) dk \quad (2)$$

which, from Eq. (1), is seen to be a weighted sum of site-site distribution functions modified by products of scattering factors.

Neopentane. The x-ray diffraction pattern of liquid neopentane has been measured at eight different temperatures, listed in Fig. 11.15, between the melting point (-17°C) and the critical point (161°C). The data have been analyzed to yield the molecular structure. This structure is not significantly different from that found from the low-density vapor. Subtraction of the molecular structure function from the measured total structure functions yields the distinct structure functions defined in

Fig. 11.15. Structure functions for neopentane at eight different temperatures and densities. The points and open circles are experimental results. The solid curves were obtained from the zeroth-order, blip-function expansion method.

Eq. (1) and shown in Fig. 11.15. The functions $H(k)$ are sufficiently accurate to provide a sensitive test of statistical mechanical theories of molecular fluids.

We have calculated distinct structure functions for three models of neopentane, namely a one-site hard-sphere model, a one-site soft-sphere model, and a five-site fused-sphere model.

One-site models. For the hard-sphere model the distinct structure function depends only on the density and the hard sphere diameter, D . For each density and temperature, D was chosen such that the difference between the experimental and computed structure functions was minimal with respect to variation of D . The hard-sphere-model, distinct-structure function was computed using computer simulation results. These hard-sphere model $H(k)$ s are in good agreement with the experimental $H(k)$ s for $k < 2 \text{ \AA}^{-1}$.

The interaction site for the soft-sphere model of neopentane was the repulsive part of the Lennard-Jones pair potential. The distinct structure functions were computed using the zeroth order blip function expansion method. The Lennard-Jones parameter σ was set equal to the value of D found for the hard-sphere model of neopentane at $T = -17^\circ\text{C}$ and $\rho = 0.00528 \text{ \AA}^{-3}$. For this state $D = 5.5 \text{ \AA}$. The parameter ϵ was chosen such that, at -17°C , the difference between experimental and computed structure functions was minimal with respect to variation of ϵ . The value thus found was $\epsilon/k_B = 200 \text{ K}$. The repulsive Lennard-Jones system with $\sigma = 5.5 \text{ \AA}$ and $\epsilon/k_B = 200 \text{ K}$ was also treated using the Optimized Cluster Theory (OCT). The OCT results agreed well with those obtained by the blip function method shown in Fig. 11.15.

The functions $H(k)$ computed for the soft-sphere model (Fig. 11.15) reproduce the first maximum near $1.2 \text{ \AA}^{-1}$ in the curves derived from experiment, and the model predicts the temperature (and density) dependence of this feature correctly. Beyond values of $k > 2 \text{ \AA}^{-1}$, the computed curves disagree with those derived from experiment. The radial distribution functions [Eq. (2)] for liquid neopentane are compared with the corresponding curves for the soft-sphere model in Fig. 11.16. It is seen that the model describes the site-site distributions in neopentane well for distances $r > 5 \text{ \AA}$, but at shorter distances discrepancies are apparent. In particular, the peak near $4 \text{ \AA}$ in the curve for neopentane at -17°C is not reproduced by the model. This peak must be assigned to a contact between methyl groups from neighboring molecules.

Five-site models. The procedure used was to model the CMe₃ molecule by four hard spheres of

Fig. 11.16. Radial distribution functions for neopentane at eight different temperatures and densities. The solid curves are experimental results. The dashed curves were obtained from the zeroth-order, hsp-function expansion method.

equal diameter fused in tetrahedral locations to a central sphere (of smaller diameter) with $R_{\text{eff}} = 1.55$ Å. The site-site structure functions for this model were then computed using RISM theory, with the methyl group and carbon atom sphere diameters (σ_{CH_3} and σ_{C}) adjusted to give the best agreement between theory and experiment for $H(k)$ at -17°C ; the values thus found were $\sigma_{\text{CH}_3} = 3.2$ Å and $\sigma_{\text{C}} = 4.0$ Å. The functions $H(k)$ computed for this model (not shown in Fig. 11.15) agree well with the curve derived from the x-ray data at -17° below $k \lesssim 2$ Å $^{-1}$; but, as expected for a hard-sphere model, the temperature dependence of the first peak in $H(k)$ is not predicted correctly. For values of $k \gtrsim 2$ Å $^{-1}$ the structure functions computed for the fused-sphere model reproduce the experimental curves somewhat better than those computed for the one-center models. However, large discrepancies remain, and it is not yet clear whether these disagreements arise from the assumed hard-sphere

nature of the interactions or from the description of a CMe₃ molecule in terms of only five interaction sites.

***t*-Butyl alcohol.** The x-ray diffraction pattern of liquid CMe₃OH has been measured at 26°C , just above the melting point of 25.5°C . The data have been analyzed¹² as described for neopentane to yield the distinct structure function [Eq. (1)]. The function $H_s(k)$ will be used to test interaction models for CMe₃OH after a successful model for liquid CMe₃ has been found. In the meantime, the radial distribution function $G_s(r)$, obtained through Eq. (2), yields directly some valuable insight into the structure of liquid CMe₃OH (Fig. 11.17).

The most striking feature of the functions $G_s(r)$ shown in Fig. 11.17 is the presence of a well-defined peak at 2.75 Å for CMe₃OH which is absent in CMe₃; this peak is due to hydrogen-bonded hydroxyl groups, and the area under the peak corresponds to $2 \text{ OH} \cdots \text{OH}$ interactions.¹² Also, there is a shift at the Me $\cdots$ Me peak clearly evident at 4.0 Å in the -17°C CMe₃ curve to 3.73 Å in CMe₃OH. The

Fig. 11.17. Radial distribution functions for neopentane at -17°C and *t*-butyl alcohol at 26°C . The lower curve is the neopentane distribution function and the upper curve is the *t*-butyl alcohol distribution function.

fact that each OH group in a CMe₃OH molecule has two OH neighbors from other molecules suggests strongly that the alcohol molecules are associated into chains in the liquid.

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11.1.14 Structure in Molten Salts

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The structure of nonassociated liquids is qualitatively well understood as determined by the shape of the constituent molecules and the harsh repulsions between them. Attractive forces can be treated as perturbations of the repulsions, and thus, for many van der Waals fluids, a quantitative description of the equilibrium properties seems feasible.

Liquids with polar molecules as well as ionic liquids remain intriguing. A theory for these fluids must be able to describe the effects of repulsive and attractive forces on equal footing, and this has not yet been achieved. To advance our understanding of these liquids, we have chosen two relatively low-melting salts for study, namely, antimony trichloride and zinc chloride.

Antimony trichloride.¹ Gaseous antimony trichloride consists of pyramidal SbCl_3 molecules having a bond distance of 2.37 Å, a bond angle of 96°, and a dipole moment of 3.93 D. The physical properties of liquid SbCl_3 are not unlike those of water. The liquid is sometimes described as associated, and its large dielectric constant (33.2 at 75°C) and low autoionization make it a good solvent for inorganic solutes.

We have measured the diffraction pattern of liquid SbCl_3 at 80°C, just above the melting point

of 73.4°C, with both x rays and thermal neutrons. The data have been analyzed to yield the molecular structure, which is not significantly different from that found for the low-density vapor. Subtraction of the molecular structure from the measured total structure functions yields the distinct structure functions. Combination of the results from x-ray and neutron diffraction then made possible the extraction of structure and distribution functions for intermolecular $\text{Sb} \cdots \text{Sb}$, $\text{Sb} \cdots \text{Cl}$, and $\text{Cl} \cdots \text{Cl}$ interactions. The atom pair distribution functions for liquid SbCl_3 are shown in Fig. 11.18. Inspection of the curves in Fig. 11.18 shows that the $\text{Sb} \cdots \text{Cl}$ distance of 3.40 Å between atoms from neighboring molecules is much shorter than the distance of 4.0 Å expected from the van der Waals radii of antimony (2.2 Å) and chlorine (1.8 Å) atoms. Each antimony atom has three chlorine neighbors from other molecules in a very well defined distribution centered around 3.40 Å in

Fig. 11.18. Intermolecular atom pair distribution functions $g_{\alpha\gamma}(r)$ derived from x-ray and neutron scattering (solid lines); $n_{\alpha\gamma}(r)$ is the average number of γ atoms in a sphere of radius r around any α atom in liquid SbCl_3 .

addition to the three-bonded chlorine atoms at 2.35 Å. These numbers suggest a distorted octahedral arrangement of chlorine atoms around each antimony atom in the liquid. This arrangement must be such that each chlorine atom "sees" only one nearest antimony atom from a neighboring molecule. Each antimony atom has two close antimony neighbors in a sphere of radius 4.3 Å (Fig. 11.18). This short Sb...Sb contact in liquid SbCl₃ can only be accommodated if all three near neighbor chlorine atoms belong to one SbCl₃ molecule. If pairs of molecules are stacked like umbrellas (Fig. 11.19) so that all three intermolecular Sb...Cl distances are 3.40 Å, the Sb...Sb distance would be 3.94 Å. Whether such neighboring molecules have their Sb-Cl bonds staggered or eclipsed cannot be inferred directly from the curves in Fig. 11.18. However, the staggered geometry seems likely from the known preference of hexacoordinate antimony for pseudooctahedral geometry. The shortest Cl...Cl distances in a pair of molecules stacked in a staggered umbrella configuration (Fig. 11.19) would be 4.43 Å, a distance that correlates well with the shoulder on the function $g_{\text{Cl-Cl}}(r)$ in Fig. 11.18.

There are, in addition, shorter Cl...Cl contacts from other neighboring molecules at 3.85 Å. Since the corresponding Sb...Cl distances cannot be much shorter than 4.5 Å, the Cl...Cl-Sb angles

in such contacts must be at least 90°. A possible configuration of this type is also shown in Fig. 11.19.

The structure of liquid SbCl₃ just above the melting point might then be described in terms of chains of SbCl₃ molecules stacked in the umbrella configuration, with interaction between chains through van der Waals forces. The interaction between pairs of molecules within a given chain must be much stronger than these van der Waals forces, and the dipole axes of these molecules are strongly correlated, at least over one or two molecular diameters. This might explain the large dielectric constant of liquid SbCl₃.

As mentioned in the introduction, statistical mechanical theories capable of predicting the structure of polar liquids have not yet been developed. We have tested a wide variety of four-center, fused-sphere models of SbCl₃ using RISM theory. The structure functions computed for all of these models were in very poor agreement with experiment. A pair potential with electric charges distributed on the molecule might be a more suitable model of SbCl₃. Such pair potentials were not treated with the RISM theory, because, when the charges are large enough to affect significantly the liquid structure, the RISM results appear to be inaccurate. We are testing realistic interaction potentials in computer experiments, using the molecular dynamics method.⁷

Zinc chloride. Among pure liquid inorganic halides, ZnCl₂ (like BeF₂) is unusual for its high viscosity at the melting point (318°C) and for its consequent ability to supercool into a glass, metastable at room temperature. We here report first results of a comprehensive study of liquid and amorphous solid ZnCl₂ by neutron and x-ray diffraction.

We have measured the x-ray diffraction pattern of ZnCl₂ at 323°C, just above the melting point. The data have been analyzed to yield a radial distribution function $G(r)$, shown in Fig. 11.20, which yields directly some valuable insight into the structure of the melt. The most striking feature of the function $G(r)$ for liquid ZnCl₂ is a completely resolved peak at 2.29 Å; this peak is completely described (Fig. 11.20, circles) by a curve computed for four Zn-Cl interactions. The second maximum in $G(r)$ occurs at 2.74 Å and must be ascribed predominantly to Cl-Cl interactions. The distance ratio for these two peaks is equal to the value (8/3) typical of tetrahedral coordination. Our

Fig. 11.19. A typical configuration of SbCl₃ molecules in the liquid consistent with the experimental data. There are, of course, sizeable local and instantaneous deviations from this configuration, and hence the correlations pictured extend only a few molecular diameters from any given origin. The spheres representing individual atoms are of arbitrary diameter, but the distances between their centers (in Å) are to scale.

Fig. 11.20. Radial distribution functions for liquid ZnCl_2 derived from x-ray diffraction (solid line) and calculated for a model which assumes that the Cl^- ions are close-packed and the Zn^{2+} ions are located in the tetrahedral holes of such a structure (circles).

first conclusion then is that liquid zinc chloride does not consist of ZnCl_2 molecules but of Zn^{2+} and Cl^- ions arranged as ZnCl_4 tetrahedra.

The peak at 2.74 Å is not completely described by the maximum number, $N = 12$, of Cl neighbors per Cl ion, but a curve (Fig. 11.20) calculated for 12 Cl per Cl ion plus four Zn^{2+} neighbors per Zn^{2+} ion agrees well with the experimental radial distribution function to ~ 4 Å. These numbers indicate that in liquid ZnCl_2 the Cl ions are close-packed and that the Zn^{2+} ions are located in the tetrahedral holes typical of such a structure. Such an arrangement is typical of the known crystalline phases of ZnCl_2 .

11.1.15 The Structure of Liquid Bromine

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A. H. Narten

Our knowledge of the liquid state has increased rapidly in the last 15 years. Important ingredients in this increased understanding have been accurate x-ray and neutron diffraction studies of liquids, advances in theory, and computer-simulation studies of increasingly more complicated molecular fluids. For relatively simple liquids with homonuclear diatomic molecules such as oxygen and nitrogen, the agreement between experimental results, computer simulations, and theoretical predictions has been quite satisfactory. For bromine the situation is not so clear, and there were several reasons for choosing to study this liquid. First, there is relatively little physical properties information for bromine. In fact, not even the second virial coefficient of gaseous bromine has been measured, so that we have little information on the intermolecular potential. Next, the bromine molecule is highly polarizable with a large quadrupole moment (8.2×10^{-27} esu cm²). Consequently, a study of bromine should yield information on the importance of these forces in determining the structure of liquids as well as provide a severe test of liquid state theories and molecular interaction models. Finally, there existed large discrepancies between published x-ray and neutron diffraction data from liquid bromine.

We have measured the diffraction pattern of liquid bromine at 20°C with both x rays and thermal neutrons. The structure and correlation functions derived from the two data sets are in good agreement, a result not in general achieved in other laboratories. One way of describing intermolecular correlations is through the atom pair correlation function $g(r)$ defined so that $\rho_A g(r) dr$ is the number of atoms in a volume element dr a distance r from an atom on another molecule in a fluid of bulk atomic number density ρ_A . The atom pair correlation function for liquid bromine, derived from our x-ray data, is shown in Fig. 11.21 as a function of $R^* = r/\sigma_{\text{Br-Br}}$, with $\sigma_{\text{Br-Br}}$ the distance at which $g(r)$ has its first maximum. Also plotted in Fig. 11.21 are the functions $g(R^*)$ for liquid oxygen and nitrogen. It is evident that the atom pair correlations in bromine are quite different from those in oxygen and nitrogen in that, while the heights of the first peaks in $g(R^*)$ are similar, the location of the second peak and the

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2. Defined in Eq. (1), Sect. 11.1.13 of this report.

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Fig. 11.21. The intermolecular atom pair correlation functions for liquid bromine (solid line), oxygen (circles), and nitrogen (squares) near their respective melting points. The curves are plotted as a function of R^*/r_0 , where r_0 is the location of the first maximum in g(r).

breadths of the first and second peaks in liquid bromine are quite different from those for oxygen and nitrogen. These observations suggest that the molecular forces present in bromine are quite different from those found in less polarizable molecules without appreciable electrostatic moments and that these forces have a pronounced effect in the liquid structure.

The atom pair correlation function for liquid bromine, derived from our x-ray data, is compared with results of Monte Carlo computer simulations for various interaction potentials in Fig. 11.22. The models used included a two-center, Lennard-Jones interaction model, both by itself and with idealized point quadrupole and quadrupole-induced dipole interaction terms. The most important conclusion of our study is that none of the atom pair potential functions (with the force center coincident with the atomic nucleus) considered yield atom pair correlation functions that agree with those derived from our x-ray diffraction study (Fig. 11.22). The failure of an atom-atom potential is surprising in view of the success of such interaction models for oxygen, nitrogen, and other molecular fluids. Thus, we conclude that because of the charge distribution in a bromine

Fig. 11.22. Comparison of the experimental atom pair correlation function for liquid bromine (circles) with results from Monte Carlo computer simulations; simulation result with the two-center, Lennard-Jones potential and parameter, of krypton, $\epsilon/k_B = 166.7^\circ\text{K}$, $\sigma = 3.679 \text{ \AA}$ (—); the point quadrupole moment of $Q = 8.2 \times 10^{-26} \text{ esu cm}^2$ has been added to the above potential (■); the result of the further addition of the quadrupole-induced dipole interaction term (▲▲▲).

molecule (which is responsible for its large quadrupole moment and polarizability), a diatomic atom-atom potential function does not adequately represent the interaction between two bromine molecules. Hence, a complete unfolding of the liquid bromine structure will have to await further refinements in the intermolecular potential function.

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11.2 ATOMIC AND MOLECULAR COLLISIONS

11.2.1 Carbon Reactions in Crossed Molecular Beams: $\text{C}_2 + \text{NO} \rightarrow \text{CN}^*(B) + \text{CO}$

H. F. Kramers and S. Datz

Gas-phase reactions involving carbon atoms and polymers (C , C_2 , C_3 , C_4 , and C_6) are of basic interest in

interest, and they occur in a wide variety of man-made and natural environments. Basic understanding in this area is particularly applicable in combustion and high-temperature environments such as in flames, shock-tubes, MHD, and stellar atmospheres. Unfortunately the study of isolated reactions has proven to be most difficult, even in the least complicated surroundings. The unambiguous identification of specific reactants and products for several carbon atom reactions has been achieved only recently. Bulk rate constants for some of these processes have been measured, but little is known about the detailed state-to-state partitioning of reaction energy among products. Our knowledge of carbon polymer reactions is most limited.

Molecular-beam techniques are well suited to the study of carbon reactions, but they have not been applied previously. The chemiluminescent four-center exchange reaction reported here is the most detailed energy transfer study reported for any carbon reaction. Since it has been shown to be specific to the C_2 reactant, it also forms the basis for a simple, remote, and very sensitive detector ($\sim 10^{-11}$ torr) for the C_2 radical.

The chemiluminescent reaction $C_2 + NO \rightarrow CN^*(B^2\Sigma^+) + CO + 1.69$ eV has been studied. The carbon beam was obtained from a graphite sublimation source operating at 2550 K. The beam (principally C , C_2 , C_3) was pulsed by a rotating slotted disk before it crossed the NO beam. Each of the carbon beam constituents arrived at the beam interaction zone in different time-dispersed packets. Electronically excited molecules formed in reaction $CN^*(B^2\Sigma^+)$ were detected as they rapidly decayed to the ground state. Photon time-of-arrival measurements identified the reactant as C_2 . The vibrational energy disposal within $CN^*(B^2\Sigma^+)$ was derived from wavelength resolved measurements. Reaction energetics and the signal intensity indicated the companion product, $CO(X^1\Sigma_g)$.

The spectrum of the $CN(B^2\Sigma^+)$ state produced in reaction is shown in Fig. 11.23; the lowest five vibrational states ($v' = 0-4$) are produced. This emission depended on the graphite sublimation source temperature in a manner most consistent with the C heat of sublimation (8.241 eV) and depended linearly on the NO concentration. Unambiguous evidence for the C_2 reactant is shown in Fig. 11.24. The time of arrival for the $CN(B^2\Sigma^+ \rightarrow X^2\Sigma^+)$ emission is in good agreement with that predicted, assuming a reaction cross section for the

Fig. 11.23. Chemiluminescent spectrum produced by collisions C_2 with NO [$\Delta\lambda(\text{FWHM}) = 38 \text{ \AA}$, $T(C_2) = 2550^\circ \text{K}$].

Fig. 11.24. $CN(B^2\Sigma^+ \rightarrow X^2\Sigma^+)$ emission vs the time of arrival. The data are compared with that expected for the reactants C , C_2 , and C_3 at a temperature of 2575 K.

C_2 reactant which is weak [$\sigma(v) \sim v^{-1}$ as expected for an exoergic reaction with an r^{-6} interaction potential]. The total reaction cross section exceeds 10^{-16} cm^2 .

Detailed partitioning of the reaction energy into vibrational and rotational states of the $CN(B^2\Sigma^+)$ has been studied by spectral simulation techniques. Using such methods, one can derive the approximate rotational temperatures for each vibrational state formed and the relative vibrational populations characteristic of the collision. The effective rotational temperatures are found to decrease monotonically from about 7000°K to 3500°K as the vibrational quantum number increases ($v' = 0-4$). The fractional energy in rotation within a given vibrational manifold, however, is essentially constant ($\approx 27\%$) for all vibrational manifolds. The vibrational population approximately fits an effec-

tive vibrational temperature. $T_{\text{vib}} \sim 7000^\circ\text{K}$. On the average, about 14% of the energy available to products ($\approx 2.25\text{ eV}$) is deposited in $\text{CN}(B^2\Sigma^+)$ vibration. The energy partitioning in $\text{CN}(B^2\Sigma^+)$ disagrees mildly with that predicted by the methods of "prior expectation," a behavior that is similar to that expected for unimolecular decay of products from a long-lived complex.

This reaction probably proceeds on a potential energy surface that correlates to $\text{C}_2(X^3\Pi_u) + \text{NO}(X^2\Pi)$. The electronically excited $\text{C}_2(X^3\Pi_u)$ state (600 cm^{-1}) is the most abundant reactant at 2550°K , and this potential energy surface correlates to the product channel forming $\text{CN}(B^2\Sigma^+)$ adiabatically. By similar reasoning, formation of CN in the $X^2\Sigma^+$ ground state is expected to occur in reactions involving the $X^1\Sigma_g^+$ and $X^3\Pi_u$ states of C_2 with NO .

11.2.2 Ion Pair Formation and Atom Abstraction in

Collisions of Cs and UF_6

B. K. Annis S. Datz

The ion pair formation reaction $\text{Cs} + \text{UF}_6 \rightarrow \text{Cs}^+ + \text{UF}_6^-$ and the atom abstraction reaction $\text{Cs} + \text{UF}_6 \rightarrow \text{CsF} + \text{UF}_5$ were studied over the relative kinetic energy range 0.2 to 1.3 eV, using a seeded nozzle source for UF_6 . Although preliminary results of ion pair formation study have been reported previously,¹ it may be added that there was no indication that electronically excited states of UF_6 were involved in the electron transfer process.

The angular distributions of CsF were found to be significantly different from those obtained earlier at thermal energy ($\sim 0.08\text{ eV}$ relative kinetic energy). At hyperthermal energies the product peaks were found in the backward direction as illustrated in Fig. 11.25. This behavior indicates that the collision proceeds by a direct rebound mechanism rather than by the complex formation that characterized the thermal reaction. Since the lowest relative kinetic energy attainable with the nozzle source was 0.19 eV, it is apparent that the transition from complex formation to direct reaction occurs in a very limited energy range (i.e., $\sim 0.1\text{ eV}$) and thus substantiates our earlier conclusion that the binding energy of the CsUF_6 complex must be less than about 0.9 eV.

Estimation of the magnitude of total cross sections for the atom abstraction processes from the

Fig. 11.25. Laboratory angular distribution of CsF correspond to various models for CsF velocity distributions.

angular distribution data is sensitive to the model chosen for the product velocity distributions. However, it was clear that product was substantially favored over the energy range investigated.

I. B. K. Annis and S. Datz, *Chem. Div. Annu. Mar. 31, 1977, ORNL-5297*, p. 126; B. K. Annis, p. 1154 in *Proc. 10th Internat. Conf. Physics of E. Atomic Collisions*, vol. II, Commissariat à l'Énergie Paris, 1977.

11.2.3 Hydrogen Recycle Chemistry: Interactions of Low-Energy Proton Beams with Carbon

S. H. Overbury R. S. Thoe
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In MFE reactors, charge-exchanged neutral hydrogen atoms leave the plasma, first wall, and are reemitted into the plasma with the initial energy of the atomic hydrogen rather than thermal up to plasma temperature and is a sharp peak at $\sim 200\text{ eV}$ in some Tokomaks and at lower energies in others. During this report period we have been studying the physics of transmission and "reflection" of 2500-eV H^+ and D^+ from carbon in order to obtain information pertinent to plasma-wall interactions in Tokomaks.

Transmission. The scattering of low-energy hydrogen from carbon has been investigated by exact transmission of H^+ through thin amorphous foils. These foils were mounted in an ion spectrometer, which was completed last year. The system contains an ion source capable of ge-

monoenergetic, focused, and mass analyzed beam of H^+ or D^+ with energies from 100 to 3000 eV. The thicknesses of the foils were determined by a correlation of light-transmission measurements with Rutherford backscattering measurements.

As ions penetrate a solid, they lose energy inelastically to electrons and elastically due to collisions with nuclei. At high energies, collisions with nuclei occur with low probability, and most of the energy of an ion is lost continuously through electronic stopping. In the energy range of these experiments, theory predicts that the energy lost per increment of penetration depth (dE/dx) is proportional to the velocity $v \propto E^{1/2}$ of the ion, that is,

$$(dE/dx) = KE^{1/2} \quad (1)$$

The integral form of this equation is given by

$$E_f^{1/2} - E_i^{1/2} = 1/2 Kt, \quad (2)$$

where E_f and E_i are the final and initial energies of the transmitted ion and t is the thickness of the transmitted foil. Results for H^+ through carbon are shown in Fig. 11.26 and agree well with the theoretical form predicted by Eq. (2). The intercept of the line in Fig. 11.26 gives a value of the constant K , which is found to be in good agreement with that predicted by the theory of Lindhard et al.

An important aspect of this problem is that the particles transmitted through the carbon foils emerge as H^0 , H^+ , or H^- . Since the electrostatic analyzer can detect only charged particles, it is important to know the fractions f^+ , f^- , and f^0 of hydrogen species which emerge positive, negative, or neutral. To measure these fractions, it is necessary to know the fraction f_t of the particles that pass through the foil without being reflected by the foil or stopped within it. The energy dependence of $f_t(E)$ was calculated for us by M. T. Robinson of ORNL, using his computer code MARLOWE. By counting all charged particles emerging from the foil and using the known incident beam current and the calculated value of f_t , the charge fractions f^+ , f^- , and f^0 could be deduced. This was done as a function of the emergent energy of the hydrogen. It was found that $f^+(%) \approx 2.6 E$ and $f^-(%) \approx 1.9 E$, where E is in keV.

Reflection. Since completing the transmission experiments, we have investigated the energy spectra of H^+ particles that are back reflected from thick carbon samples. We have obtained spectra as a function of incident energy, incident angle, and total scattering angle. The energy distributions of back-scattered H^+ are found to be quite broad, although the width decreases with increasing energy. In all

Fig. 11.26. The square root of the final energy, E_f (in $eV^{1/2}$) plotted as a function of the square root of the initial energy, E_i , for H^+ and D^+ transmitted through a $2.66\text{-}\mu\text{g}/\text{cm}^2$ foil. The solid lines are least-squares fits to the data, but they are constrained to have unity slope. The close agreement between the data and the lines is experimental confirmation that the stopping power dE/dx is proportional to the velocity in this energy range.

cases a high energy cut-off is found, which begins at an energy just below the maximum energy obtainable from a single elastic surface scattering event. This high energy "knee" has been fitted numerically to a Gaussian peak shape whose intensity yields a positive charge fraction for surface-scattered hydrogen which is different from that for hydrogen transmitted through thin foils. Current work is aimed at obtaining greater qualitative understanding of the shape of the energy distributions, and use of the computer code MARLOWE should aid in this endeavor.

The angular intensity distributions are found to depend strongly on the incidence angle of the beam. For normal incidence, the angular distributions are found to be cosine; whereas, for grazing angles of incidence, the intensity is peaked in a direction forward of the specular scattering angle. Using the charge fractions obtained from the thin foil measurements, the "reflection" coefficient for normally incident H^+ was determined and is in agreement with the predictions obtained from MARLOWE.

1. Consultant, Physics Department, University of Tennessee, Knoxville

2. J. Linhard, M. Scharff, and H. E. Schmitt, *K. Dan. Vidensk. Selsk. Mat-Fys. Medd.* **36**, 10 (1968).

11.2.4 Resonant Coherent Excitation of Channeled Ions

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A channeled ion passing between ordered rows of atoms in a crystal lattice with a velocity v experiences a coherent periodic perturbation of frequencies $\nu = k(v/d)$, $k = 1, 2, 3, \dots$, where d is distance between atoms in a row. When one of these frequencies coincides with $\nu_{ij} = \Delta E_{ij}/h$, where ΔE_{ij} is the energy difference between electronic states i and j of the ion, a resonant coherent excitation might occur.

To probe for this effect we have utilized our previous observations that, for ions of $Z = 5$ through 9 ($E \geq 1.5$ MeV/amu), an appreciable fraction of zero-, one-, and two-electron systems can pass through the central channel cores ($\leq 1 \mu\text{m}$ thick) without charge change and that ions maintaining their input charge state can be identified by a characteristic energy loss peak. The probability of an ion remaining in a fixed charge state depends on the integrated flux of electrons encountered and, very sensitively, on the state of the attached electron. For example, if an electron bound to a channeled ion makes an $n = 1$ to $n = 2$ transition, we should observe an increased probability for electron loss. We therefore measured the surviving fraction of ions in fixed-charge states for a number of ionic species passing through channels in silver (1000 Å thick) and gold (850 Å thick) as a function of velocity.

In Fig. 11.27 we show an example of some observed resonances for incident N^{7+} . We display the total population fraction of N^{7+} emerging from an 850-Å-thick gold crystal as a function of the incident energy. The spacing along a $\langle 111 \rangle$ row is 7.064 Å. Resonances are shown for $k = 4, 5$, and 6. The additional scales shown are given in terms of v/v_r , where v_r is the calculated resonant velocity.

Consider first the processes occurring in the absence of resonant excitation. For example, 35-MeV N^{7+} ions passing on a well-channeled course through ~ 1000 Å of gold will encounter an electron target thickness of $\sim 5 \times 10^{17} \text{ cm}^{-1}$ (~ 10 electrons per gold atom), and the center-of-mass energy is 1400 eV. By electron collision, the ion can be directly ionized ($\sigma_i \sim 5 \times 10^{-20} \text{ cm}^2$) or excited to $n = 2$ ($\sigma_{2p} \sim 5 \times 10^{-20} \text{ cm}^2$) and then ionized ($\sigma_{2p} \sim 5 \times 10^{-20} \text{ cm}^2$). Once ionized, the probability of recapturing an electron is

Fig. 11.27. Ratio of N^{7+} counts to the sum of N^{7+} and N^{6+} counts as a function of initial energy for (111) axial channeling in gold. The abscissa is linear in velocity. The incident beam is N^{7+} .

small; the passage would leave $\sim 50\%$ of the N^{7+} ions unchanged, in rough accord with the observations. The coherent resonant excitation process to $n = 2$ effectively supplies an additional ionization channel.

For all the simpler features of the resonances, some generalizations can be made: (1) narrower channels give stronger resonances, (2) higher harmonic resonances are weaker, (3) there are slight shifts in the resonance peaks to lower (v/v_r), and (4) the peaks are asymmetric toward lower (v/v_r). The first is easily understood, since ions moving through narrower channels experience stronger perturbations. The remaining three can all be seen in Fig. 11.27. The peak shifts may be caused by the decreased $n = 1$ to $n = 2$ energy spacing due to the presence of the crystal field. The spreading is asymmetric since the energy spacing is maximum at the exact channel center and decreases as the rows are approached.

More subtle features of the resonances are shown in Figs. 11.28 and 11.29 for the $\langle 100 \rangle$ channel ($d = 4.078 \text{ Å} = a$, the lattice constant). In Fig. 11.28 we show a third (odd) harmonic excitation for O^{7+} and the splitting of the single central feature as the crystal axis is tilted in the (100) planar direction. In Fig. 11.29 we show a double peak seen for the second

Fig. 11.28. Ratio of O^{++} counts to the sum of O^{++} and O^{+} counts as a function of initial velocity for (100) axial channeling in gold and for three tilt angles. The incident beam is O^{++} .

harmonic of N^{++} directly on axis and its insensitivity to tilt angle. Evidence for doublet structure has been seen for all ions in even harmonics in the $\langle 100 \rangle$ and $\langle 110 \rangle$ axes. We will show that the splitting in Fig. 11.28 is due to sidebands produced by modulation of the central frequency when the crystal is tilted, whereas the splitting in Fig. 11.29 is due to Stark splitting of the $n = 2$ levels of the ion.

An ion channeled along the $\langle 100 \rangle$ axis (z direction) generates an electron wake. This produces a field that can be shown to split the $n = 2$ manifold of the ion into three levels, the central one of which is $2p_z$, $2p_x$ (degenerate), whereas the outer ones arise from mixed $2s$, $2p_y$ states. We attribute the central minimum in Fig. 11.28 to transitions to the degenerate $2p_z$ and $2p_x$ states and the two large minima in Fig. 11.29 to transitions from $1s$ to the mixed $2s$, $2p_y$ levels.

Selection rules have been derived from the electric potential, which in an unperturbed face-centered

Fig. 11.29. Ratio of N^{++} counts to the sum of N^{++} and N^{+} counts as a function of initial velocity for (100) axial channeling in gold and for three tilt angles. The incident beam is N^{++} .

cubic crystal can be shown to have the following form:

$$V = \sum_{k \text{ (even)}} V_{kz} \cos(2\pi kz/a) \cos(2\pi lx/a) \cos(2\pi my/a) + \sum_{k \text{ (odd)}} V_{ky} \sin(2\pi kz/a) \sin(2\pi lx/a) \sin(2\pi my/a), \quad (1)$$

where the z , x , and y axes are centered in $\langle 100 \rangle$, $\langle 010 \rangle$, and $\langle 001 \rangle$ channels. The two sums are overall sets of positive even and positive odd integers. The first sum contains the even harmonics and the second sum the odd harmonics of the fundamental frequency, v/a . One finds, for sufficiently small x and y , that the oscillating field is predominantly in the x and y directions for odd harmonics (odd k) and in the z direction for even harmonics. Dipole selection rules have been shown to apply. Thus, when the ion comes into resonance with an odd harmonic as in Fig. 11.28, the strongest transitions should be those to the degenerate $2p_z$ and $2p_x$ states. It follows that the separation between the two minima in Fig. 11.29 is a

measure of the wake field in the vicinity of the moving ion. If we assume a uniform field ξ , the first-order Stark splitting is $6e\xi a$. The data of Fig. 11.29 give a value of $0.10e^2/a$ for this splitting, from which we deduce $\xi = 0.12e/a$, which is of the expected order of magnitude. A more refined treatment is in progress.

If the crystal is rotated through an angle θ about the y axis, a similar analysis (assuming only small γ) shows that, for even k , the field contains the following frequencies:

$$(v/a)(k \cos \theta \pm \epsilon \sin \theta), \quad \epsilon = 0, 2, 4, \dots \quad (2)$$

where the central ($\epsilon = 0$) frequency component is mainly in the z direction. Therefore, for small tilts, one should find the same spectrum as for $\theta = 0$, with the possible addition of small sidebands. Hence the curves in Fig. 11.29 show little change with tilt.

Odd harmonics behave differently: Fig. 11.28 shows a central minimum breaking into two minima. This breaking occurs because the frequencies for odd k are as in Eq. (2), but here with only odd ϵ . The ion steps through a succession of $\langle 100 \rangle$ channels. Since fields vary across a channel, an amplitude modulation results, and sidebands appear. The central frequency is missing when k is odd because the strings of atoms which define the $\langle 100 \rangle$ channels in a face-centered cubic crystal are staggered in z in such a way that the odd- k signals change phase by one cycle as the trajectory progresses sideways a distance a . A tilt of 0.7° causes the ion to step over a distance a once every 80 atoms of its passage (thus once per 240 cycles of the third harmonic), giving sidebands 0.4% above and below the frequency $k(v/a)$ ($\pm 0.4\%$ in v/v) in agreement with Eq. (2), with $\epsilon = 1$.

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11.3 REACTIVE INTERMEDIATES BY ELECTRON SPIN RESONANCE

11.3.1 Studies of Free Radicals Formed by Pyrolysis

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M. Conradi

Several approaches have been investigated for the study of pyrolytically formed radicals by electron spin resonance. A spin trapping method was examined in which vapors of organic substances were pyrolyzed as they passed through a heated tube and then over a spin trapping agent. The agents tried were

phenyl-*N*-*t*-butylnitron and 2-methyl-2-nitrosopropane. There was too great a variability of efficiency for trapping of mixtures of radicals, and the final radical products did not show adequate resolution for definitive identification of the radicals. The method was not explored further. A method of supplying short-time, high-current pulses through a filament immersed in a flowing liquid in the active region of the spectrometer was examined as a possible technique for seeing short-lived radicals. Although a filament pulsed in this manner showed interesting properties, tests and calculations showed that it is not suitable as the primary heat source to form radicals. It may be of later use as a temperature-jump technique for kinetic studies when applied to other pyrolytic approaches. A rapid flow technique was tried in which a gaseous organic substance was pyrolyzed in a hot tube and then rapidly blended with a high-velocity liquid stream where the blending occurs near the sensitive region of the spectrometer. Radical signals have not yet been seen, but additional tests will be made. A successful approach that has been developed is the heating of a liquid at high pressure as it slowly flows through the microwave cavity of the spectrometer. The results that follow were obtained with this approach.

The pyrolytic cell consists of a length of fused silica capillary that spans the microwave cavity of the spectrometer. The sample flow system contains a reservoir for the liquid sample. In all work reported here, unless otherwise stated, helium was bubbled through the liquid in the reservoir in order to remove dissolved oxygen. The liquid flows to a high pressure pump and then to the pyrolytic cell. A throttling valve is located at the exit side of the cell to permit setting of the pressure. After the throttling valve, the liquid sample at atmospheric pressure is returned to the reservoir. In the present configuration, pressures up to 2000 psi have been used, and the flow rates have usually been 1 ml/min. The pyrolytic cell is contained within a vacuum-jacketed, fused-silica tube, and heating is accomplished by passing electrically heated air through the annular space between the cell and the surrounding vacuum-jacketed tube. A thermocouple is located in the annular space just below the active region of the microwave cavity, which provided the temperature values reported here. Temperatures up to 560°C have been used, and it appears that even higher temperatures are readily attainable with this technique.

In preliminary experiments a strong, well-resolved spectrum was obtained for $(\text{CH}_3)_2\text{CCN}$ resulting from the thermal decomposition of α, α' -

azobisisobutyronitrile at $\approx 150^\circ\text{C}$ and 1000 psi. Solvents used for the nitrile were dibutylphthalate and isopropyl alcohol. A good spectrum was also obtained from $(\text{CH}_3)_2\text{COH}$ obtained by heating a solution of 3% di-*t*-butyl peroxide in isopropyl alcohol at 220°C , 1000 psi. In this case the peroxide is thermally decomposed to give highly reactive radicals that abstract hydrogen from the isopropyl alcohol. Much of the work thus far has centered on a number of benzylic-like radicals that are of interest in coal conversion processes and in combustion. Figure 11.30 summarizes many of these results. To maintain a high enough steady-state concentration of the radicals from indene and from bibenzyl, a high temperature was chosen, which caused a very high burn-up rate of the substance being pyrolyzed. In the case of indene, a second ESR signal appeared and became progressively stronger during each run. This signal was a broad, intense line, which remained at room temperature and resulted from a coating on the cell wall, presumably the result of polymerization. The radical from bibenzyl is believed to form by decomposition to benzyl radicals with subsequent abstraction of hydrogen from other molecules of bibenzyl, giving the observed radical. Sharp, intense spectra of the diphenylmethyl radical were obtained from diphenylmethane from three sources of supply, but the radicals were found to be initiated by low concentrations of impurities. Spectra were not obtained from purified diphenylmethane. Addition of a small amount of benzophenone or pretreating the diphenylmethane by bubbling air through it did give the diphenylmethyl spectrum. In these cases the radical is apparently at equilibrium with tetraphenylethane, which is only slightly dissociated at 420°C . Its dissociation in benzene solution has also been observed, but a yet unexplained observation is that a manyfold stronger spectrum is obtained when diphenylmethane is present. Work on cumene is still under way; it appears, however, that the cumyl radical reported in Fig. 11.30 is not at equilibrium with other substances but is a consequence of continuous slow pyrolysis of cumene. A sulfuric acid treatment of the cumene to remove oxidizing impurities and substances with olefinic linkages such as α -methylstyrene did not change the intensity of the spectrum. Moreover, addition of the dimer, 2,3-dimethyl-2,3-diphenylbutane, produced negligible change in intensity of the spectrum. Cumyl radical has been prepared in other ways where it was evident that the radical was disappearing largely by irreversible processes. A solution of 4% di-*t*-butylperoxide in

Fig. 11.30. Radicals observed during pyrolysis with the indicated conditions. Hyperfine couplings are given in units of gauss.

cumene gives an excellent cumyl spectrum at 230°C , and rapid burnup of the peroxide has been followed. A weak cumyl radical spectrum is obtained by heating cumene with dissolved oxygen at 350°C . At higher temperatures the oxygen is burned out before the sample reaches the active region of the spectrometer, and no spectrum is seen until 450°C is reached, whereupon the mechanism responsible for the results in Fig. 11.30 starts to become important. If the cumyl radical is observed with the conditions of Fig. 11.30 and bibenzyl is added to the solution, there is a large enhancement in intensity of the cumyl radical signals.

This is presumably a consequence of dissociation of bibenzyl to give the benzyl radical, which then abstracts hydrogen from cumene. Studies of *p*-cymene and ethylbenzene are not complete, and it is not known what role impurities may play and whether or not the radicals are seen as part of an equilibrium system.

11.3.2 Exchange in Basic Aqueous Solution of the NH-Hydrogen of a Substituted *N*-Hydropyridinyl Radical

H. Zeldes R. Livingston

A study of the 1-hydro-3,5-pyridinedicarboxylate anion radical has now been completed.¹ This study is similar to that reported previously for the 1-hydro-2,5-pyridinedicarboxylate anion radical.² The radical was produced photolytically in aqueous solution, and its electron spin resonance spectrum was studied over a broad range of NaOH concentrations near room temperature. Effects of the dissociation of the NH-hydrogen in basic aqueous solutions were interpreted quantitatively. At high concentrations of NaOH, the radical interchanges rapidly between its undissociated and dissociated forms, resulting in a single sharp-lined spectrum whose couplings depend on the degree of dissociation. This result made it possible to determine the thermodynamic equilibrium constant for the base-catalyzed equilibrium, from which the constant for the ionization in aqueous solution was calculated. The latter at 25°C, expressed in *pK* units is 16.82 ± 0.05 . For a range of lower concentrations of NaOH, the radical is essentially completely undissociated, but the NH-hydrogen is reoriented by the equilibrium reactions. In this range, lineshape effects occur which depend on the second-order rate constant for the reaction between OH⁻ and the undissociated form of the radical. This constant was determined for a range of dilute NaOH concentrations with the help of spectral simulations, which included corrections for the finite amplitude of the field modulation. The value of the rate constant extrapolated to infinite ionic dilution was found to be $(5.0 \pm 0.5) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ at 30°C. The *g*-values and couplings of both forms of the radical were determined.

1. Expanded abstract of paper prepared for publication.
2. H. Zeldes and R. Livingston, *Chem. Div. Annu. Prog. Rep. Mar. 31, 1977*, ORNL-5297, p. 133.

11.3.3 Ring Inversion of Tetralin-1-yl and Studies of Related Benzylic Radicals

M. Conradi H. Zeldes
R. Livingston

During a study of substituted benzyl radicals of importance in coal chemistry, we observed the ESR spectrum of tetralin-1-yl (or, α -tetralyl).¹ Photoexcited benzophenone abstracted a hydrogen atom from tetralin (1,2,3,4-tetrahydronaphthalene) to form the radical. The absence of certain lines from the room temperature ESR spectrum indicated the occurrence of an alternating linewidth effect. This effect resulted from inversion at an intermediate rate of the ring puckering in the saturated portion of the radical. Subsequently, ESR spectra of tetralin-1-yl were obtained in the slow and fast ring inversion regimes. The linewidths at low and high temperatures were analyzed to yield values of the inversion rate and the Arrhenius parameters of the inversion. The activation energy is $30 \text{ kJ mol}^{-1} \pm 12\%$ and the frequency factor is $1.2 \times 10^{11} \text{ s}^{-1}$, uncertain within a factor of 5.

The proton hyperfine splittings and *g* value of tetralin-1-yl were measured from -69 to 146°C. The values of angles descriptive of the ring puckering in the radical were determined from the values of the splittings at low temperatures. The values of the angles agreed well with a simple model of the structure.

The proton hyperfine splittings and *g* values of meta- and ortho-xylyl and α -methylbenzyl were also measured. These values confirmed the assignment of proton hyperfine splittings in tetralin-1-yl. The methyl group splittings in meta- and ortho-xylyl indicate an unusual methyl substitution effect.

1. Abstract of paper submitted for publication in *J. Phys. Chem.* and talk presented at Tenth Southeastern Magnetic Resonance Conference, Knoxville, Tenn., October 1978.

11.3.4 Radicals Produced Photolytically from Hydrocarbons

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R. Livingston

A number of radicals made pyrolytically (Sect. 11.3.1) have also been prepared photolytically at room temperature. This gives added confirmation of the identification of many of the pyrolytically formed

radicals and also allows a comparison of room-temperature and high-temperature spectral parameters. Many of the radicals reported in Fig. 11.30 were made by photolyzing the following systems at room temperature: indene in acetone, bibenzyl in benzene with a small amount of benzophenone, cumene with a small amount of di-*t*-butylperoxide, and ethylbenzene with a small amount of benzophenone. In general, the *g*-values do not change, whereas the changes in hyperfine couplings are small and appear reasonable. The most notable effect appears in the radicals from bibenzyl and ethylbenzene. At room temperature, the ortho hydrogens are inequivalent because of a lack of rapid rotation of the aromatic ring about the bond to the carbon with high spin density, whereas at high temperature the ortho hydrogens appear equivalent.

11.4 PHOTOCHEMISTRY AND RADIATION CHEMISTRY

11.4.1 Studies of Elementary Reactions of Small Free Radicals in the Gas Phase by Flash Photolysis

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P. J. Ogren

Flash photolysis was used to study reactions of small free radicals of importance in combustion and other systems of interest in the energy field. Here we report results on reactions of CH_3 , HCO , and HO_2 produced by photodissociation of water vapor in the presence of CH_4 , CO , and O_2 respectively. The mechanisms developed, even for these relatively simple systems, involve several competing reactions. Consequently, it was necessary to employ numerical integration to fit the data by the method of least squares. Absolute rate constants were evaluated for several important elementary reactions. Realistic error limits were determined by detailed sensitivity analyses, which took into account both the error in the computer fit to the experimental measurements and the accumulated error arising from uncertainties in the assumed values for fixed parameters. Five different systems have been studied.

$\text{H}_2\text{O} + \text{CH}_4$. Methyl radicals that are produced by reaction of OH with CH_4 decay by reaction with H , CH_3 , and OH. By measuring CH_3 decay kinetics as a function of CH_3 concentration, using N_2 and H_2 as diluents and pressures from 1 to 3 atm, we were able to evaluate absolute rate constants for the reactions of CH_3 with H and OH and the reactions of OH with CH_3 and H_2 . A typical set of results with N_2 as inert

diluent is shown in Fig. 11.31. The solid curves were fit to the data by computer, using the mechanism listed in Table 11.2. A similar set of results was obtained with H_2 as diluent; the kinetic behavior was somewhat different, however, because of reaction 5.

Fig. 11.31. Decay of CH_3 absorption (216 nm) in the flash photolysis of $\text{H}_2\text{O}-\text{CH}_4-\text{N}_2$ mixtures.

Table 11.2. Reactions in the $\text{H}_2\text{O}-\text{CH}_4$ systems
Underlined values were determined in this work

1. $\text{H}_2\text{O} \xrightarrow{h\nu} \text{H} + \text{OH}$	
2. $\text{OH} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{H}_2\text{O}$	$4.2 \pm 0.4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$
3. $\text{CH}_3 + \text{CH}_4 \xrightarrow{M} \text{C}_2\text{H}_6 (\text{atm})$	$3.1 \pm 0.6 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$
4. $\text{H} + \text{CH}_3 \xrightarrow{M} \text{CH}_4 (\text{atm})$	$1.2 \pm 0.3 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$
5. $\text{OH} + \text{H}_2 \rightarrow \text{H} + \text{H}_2\text{O}$	$5.1 \pm 1.1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$
6. $\text{H} + \text{CH}_3 \rightarrow \text{CH}_4 + \text{H}_2$	$2.6 \pm 0.3 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$
7. $\text{H} + \text{H} \xrightarrow{M} \text{H}_2$	
(a) (<i>M</i> = H_2O)	$9.0 \pm 2.0 \times 10^{10} \text{ M}^{-2} \text{ s}^{-1}$
(b) (<i>M</i> = CH_3)	$5.5 \pm 0.3 \times 10^9 \text{ M}^{-2} \text{ s}^{-1}$
(c) (<i>M</i> = H_2)	$2.9 \pm 0.2 \times 10^9 \text{ M}^{-2} \text{ s}^{-1}$
(d) (<i>M</i> = N_2)	$3.3 \pm 0.2 \times 10^9 \text{ M}^{-2} \text{ s}^{-1}$
8. $\text{OH} + \text{CH}_3 \rightarrow \text{products}$	$5.6 \pm 1.3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$
9. $\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}$	$1.4 \pm 0.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$
10. $\text{OH} + \text{OH} \xrightarrow{M} \text{H}_2\text{O}_2$	
(a) (<i>M</i> = H_2 , CH_3)	$3.4 \pm 1.3 \times 10^{11} \text{ M}^{-2} \text{ s}^{-1}$
(b) (<i>M</i> = N_2 , H_2)	$6.2 \pm 2.3 \times 10^{10} \text{ M}^{-2} \text{ s}^{-1}$
11. $\text{OH} + \text{H} \xrightarrow{M} \text{H}_2\text{O}$	
(a) (<i>M</i> = H_2O , CH_3)	$9.5 \pm 3.5 \times 10^{11} \text{ M}^{-2} \text{ s}^{-1}$
(b) (<i>M</i> = N_2 , H_2)	$1.7 \pm 0.6 \times 10^{11} \text{ M}^{-2} \text{ s}^{-1}$

Note: $\epsilon(\text{CH}_3, 216 \text{ nm}, 6 \text{ Å band}) = 9000 \pm 800 \text{ M}^{-1} \text{ cm}^{-1}$.

From these measurements the four underscored rate constants were evaluated; the other values were fixed values taken from the literature. In addition to the four rate constants, the amount of water dissociated by the flash was evaluated. The $\text{H}_2\text{O} + \text{CH}_4 + \text{N}_2$ and $\text{H}_2\text{O} + \text{CH}_4 + \text{H}_2$ mixtures gave the same value for the amount of H_2O dissociated by the flash. The rate constant k_2 was invariant with either CH_4 , N_2 , or H_2 as third body M , indicating that the reaction is near the second-order limit at 1 atm; our value agrees with recent theoretical estimates of this limit. Our value for k_2 is the only measured value and is about three times higher than previous estimates. A number of values have been reported for k_2 and k_3 ; our values differ by -18% and $+30\%$, respectively, from recently reported values. The $\text{H}_2\text{O} + \text{CH}_4$ system was used as an actinometer for the other systems discussed below.

$\text{H}_2\text{O} + \text{CO}$. Last year we reported the uv spectrum of HCO and preliminary values for the molar extinction coefficient ϵ and the rate constant for the bimolecular combination. The predominant reactions in this system, following the dissociation of H_2O , are $\text{OH} + \text{CO} \xrightarrow{k_1} \text{CO}_2 + \text{H}$, $\text{H} + \text{CO} + \text{CO} \xrightarrow{k_{12}} \text{HCO} + \text{CO}$, $\text{HCO} + \text{HCO} \xrightarrow{k_{13}}$ products, and $\text{H} + \text{HCO} \xrightarrow{k_{14}} \text{H}_2 + \text{CO}$. Measurements of HCO kinetics as a function of CO concentration, by using H_2 and CH_4 as diluents and pressures of 1 to 3 atm, have allowed us to evaluate k_{14} and thereby obtain a more accurate value for k_{12} . Our value for $k_{12} = 5.6 \pm 1.8 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ is about three times higher than a published estimate based on modeling of flames. Our value for k_{13} is $1.5 \pm 0.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ and for k_{14} is $3.4 \pm 0.7 \times 10^7 \text{ M}^{-2} \text{ s}^{-1}$.

$\text{H}_2\text{O} + \text{CO} + \text{O}_2$, $\text{H}_2\text{O} + \text{H}_2 + \text{O}_2$, and $\text{H}_2\text{O} + \text{O}_2$. These three systems were studied in order to check our published values² for $\epsilon(\text{HO}_2)$, $k_4(\text{HO}_2 + \text{HO}_2)$, and $k_5(\text{HO}_2 + \text{OH})$. In the first two systems, both CO and H_2 convert OH to H , which is then converted to HO_2 . The HO_2 then reacts to form H_2O_2 and O_2 . In the $\text{H}_2\text{O} + \text{O}_2$ system the reaction of $\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$ is a predominant reaction. We are particularly interested in establishing a more accurate value for k_5 , since this is an important termination reaction in several systems. There is still serious discrepancy among the few published values, our value being the highest. In our new measurements, we employ the $\text{H}_2\text{O} + \text{CH}_4$ system as actinometer and are making more accurate and more extensive measurements and more detailed computer calculations. Although final values have not been obtained, we still find k_5 to be very large but probably somewhat lower than our reported value.

We have also confirmed the interesting effect of water vapor on k_1 , which has been reported by Hamilton.³ He produced HO_2 by pulse radiolysis of H_2 in the presence of O_2 , while we produced HO_2 in a dry system by photolysis of O_2 in the presence of H_2 : $\text{O}_2 \rightarrow \text{O}(^1\text{D}) + \text{O}(^3\text{P})$, $\text{H}_2 + \text{O}(^1\text{D}) \rightarrow \text{H} + \text{OH}$, $\text{H}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{H}$, and $\text{H} + \text{O}_2 \rightarrow \text{HO}_2$.

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12. Theoretical Chemistry

12.1 ATOMIC AND MOLECULAR COLLISION THEORY

12.1.1 Variational Method for Reaction Cross Sections

O. H. Crawford

Relations between chemical reaction cross sections and potential energy surfaces have long been subjects of thought and speculation among chemical kineticists. A body of important results of an approximate or qualitative nature are in hand, such as the effect of a barrier on the energy dependence of a total reaction cross section and the influence of the gross shape of the surface upon the disposal of energy in reaction products, all based on the assumption of classical motion of atoms. It is important to bring quantum mechanical scattering theory to bear on chemical reaction dynamics in order to test general ideas of the kind discussed above, to modify them when necessary, and to extend them. Furthermore, in nonequilibrium applications such as chemical lasers and combustion, the rates of reaction out of or into specific quantum states are important.

The close-coupling method has been the most popular quantum mechanical method for molecular collisions. However, a close-coupling calculation for a chemical reaction involves such a lengthy computation that its application to the simplest case, $H + H_2$, is considered a tour de force. For further progress, it is essential to develop a more practical computational method, and various alternative approaches, including a Faddeev method, R -matrix propagators, and finite elements, are being investigated at other institutions.

We have previously suggested that variational methods are especially promising for this problem, have studied the general properties of suitable variational principles, and have computed reaction probabilities in collinear $H + H_2$. This year has seen the development of some of the algorithms and computer codes necessary for full three-dimensional

calculations. Working with a one-dimensional reaction model, we have found that a certain optimal choice of a basic set allows one to reduce the Hamiltonian and overlap matrices to band matrices of width five (by ignoring the remaining elements) without serious error in calculated reaction probability, thus greatly diminishing the computer storage and time requirements.

12.1.2 Atomic Physics of Channeled Ions

O. H. Crawford R. H. Ritchie

I. L. Thomas

Recent experiments performed in this laboratory, which demonstrated resonant coherent excitation of channeled ions, offer an opportunity to gain new insight into the atomic physics of channeled ions. In this study, we have developed a time-dependent effective Hamiltonian formalism that provides a means of estimating the energy positions and widths of low-lying electronic states of channeled ions and also furnishes a conceptually simple interpretation of resonant coherent excitation. Calculations are compared with experimental results.

We consider the ion's nucleus to follow a prescribed classical path, $r_c(t) = r_0 + vt$. The remaining degrees of freedom are treated quantum mechanically. The Hamiltonian, H , is

$$H = H_e(r_e, t) + H_c(r_c) + V(r_e, r_c, t), \quad (1)$$

where H_e , H_c , and V are, respectively, the electronic Hamiltonian of the ion, the Hamiltonian of the crystal, and the ion-crystal interaction potential. The arguments are r_e , the position of the ion's electron (for simplicity, a one-electron ion is assumed); r_c , the positions of the electrons and nuclei of the crystal; and t , time.

We define a potential operator $U(r_e, t)$, which is the interaction energy between the crystal, and a

hypothetical point charge $(Z - 1)e$ moving with the nucleus. Note that V approaches U asymptotically at a large distance from the ion and that U includes most of the ion-crystal interaction (especially for small r) but is independent of r_z .

Let us define the P and Q subspaces by the projection operators

$$P = \sum_i |\psi_i\rangle\langle\psi_i|, Q = 1 - P, \quad (2)$$

where

$$\psi_i = \chi(r_z, t) \phi_i(r_z, t), i = 1, 2, \dots, n, \quad (3)$$

where ϕ_i is a hydrogenic wave function on the moving ion, with energy ϵ_i , and χ is the wave function for the crystal, beginning with appropriate initial value at some time t_0 and evolving under the influence of the H , and U . P and Q spaces are coupled only by $V - U$, whose expansion in multipole operators of the ion begins with the dipole operator. Therefore, transition rates between P and Q space decrease with increasing Z , because the orbitals are more compact. It follows that, for large enough Z , P space should have a large enough lifetime for its properties to have experimental implications.

It is argued that transitions from P to Q space are, to a good approximation, irreversible. Writing $P\psi = \chi(r_z, t)f(r_z, t)$, the following Schrödinger equation is derived for f alone, the atomic part of the wave function $P\chi$:

$$[i\hbar \partial/\partial t - H_{\text{eff}}]f = 0, \quad (4)$$

where the effective one-body Hamiltonian is

$$H_{\text{eff}} = H_0 - ep\phi p - ipVp, \quad (5)$$

where p is the projection operator onto the n atomic states of P space, ϕ is the electric potential in the crystal (taking into account the response of the crystal to the moving potential U), and the V term is purely dissipative, arising from $P \rightarrow Q$ transitions.

According to Eqs. (4) and (5), the ion's electronic states are mixed by ϕ , the dc part of ϕ (as sensed by the ion) producing new quasi-stationary states whose energies are the eigenvalues E of $H_0 + \phi$. The V term produces lifetime broadening of these energies. The ac part of ϕ , ϕ_{ac} , causes transitions between these states if one of the (angular) frequencies ω in ϕ_{ac} satisfies the following relation to the difference between a pair of energies:

$$\hbar\omega_j = E_i - E_j, \quad (6)$$

The last sentence above is a description of what we call resonant coherent excitation. It is coherent because transition amplitudes for transitions occurring in successive intervals along a trajectory interfere with each other. It is resonant because only near resonance [Eq. (6)] does the interference remain constructive over a long section of the trajectory.

The electric potential ϕ may be written as the sum of an unperturbed part ϕ_0 and the polarization part ϕ_{pol} arising in response to U . The dc components are

$$\phi_0 = \phi_{0,\text{ion}} + \phi_{0,\text{cr}}. \quad (7)$$

In our calculations, $\phi_{0,\text{cr}}$ was obtained from existing quantum mechanical results for free gold atoms under the assumption that the potential in the crystal is the sum of free-atom values, averaged over thermal vibrations by the Debye-Waller prescription. The polarization term ϕ_{pol} was calculated in the plasmon pole approximation, which treats the medium as being approximately an electron gas moving in a rigid uniform distribution of positive charge.

It is found that, in channeling down the center of an axial channel of at least threefold symmetry, the $\phi_{0,\text{cr}}$ potential lowers the energies of the $2s$ and $2p$ levels by differing amounts relative to the $1s$ level. When the polarization term ϕ_{pol} is considered, we find some additional lowering of the levels, but the main effect of ϕ_{ac} is due to a matrix element $\langle 2s|\phi_{\text{ac}}|2p \rangle$ that mixes the $2s$ and $2p$ states to form a new pair, $2sp$ and $2sp^*$, with an increased energy splitting.

The shifts in the degenerate $2p_x, 2p_y$ pair and in the center of the $2sp$ and $2sp^*$ pair are predicted to be due mainly to the $\phi_{0,\text{cr}}$ potential. Moreover, for trajectories down the channel center line, these shifts are sensitive mainly to the curvature of $\phi_{0,\text{cr}}$, which is directly related to the mean electron density in the (unperturbed) channel. Experimental shifts were found to be consistent with theoretical electron densities for (111) axial channeling, but the shifts are not consistent with a unique density in the case of (100) axial channeling. The relation used to derive densities from energy shifts is strictly valid only on the channel center line, and the above inconsistency in the (100) shifts indicates that a better treatment will require calculations for trajectories spanning a range of displacements from the channel center line.

The $2sp, 2sp^*$ splitting is due mainly to the asymmetric part of the polarization, which part

arises from a wake of electrons in the crystal behind the moving ion. The $2p$, $2p^*$ splitting is therefore a measure of the wake field in the region of the electron orbitals. The experimentally determined splittings are roughly consistent with the predictions of the plasmon pole model of the wake, but there are differences between the (100) and (111) channels which suggest that it would be useful to consider a dielectric response model that takes more account of the structure of the crystal.

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12.2 THE STRUCTURE OF MOLECULAR FLUIDS

E. Johnson

The Reference Interaction Site Model (RISM) theory¹ is the best method available for the theoretical study of molecular fluids. It was assumed that this method was directly applicable only when the atoms of the molecular fluid were treated as hard spheres. We have shown that the RISM method is directly applicable to molecular fluids with "soft sphere" atoms,² which has made the RISM method more versatile and convenient.

One model for a benzene molecule consists of a Lennard-Jones interaction site at each vertex of a regular hexagon.³ The radius of the circle which circumscribes this hexagon is 1.756 Å. In this model the interaction sites are not located at atomic positions. The Lennard-Jones parameters are $\sigma = 3.5$ Å and $\epsilon = 77 K_B$, where K_B is the Boltzmann constant. The RISM and the "experimental," computer-simulation⁴ site-site distribution function $g_{ii}(r)$ for this model liquid at $T = 328$ K and molecular number density equal to 0.00633 Å^{-3} are shown in Fig. 12.1. The largest difference between the RISM (solid curve) and computer-simulation (circles) distribution functions is 0.08. This difference, which occurs at $r = 6.5$ Å, is about 7% of the value of the computer-simulation distribution function at this point.

The RISM method yields site-site or atom-atom distribution functions. The atom-atom distribution

Fig. 12.1. Pair distribution functions for benzene at $T = 328^\circ \text{K}$ and number density equal to 0.00633 Å^{-3} . The circles are computer simulation results. The solid curve was obtained from the RISM theory.

function is the probability density for finding two specified atoms of different molecules at given positions. X-ray and neutron scattering experiments on fluids yield atom-atom distribution functions or linear combinations of atom-atom distribution functions. The "full distribution function" is the probability density for finding two molecules with given positions and orientations. The atom-atom distribution functions contain less information than the full distribution function. The atom-atom distribution functions are of much interest because they are relatively easy to obtain experimentally and to treat theoretically.

Before the RISM theory was developed, all distribution-function theories were theories for the full distribution function. We have developed a method for obtaining an integral equation for atom-atom distribution functions from a given integral equation theory for the full distribution function.¹ The RISM method is applicable to model fluids for which the force between molecules takes a special form. The methods mentioned above are not limited to these models. For the cases treated, diatomic molecular fluids, the results from one of these analogues of the RISM method are about as accurate as RISM results.¹

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12.3 THEORETICAL CHEMICAL KINETICS OF UNIMOLECULAR PROCESSES

12.3.1 Theoretical Investigation of Vibrational Energy Transfer in Polyatomic Molecules

D. W. Noid

J. D. McDonald

M. L. Koszykowski

R. A. Marcus

Many trajectory studies have been made of the behavior of dynamical systems whose Hamiltonians are similar to those of molecules. The astronomical literature in particular is replete with studies of anharmonically coupled oscillators. Such studies, in accordance with the fundamental theory of Kolmogorov, Arnold, and Moser for nonlinear systems, illustrate that at low energies the motion of the system is quasi-periodic (i.e., multiply periodic); any coordinate q , depends on time only via "angle" variables w . It depends on w in a periodic manner with unit period:

$$q = q(w_1, \dots, w_n, J_1, \dots, J_n), \quad w_i = \nu_i t + \psi_i,$$

where ψ is the phase angle at zero time. The number of nonzero frequencies ν is equal to the number of

degrees of freedom n in the nondegenerate case and less than that number in the degenerate case. (In the degenerate case, some of the w 's are therefore constants of the motion.) Canonically conjugate to these angle variables w are action variables J . They are constants of the motion and, for vibrational problems, serve in effect as generalizations of the usual amplitudes for harmonic oscillator (normal mode) systems. This generalization for anharmonic systems is also applicable to systems that do not permit separation of variables.

Trajectory studies reveal that at higher energies the dynamical system behaves in an ergodic-like manner, yielding a shotgun pattern of the surface of section instead of a regular pattern. There is, as yet, no rigorous theory for treating systems in the ergodic or nearly ergodic regime, unlike the quasi-periodic regime at low energies (and low couplings), but action variables J can no longer be rigorously defined (or evaluated). The onset of ergodicity has been treated in Chirikov's theory of overlapping resonances as well as by other methods.

To get the classical spectrum (and so the approximate quantum) directly from the trajectory, one merely calculates from the trajectory the appropriate

Fig. 12.2. Spectra of OCS, which is quasi-periodic.

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Fig. 12.3. Spectra of OCS, which exhibits stochastic behavior.

autocorrelation function and then computes the Fourier transform. The quasi-periodic regime of such a spectrum consists of sharp lines, peaked at the ν 's, at the overtones, and at the combination frequencies. The sharpness of the spectrum has nothing to do with any approximation in the separation of variables and should apply equally to the spectrum of any molecule that is in the quasi-periodic regime.

In the ergodic regime there are no well-defined variables J and w , and classically one would expect the sharpness of the spectrum to decrease. It was interesting, therefore, to compute the spectrum of a high-energy molecule obtained from a classical mechanical trajectory. The spectrum obtained indicated a broadening of the formerly sharp lines and the appearance of an underlying continuum. Comparisons with a quantum mechanically calculated spectrum of a high-energy molecule are in progress.

Recently we applied this technique to the vibrational Hamiltonian of molecules. A quasi-periodic spectrum for the ground vibrational state of OCS is shown in Fig. 12.2. An excited-state spectrum of OCS

is shown in Fig. 12.3. We plan to calculate the width of this spectrum and to study other molecules.

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12.3.2 Quantum Mechanical and Semiclassical Study of Infrared Multiphoton Dissociation

D. W. Noid¹ M. I. Koszykowski²
J. R. Stine³

There has been much interest recently in the interaction of intense electromagnetic radiation with chemical systems. In particular, the discovery that polyatomic systems may be dissociated with intense laser radiation has required an examination of the classical and semiclassical methods that describe intermolecular energy transfer. Indeed, it has been

Fig. 12.4. Internal energy of a single molecule of CD_3Cl in a laser field.

successfully demonstrated that semiclassical methods may be used to calculate spectra and eigenenergies that are in good agreement with quantum mechanical methods, for systems containing many degrees of freedom.

The addition of the laser field can change the character of the motion from quasi-periodic to stochastic. A classical trajectory calculation of the energy in the molecule CD_3Cl in a laser field is shown in Fig. 12.4. Initially the molecule undergoes stimulated adsorption and emission as shown by the "beats." After a period of time, the beats disappear, and the motion becomes stochastic. Currently, we are looking at the effect of two laser terms on model

systems. The comparison of the semiclassical calculation with a full quantum calculation is in progress.

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12.3.3 Development of Semiclassical Methods for the Calculation of Bound-State Eigenvalues

D. W. Noid M. L. Koszykowski
R. A. Marcus

The calculation of bound-state properties using semiclassical concepts has been of interest for many years. This problem has a well-known WKB solution for systems permitting separation of variables. Recently several methods of calculating eigenvalues for nonseparable systems that are quasi-periodic have been presented. One of the most successful methods¹ involves the use of classical trajectories for the calculation of the path integrals used to quantize the system and hence find the semiclassical eigenvalues.

An example of a trajectory where the coordinates q are two in number, x and y , and where the frequencies ν are rather different is given in Fig. 12.5. The method used to obtain the J was to first obtain a Poincaré surface of section from the trajectory.

Fig. 12.5. A typical quasi-periodic trajectory for a Hamiltonian with two degrees of freedom.

Fig. 12.6 A Poincaré surface of section for trajectories such as those in Fig. 12.5.

Denoting the momenta that are conjugate to x and y by p_x and p_y , one notes the values of p_x and x each time the trajectory crosses the $y = 0$ plane with p_y positive. The plot of this p_x vs x is in Fig. 12.6, yield-

the value of J for this degree of freedom J_x by calculating the area under the curve

$$J_x = \oint p_x dx. \quad (1)$$

Similarly,

$$J_y = \oint p_y dy. \quad (2)$$

Once the values of J_x and J_y are found from a set of three trajectories, the value of the eigenvalues I_n can be found by interpolation of J_x and J_y for which

$$J_x = 2\pi(n_x + 1/2), \quad (3)$$

$$J_y = 2\pi(n_y + 1/2). \quad (4)$$

Recently we have been able to extend the applicability of this method to systems that have Fermi resonance and systems with more degrees of freedom. The system that exhibits Fermi resonance has frequencies of the unperturbed problem in a ratio of 1:2 and also a perturbation term that couples the two degrees of freedom resonantly. A trajectory of this type is shown in Fig. 12.7. Using now a parabolic

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Fig. 12.7 A Fermi resonance-type trajectory

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Fig. 12.8. The path integrals and surface of section for a Hamiltonian with three degrees of freedom.

surface of section instead of the Poincaré surface of section, we were able to calculate the semiclassical eigenvalues. It was found that the agreement with quantum mechanical calculation of the eigenvalues

was usually within 1 part in 500. This system exhibits stochastic-type motion when the energy exceeds a critical energy. As of yet no semiclassical method has been developed for trajectories of this type.

A method for calculating eigenvalues for systems with more degrees of freedom has also been developed. This method is an extension of the Poincaré surface of section method. However, now we use a line surface of section in $2N$ phase space. This surface of section with the appropriate path integrals is shown in Fig. 12.8. A surface of section calculated this way for the Hamiltonian

$$H = \frac{1}{2}(P_x^2 + P_y^2 + P_z^2 + \omega_x^2 X^2 + \omega_y^2 Y^2 + \omega_z^2 Z^2) + \lambda(xy - \eta x^2) + \lambda(yz - \eta y^2) \quad (5)$$

is shown in Fig. 12.9. Upon calculation of the three path integrals

$$J_x = \oint p_x dx,$$

$$J_y = \oint p_y dy,$$

$$J_z = \oint p_z dz.$$

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Fig. 12.9. A surface of section for the Hamiltonian III.1.

the values of J 's can be interpolated for $J = 2\pi(n + 1/2)$, and the energy eigenvalue can be obtained. The agreement with the quantum mechanical eigenvalue is excellent. We hope in the future to begin applying this method to molecular Hamiltonians of interest.

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13. Electrochemistry

13.1 ELECTROCHEMICAL BEHAVIOR OF TITANIUM IN ACIDIC CHLORIDE SOLUTIONS

L. J. Kelly

The results of a study of the electrochemical behavior of titanium in deoxygenated acidic chloride solutions are presented. The work complements an earlier study of the mechanisms of titanium dissolution in acidic sulfate solutions¹ and provides the basic electrochemical information required for understanding the notorious association of halide ions with localized corrosion phenomena.

Steady-state anodic polarization curves for titanium in the active state and in the active-passive transition region have been determined for chloride solutions ($[Cl^-] = 1\text{ }M$) having pH values ranging from 0.08 to 2.00 and are shown in Fig. 13.1. The metal spontaneously activates in these solutions (pH = 2.3) and exhibits an active-state corrosion potential (*volts vs. SCE*) given by the expression $E = 0.665 - 0.024\text{ pH}$. At constant pH, as the potential *E* of the metal is made increasingly positive relative to the corrosion potential, the anodic current density rises to a maximum and then decreases as the metal is transformed from the active to the passive (TiO_2 film) state. To obtain the current density i corresponding solely to the dissolution of the metal to form $Ti(III)$ ions in solution, each of the curves shown in Fig. 13.1 must be corrected for the hydrogen evolution reaction, that is, the current density i_H due to the hydrogen evolution reaction must be added to the observed current density i , as illustrated in Fig. 13.2 for pH = 1.0. The resultant partial anodic polarization curve $\log i$ vs. *E* then exhibits a maximum current density i_m that is greater than the observed maximum i and that occurs at a more negative potential (E_m) as compared with *E*. The higher the pH, the more significant the hydrogen evolution reaction correction becomes. In Fig. 13.3, it is observed that $\log i_m$ is a linear function of both E_m and pH; that is,

Fig. 13.1 Anodic polarization of titanium in 1 *M* chloride solutions ($T = 30.0^\circ\text{C}$)

$$d \log i_m / d \text{pH} = -1 \quad (1)$$

and

$$d \ln i_m / dE_m = -1 / 2RT \quad (2)$$

from which it follows (and was observed) that

$$dE_m / d \text{pH} = -C / (2.30RT) \quad (3)$$

The highly restrictive diagnostic relationships given by Eqs. (1-3) are identical to those observed for the

Fig. 13.2 Effect of hydrogen evolution reaction E_H on anodic polarization data, observed i_m , E_m and corrected $i_{m,0}$, $E_{m,0}$ values of current density maximum and corresponding potential for $\text{pH} = 1.0$

dissolution of titanium in acidic sulfate solutions and may be derived on the basis of the following mechanism

Among the requirements satisfied by the mechanism, are the following: the oxidation of the metal must occur in a sequence of single-electron transfer reactions; corresponding to each of the four valence states, a surface intermediate exists (indicated by subscript a), and only one proton or water molecule is involved in any single reaction. In addition, it is recognized that, in the pH region of interest, Ti(III) ions in solution exist as Ti^{3+} and its first hydrolysis product Ti(OH)^+ , whereas Ti(IV) exists only as $[\text{Ti(OH)}]^+$ (ref. 3). Coulometric weight-loss experiments demonstrated that, in the vicinity of E_m , only Ti(III) ions are formed in solution. According to the mechanism, the steady-state current density is given by

$$i = 3Fk_0 \exp(H/2RT) \quad (14)$$

Fig. 13.3 Variation of i_m with pH (curve II) and with E_m (curve I).

where θ represents the fraction of surface covered by Ti(OH)_3 and θ_{∞} is the surface coverage at the conventional saturation. It can also be shown that in the case of I_{corr} the governing equation

$$I_{\text{corr}} = I_0 [1 + K_1] \exp(3H/2.819) \quad (15)$$

If θ from Eq. (15) is substituted into Eq. (14), the diagnostic relationships given by Eqs. (1) to (3) are satisfied.

Titanium dissolution has been shown to follow the same general mechanism in either acidic chloride or acidic sulfate solutions. However, for any specified pH, the dissolution rate in sulfate media is greater than that in chloride solutions in both the active and passive states, that is, for any value of potential. Nevertheless it is the sulfate ion that promotes severe localized (pitting, crevice corrosion, etc.) corrosion. The explanation for this seemingly contradictory state of affairs is that, in addition to the reactions discussed above, Ti(III) ions in solution are oxidized to form Ti(IV) ions in solution at a passive titanium surface, and Ti(IV) ions in solution are reduced to Ti(III) ions in solution at an active titanium surface. These two reactions have been shown to play a critical role in determining the susceptibility to localized corrosion, with susceptibility increasing as the rate constants for the two reactions decrease. The values of the rate constants for the oxidation and reduction reactions were found to be 10 and 35 times greater, respectively, in sulfate solutions than in chloride solutions.

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13.2 CORROSIVITY OF CARBON STEEL IN CONCENTRATED CHLORIDE SOLUTION

E. A. Poser, V. A. Palko

In spite of the ubiquity of chloride-related corrosion problems with ferrous materials, relatively few investigators have carried out electrochemical kinetic measurements on active-state corrosion, either in pure chloride solutions or in solutions of other electrolytes with added chloride ions. The

purpose of these studies with wrought steels is to provide DOE-Dywidag-Geothermal Energy with a basic understanding of corrosion processes, in particular, as they pertain to carbon steel in synthetic brines that simulate the aggressive concentrated salt solutions encountered during conversion of the heat content of geothermal brines into electrical energy.

Because of the lack of an adequate data base and because it is generally impossible to extrapolate corrosion behavior from dilute to concentrated solutions with any confidence, we investigated the influence of pH (from neutral to moderately acidic solutions) and temperature (up to at least 200°C) on the corrosion behavior of carbon steel in deaerated concentrated chloride solution (4 M NaCl).

Electrochemical measurements were carried out in a refreshed, stirred titanium autoclave system. Details of the measurements and results are contained in a series of progress reports, and a paper on the subject has been accepted for publication in *Corrosion*. Corrosion rates were estimated from polarization curves both by extrapolation of anodic and cathodic Tafel lines back to the open-circuit potential and by measurement of the polarization resistance, which is inversely proportional to the corrosion rate. The rate of spontaneous corrosion of type A212B carbon steel (analysis: 0.358% C, 0.62% Mn, 0.18% Si, 0.033% S, and 0.012% P) in deaerated 4 M NaCl was determined at pH = 2, 3, 4, 5, and 7 (measured at room temperature) and at temperatures from 25 to 200°C. A summary of the experimental results is shown in Fig. 13.4. These results show clearly a change in the apparent activation energy of the overall corrosion process as a function of pH. Thus in the neutral region (pH = 5 and 7), the corrosion rate depends only on the temperature, not on pH. In this region the cathodic process consists mainly of hydrogen evolution from the solvent water, and the rate of this process is independent of pH. In this same (neutral) pH region the rate of the anodic process is also independent of pH. The apparent activation energy of the overall corrosion process in the neutral pH region is about 7.8 kcal/mol (33 kJ/mol). On the other hand, in moderately acidic solutions (pH = 3 and 2), the cathodic process consists principally of hydrogen evolution from hydrogen ions, and the rate of the cathodic process (under these stirring conditions) is controlled by convective diffusion of hydrogen ions to the metal surface throughout the temperature range 25 to 200°C. In such acidic media, the apparent activation energy of the overall corrosion reaction is

Fig. 13.4. Corrosion rate of A212B carbon steel in deaerated 4 M NaCl as a function of pH and temperature.

about 4.2 kcal/mol (18 kJ/mol), a value that is consistent with rate-determining mass transport of hydrogen ions to the metal surface. At pH = 4, a transition is observed between the two values of apparent activation energy. Up to about 75°C at this pH, the corrosion rate is controlled by the rate of convective diffusion of hydrogen ions to the electrode surface; at higher temperatures, the rate is independent of stirring, and the cathodic process is mainly reduction of the solvent water to form molecular hydrogen. These results agree qualitatively with work of other investigators in other iron corrosion systems at lower temperatures on the nature of rate control in acidic media and provide a data base for the corrosion behavior to be expected for carbon steel in strong brines such as those encountered under certain geothermal conditions.

The anodic and cathodic Tafel slopes needed for estimation of corrosion rates from values of polarization resistance were determined from the measured polarization curves. In the neutral region (pH = 5 and 7), the cathodic Tafel slope was close to $(2.3)2RT/F$ at all temperatures. On the other hand, a limiting current corresponding to the maximum rate of convective diffusion of hydrogen ions to the electrode surface under these stirring conditions was

observed for the cathodic process in acidic solutions. The Tafel slope of the anodic process was equivalent to $(2.3)RT/F$ at 25 and 50°C, but at higher temperatures it was equivalent to $(2.3)2RT/3F$, a value consistent with steady-state Tafel slopes observed in some other systems.

The data shown in Fig. 13.4 may be described by a simple numerical correlation, composed additively of pH-independent and pH-dependent terms. This expression is

$$i_{\text{corr}} = 1.90 \times 10^{-6} \exp(-3.98 \times 10^{-4} T) + 4.19 \times 10^{-6} (10^{-\text{pH}}) \exp(-2.10 \times 10^{-4} T) \quad (1)$$

Here, i_{corr} is the corrosion rate in mill per year (mpy), T is absolute temperature (K), and the numerical constants were computed from the lines drawn through the data in Fig. 13.4 at pH = 2 and at pH = 7 (or 5). [Corrosion rates computed from Eq. (1) may be converted to units of millimeters per year by use of the relation 1 mpy = 2.54×10^{-3} mm/year.] The experimental data are replotted in Fig. 13.5 as corrosion rate vs pH for several temperatures; the solid lines were calculated by use of Eq. (1). Considering the experimental errors that typically accompany measurements of this type, the data are described reasonably well by the two-term expression of Eq. (1) over the entire temperature and pH ranges. The pH-independent region seems to be more extensive at elevated temperatures; it extends nearly to (room-temperature) pH = 3 at 200°C. This behavior reflects the higher apparent activation energy of the pH-independent corrosion process compared with the pH-dependent process.

Stirring conditions that are different from those of our experiments can be expected to shift the lines in Fig. 13.4, corresponding to corrosion in acidic solutions upward or downward. Correspondingly, the numerical multiplier in the second (pH-dependent) term in the correlation of Eq. (1) can be expected to vary with the flow conditions. Conditions certainly arise for the corrosion of iron or carbon steel, in some systems, in which the hydrogen-evolution reaction is not under mass-transport control in acidic solutions, and in these cases a correlation different from that of Eq. (1) would have to be developed from the appropriate rate relations. But for corrosion systems like the one examined here, involving rate-controlling mass transport of hydrogen ions in acidic solutions, it should be possible to use the predictions of boundary-layer theory or various engineering correlations to predict the

Fig. 13.5 Variation with pH of the corrosion rate of A212B carbon steel in 4 M NaCl as a function of temperature.

maximum rate of convective diffusion for various configurations and types of flow (e.g. laminar or turbulent flow in pipes) to extend the correlation of Eq. (1) to systems of practical interest.

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13.3 METHOD FOR ANALYSIS OF POLARIZATION CURVES

F. A. Posey

Previous studies have shown the need for a convenient method for analysis of polarization curves of corrosion systems using only data obtained near the corrosion potential (polarization less than about $2RT/F$). For a large number of (but by no means all) electrochemical systems, the net or measurable current density may be described as the difference between anodic and cathodic partial processes, each of which is exponentially dependent upon the electrode potential. For these cases, one may write

$$i = i_0 [\exp(\alpha_a F \eta / RT) - \exp(-\alpha_c F \eta / RT)] \quad (1)$$

where i is the net current density (A/m²), i_0 is the corrosion current density (A/m²) at the corrosion potential (or the exchange current density at the reversible potential in the case of a reversible electrochemical system), η is the polarization (V), RT/F is the thermal volt equivalent (V), and α_a and α_c are the (dimensionless) transfer coefficients of the anodic and cathodic partial processes. In general, i_0 , α_a , and α_c are unknown and must be determined from the experimental data, which consist of corresponding values of i and η , obtained by use of steady-state (potentiostatic or galvanostatic) or non-steady-state (potentiodynamic, etc.) techniques.

The method of polarization resistance has been used extensively to estimate and monitor corrosion rates in all kinds of solutions, and a number of recent reviews on both theory and methodology are available. Differentiation of Eq. (1) leads to

$$R = \frac{d\eta}{di} = \frac{RT}{F(\alpha_a + \alpha_c) i} \quad (2)$$

where R , the polarization resistance (V·m²/A), is the slope of the polarization curve evaluated at the corrosion potential. Use of Eq. (2) for precise estimation of the corrosion rate i requires a knowledge of both α_a and α_c , which are usually determined from the late-slope regions of the polarization curve described by Eq. (1); that is, from the regions where $\eta \gg RT/F$ and where $\eta \ll -RT/F$. However, this procedure has a number of disadvantages, and some alternative approaches to the deter-

mination of α_a , α_c , and i_c from experimental data obtained near the corrosion potential have been developed during the last decade. These methods, however, also have certain disadvantages, such as restrictions on the number of data points that may be used in the computation or the necessity for use of a digital computer to establish a best fit of the experimental data. The new method allows use of as many data points as desired and may be carried out by using simple graphical procedures and a hand calculator, thereby ensuring easy application to treatment of corrosion data obtained in the field as well as in the laboratory.

It can be shown that, if i_a is an anodic current density corresponding to $\eta = +1/\eta$, i_c is the corresponding cathodic current density for $\eta = -1/\eta$, and if $y = (nF/RT)$ is defined as a dimensionless potential variable, the difference between the transfer coefficients may be determined from the relation

$$(\alpha_a - \alpha_c) = d[\ln(i_a/i_c)]/dy \quad (3)$$

Thus the difference between the transfer coefficients is determined simply by measuring the slope of a plot of the natural logarithm of the current density ratio against the dimensionless potential variable y . Furthermore, the mean of the anodic and cathodic current densities is given by

$$x = [i_a(-1)]^{1/2} = 2i_c \sinh[(\alpha_a + \alpha_c)y/2] \quad (4)$$

A plotting function exists that can be used to determine both of the quantities $(\alpha_a + \alpha_c)$ and i_c from values of x and y ; this is given by

$$x/y = L + S + G(\alpha_a + \alpha_c, y) \cdot y^2 \quad (5)$$

where $L = i_c(\alpha_a + \alpha_c)$, $S = i_c(\alpha_a + \alpha_c)^{-1/2}$, and the function G is defined by

$$G(\alpha_a + \alpha_c, y) = \sum_{n=0}^{\infty} \{3! [(2n+3)!] / [(\alpha_a + \alpha_c)y/2]^{2n}\} \quad (6)$$

For all values of $(\alpha_a + \alpha_c)$ that are likely to be encountered in practice, the series in Eq. (6) converges rapidly, and G is close to unity and varies slowly with increasing values of y . For example, with $\alpha_a + \alpha_c = 1$, $G = 1.0126$ at $y = 1$ (corresponding to a polarization of 25.6 mV at 25°C), while $G = 1.0512$ at $y = 2$. Consequently, the intercept (L) and the limiting

slope (S) of a plot of x/y vs y may be used to calculate the corrosion rate and the quantity $\alpha_a + \alpha_c$ according to the relations

$$(\alpha_a + \alpha_c) = [(4!)S/1] \quad (7)$$

$$i_c = [L/(4!)S] \quad (8)$$

Appropriate combinations of Eqs. (3) and (7) then lead to individual values of α_a and α_c .

The method promises to be useful in the investigation of effects of pH, temperature, and other variables on the kinetics of individual partial processes important in corrosion, with minimal disturbance of the corrosion system by the measurement procedure. Details of the theory and applications will be presented in a paper to be published in *Corrosion*.

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13.4 EFFECT OF REDOX COUPLES ON THE KINETICS OF TITANIUM DISSOLUTION

A. L. Bacarella

Titanium corrodes spontaneously in the active state when exposed to deaerated 0.5 M H₂SO₄ at 30°C. If the electrode potential of titanium is made increasingly positive relative to the corrosion potential -0.735 V vs S.C.F., the anodic current density increases to a maximum $i_m = 5.4 \times 10^{-4}$ A/cm² at the critical potential $E_m = -0.530$ V vs S.C.F. then decreases as the electrode potential approaches the passive region. In this case the current required to maintain the desired potential is derived from the power supply of an electronic potentiostat. Passivation may also be attained without an external power supply if the total cathodic current density of reducible substances can be made to exceed the critical anodic current density i_m . For example, admission of air (O₂) to the solution can provide the

additional cathodic current density necessary to passivate titanium. Similarly, the addition of reducible ions like Fe(III) , Ti(IV) , etc., in sufficient concentration can also increase the total cathodic current density so as to exceed i_c . When such ions or any other reducible species are added in amounts insufficient to passivate but sufficient to provide a significant cathodic current density in the potential region near the critical potential, it is observed that E_m is shifted to more positive (anodic) potentials and that the critical current density i_c is apparently decreased.

In this work, the effect of chromium dissolution products (predominantly Cr(II) , as noted below, with possibly some Cr(III)) on the dissolution kinetics of titanium in H_2 -saturated $0.5 \text{ M H}_2\text{SO}_4$ at 30°C was studied. These measurements are part of an effort to assess the influence of redox couples on active-state dissolution of titanium, with special emphasis on systems that can be expected to affect the course of localized corrosion of titanium. Pure chromium was first exposed to the H_2 -saturated $0.5 \text{ M H}_2\text{SO}_4$ at 30°C for 24 h. Corrosion of the chromium produced a solution containing $3.68 \times 10^{-2} \text{ M}$ total chromium as determined from the weight loss of the electrode in the known volume of solution and later verified by atomic absorption spectrophotometry. Steady-state polarization curves of titanium with and without chromium dissolution products present are shown in Fig. 13.6. The critical current density i_c was decreased about 30% from $5.4 \times 10^{-4} \text{ A cm}^{-2}$ to $3.8 \times 10^{-4} \text{ A cm}^{-2}$, and the critical potential E_m was shifted from -0.530 V to -0.570 V vs S.C.E. The shift of E_m to more cathodic values is opposite to the effect observed when Ti(IV) ions (or other reducible substances) are added. The possibility exists that the observed inhibition of titanium dissolution by corrosion products of chromium involves the adsorption of (probably) chromic species on the electrode surface. It is evident from Fig. 13.6 that the effect is potential dependent. As the electrode potential becomes more positive, the difference between the steady-state current densities with and without chromium present becomes larger, increasingly so at potentials anodic to E_m . Presumably, the adsorbed chromium species compete for surface coverage with adsorbed titanium species that are intermediates in the mechanism of titanium dissolution, and the effect of electrode potential may be caused by oxidation of Cr(II) to Cr(III) at the interface accompanied by adsorption on the surface.

A number of polarization measurements were also carried out on pure chromium in an attempt to

Fig. 13.6. The effect of chromium corrosion products on the steady-state anodic dissolution of titanium.

develop appropriate background data for studies on the titanium-chromium system. Some steady-state polarization curves obtained on pure chromium in H_2 -saturated $0.5 \text{ M H}_2\text{SO}_4$ at 10.7°C are shown in Fig. 13.7. Here, the critical potential was found to be $E_m = -0.569 \text{ V}$ vs S.C.E. after correcting the net anodic currents for a contribution from the hydrogen-evolution reaction. At 30°C in the same solution, the cathodic evolution of hydrogen was negligible at the critical potential, and $E_m = -0.570 \text{ V}$, essentially unchanged from the value observed at 10.7°C . Coulometric weight-loss experiments were performed at constant electrode potential in this system to determine the valence of the anodic dissolution product at a potential near the critical potential E_m and at a potential in the region of the active to passive transition. The results of these measurements, carried out at electrode potentials 5 mV more negative than E_m and 45 mV more positive than E_m , showed that the primary product of chromium dissolution is Cr(II) . Experiments are continuing on the origin of the inhibitive effect of chromium corrosion products on the anodic dissolution of titanium and on the consequences of this effect for inhibition of localized corrosion.

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Fig. 13.7. The steady-state polarization behavior of chromium in H_2 -saturated $0.5 M H_2SO_4$ at $10.7^\circ C$.

14. Inorganic Chemistry of Hydrogen Cycles

C. E. Bamberger

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The generation of hydrogen from water by means of thermochemical cycles is one of the approaches being considered for producing large amounts of hydrogen at competitive prices. This approach holds the promise of using thermal energy very efficiently. To utilize thermal energy efficiently, the chemical reactions that comprise a cycle must be simple, use relatively inexpensive reagents, and must not lead to difficult separation processes. The work described here pertains to the search for and demonstration of such chemical reactions. We have continued with our experimental approach to find suitable reactions because it yields unequivocal results. The calculational approach used by others is limited by the availability and accuracy of published thermochemical data.

1. Thermal Decomposition of Metallic Oxides

In continuation of work described previously,¹ the thermal decomposition of selected metal oxides (CuO , Co_3O_4 , and Fe_3O_4) was examined. We found that decomposition occurred at lower temperatures when the oxides were heated in a flowing stream of helium and argon rather than in argon alone. Although the effect of the stream is not fully understood, it is clear that the rate of oxygen evolution is enhanced at lower temperatures. In general, rates of evolution of oxygen are higher in helium than in argon, and for Fe_3O_4 lower than in the absence of flow. Evolution at the lower temperature has the additional advantage in the case of Fe_3O_4 that the Fe_2O_3 produced is in a finer state and consequently does not form a hard mixture with CuO as in the case at higher temperatures.

II. Two New Copper(II) Hydroxocarbonates

In the course of this research, experiments were performed which involved the equilibration, at room

temperature of copper(II) oxide with aqueous solutions of iodine and KI. It was deduced from chemical and x-ray diffraction analyses that two new hydroxiodides of Cu(II) had been synthesized. One of the compounds with the ratio Cu:I = 4, represented by the formula $\text{Cu}_4(\text{OH})_4\text{I}(2.5 \text{ H}_2\text{O})$, has an fcc structure with $a = 9.43 \text{ \AA}$. The other compound with the ratio Cu:I = 2.5, represented by $\text{Cu}(\text{OH})_2(\text{O})_{0.5}(\text{I})_{0.5}(0.74\text{H}_2\text{O})$, appears to have a hexagonal (or pseudohexagonal) structure with $a = 2.78$ and $c = 6.61 \text{ \AA}$.

III. The Enthalpy of Formation of Potassium Chromate(V), K_2CrO_5 .

In collaboration with researchers at the Department of Chemistry, the University of Lethbridge, Alberta, Canada, the enthalpy of formation of K_2CrO_4 was determined by solution calorimetry to be $370 \pm 2 \text{ kcal/mol}$.⁶

IV. Cycle Fe/N(Br,K)

The reactions of the following cycle were tested experimentally:

It is not clear whether the above cycle is a true catalytic cycle. The temperature of the reaction is 1000°C, which is too high for the use of liquid ammonia. The reaction is not reversible, and the products are not easily separated from the reaction mixture. The reaction is also very slow, and the catalyst is not stable. Because of the above drawbacks, work on this cycle was halted.

V. Cycle Ce-Ce(II,Na)

We have recently identified this cycle and are currently studying it further. Its main reactions are

where $M = \text{Na or K}$.

The solid products of reaction (5) appear to be new, and their structures have not been fully identified, but we have established that $x = 1.5$ or 2 and $\alpha = 0.7-0.9$. One interesting aspect of this reaction is that it can be performed in the temperature range 1100-1350°C, whereas the direct thermal de-

composition of CeO is at a temperature in excess of 2000°C. Additionally, we have found that the presence of some $\text{Na}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ promotes reactions (5) at lower temperatures (900-1000°C). Currently it appears that the $\text{Na}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ is only as a flux.

The replacement in reaction (5) of Ce(IV) by Fe(III) , a cheaper reagent, was investigated. Although oxygen was evolved, only about 10-25% of that expected was obtained. This was caused by the formation of solid solutions of compounds of the type

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15. Chemistry in Support of the Nuclear Fuel Cycle

15.1 ADVANCED FUEL RECYCLE AND ALTERNATE FUEL CYCLE TECHNOLOGIES PROGRAMS

L. M. Auer F. J. Smith
M. R. Bennett G. M. Brown

Fuel cycle studies concerned with the development of aqueous processes for both LWR and advanced reactor fuels are not reported here, in compliance with regulations stipulating that such information must be distributed only through limited, controlled lists. All work with breeder fuels has been included under the Advanced Fuel Recycle Program. The results of these studies are reported in topical reports and in a series of quarterly progress reports, the most recent of which is the *Advanced Fuel Recycle Program Progress Report for the Period July 1 to September 30, 1978*, ORNL TM-6557. These reports are distributed under category UC-79c Liquid-Metal Fast Breeder Reactors.

The associated efforts in LWR fuel reprocessing, done under the Alternate Fuel Cycle Technologies Program, have been reported in a separate series of quarterly progress reports with a similar controlled distribution. The most recent is the *Alternate Fuel Cycle Technologies Thorium Fuel Cycle Technology Programs Quarterly Report for the Period July 1*

to September 30, 1978, ORNL TM-6559. Task areas in the two programs are closely related; in some cases, the task areas are partially funded from both programs. Major emphasis has been on the examination of some of the schemes that enhance the nonproliferation characteristics of the fuel cycles.

15.2 PYROCHEMICAL AND DRY PROCESSING METHODS (PDPM) PROGRAM

H. E. McDuffie D. H. Smith
E. C. Douglas

The PDPM program was established at the beginning of FY 1978 as an expansion of the National Fuel Cycle Program for reprocessing fuel by methods that will reduce the risk of proliferation of nuclear weapons. Argonne National Laboratory was the lead laboratory for the PDPM program, with various work packages done at other DOE laboratories and by industrial contractors. As the program title implies, the main thrust of the PDPM program is on nonaqueous (pyrochemical) processes. Work done under the ORNL work package will be reported in a forthcoming PDPM program annual report and in topical reports. These reports will have limited, controlled distribution.

16. Thermal Energy Storage: Physical Chemistry of Phase-Change Materials

S. Cantor D. Heatherly

This research program¹ has been concerned with the study of compounds and mixtures that store and discharge energy isothermally on melting and freezing and are suitable for applications (residential, commercial, industrial, and agricultural) up to 250°C. Two areas were emphasized: (1) study of the factors that affect the performance of incongruently melting salt hydrates (especially $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) as latent-heat storage media and (2) identification and evaluation of storage materials that melt in the range, 90–250°C.

As noted previously,¹ the differential scanning calorimeter (DSC) is an efficient and versatile tool for investigating thermal behavior of storage media. For incongruently melting hydrates, the DSC measured the differences between ΔH of fusion and ΔH of solidification and recorded how these enthalpies change upon thermal cycling. In evaluating organic materials melting between 90 and 250°C, DSC measurements of time- and cycle-dependent changes in ΔH of fusion were used to detect thermal decomposition. Although exothermic measurements also provide information about supercooling, the shallow-pan configuration of DSC samples seems to increase the extent of supercooling; therefore, supercooling was also studied by temperature-time plots on more massive samples.

16.1 SALT HYDRATES

16.1.1 $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ (Glauber's Salt)

A preliminary DSC investigation² had shown that the ΔH of solidification was considerably less than the ΔH of (peritectic) fusion initially measured. In this study, three types of samples were measured: $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ alone; $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ with borax, 2–9 wt % (borax, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, structurally similar to Glauber's salt, seeds the latter from supersaturated solutions); and $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ with 4 wt % borax and additional anhydrous Na_2SO_4 . The third type of sample was studied to determine if additional Na_2SO_4 would promote equilibrium (peritectic) solidification of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$.

A summary of experimental results is as follows:

- (1) Enthalpy release in all cases is about one-half the enthalpy absorbed on first melting.
- (2) Continued cooling to temperatures less than –15°C led to the release, with supercooling, of

additional energy, often as much as 15 cal/g; immediate reheating showed that this transition occurs just below –1°C, corresponding to the eutectic melting temperature for a mixture of ice and Glauber's salt (and, where applicable, borax).

- (3) After the first thermal cycle, at least 3 d at room temperature was necessary to recover the full storage capacity of the 4–10-mg samples of Glauber's salt.
- (4) Anhydrous Na_2SO_4 added to Glauber's salt did not alter the pattern of enthalpy absorption and release.
- (5) Borax, by greatly decreasing the extent of supercooling, seemed to prevent formation of $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$; the heptahydrate, a metastable phase melting incongruently at 24.3°C, was detected only in samples without borax.
- (6) Storage and discharge of energy at or near the phase transition temperature (32°C) remained essentially constant at 30 cal/g over the first few (daily) thermal cycles between 20 and 36°C;

more frequent continuous cycling, up to 400 times, decreased energy storage and discharge of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ to a level value of 26-27 cal/g.

The observed pattern of heat release suggests that: (1) on cooling, only the sodium sulfate in solution is readily converted back to Glauber's salt and (2) solid sodium sulfate, produced by peritectic decomposition on heating or added to the sample, reacts slowly. The apparent sluggish reaction has been attributed¹ to an encapsulating layer of Glauber's salt, which acts to limit reaction of Na_2SO_4 with solution to the slow process of solid-state diffusion. An order-of-magnitude diffusion coefficient can be obtained from the DSC observations, estimating that the radius (or half-thickness) of the Na_2SO_4 crystals is roughly 0.01 cm (probably a high estimate) and given that 3 d were necessary to convert all of the anhydrous Na_2SO_4 to Glauber's salt, we obtain a diffusion coefficient from the expression,⁴ $D = (r^2/4t) = (0.01)^2/(4 \cdot 3 \cdot 86,400) \sim 10^{-10} \text{ cm}^2/\text{s}$. Diffusion coefficients in aqueous liquids are about $10^{-5} \text{ cm}^2/\text{s}$; for solids, they are orders of magnitude smaller, which appears to be the case in this instance.

The hypothesis of a Glauber's salt layer, encapsulating the anhydrous Na_2SO_4 , fails to elucidate why the layer doesn't seed Glauber's salt from solution. A possible explanation for the nonseeding follows. When a thin layer of decahydrate forms on the anhydrous salt, the heat evolved, -19.5 kcal/mol for ΔH of hydration of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ (ref. 5), raises the temperature of the crystal surface and of the adjacent liquid. Two effects of local temperature increase would be expected: the hydrate layer tends to redissolve, and more anhydrate tends to precipitate out under the driving force of the retrograde solubility.⁶ Because the low diffusion constant suggests that only part of the decahydrate redissolves, one could imagine the formation of successive layers of hydrate and anhydrate that retard the growth of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ nuclei or crystallites.

The prime relevance of these measurements is that, in static latent-heat systems, only the energy released by crystallization of the aqueous phase (about one-half that of the ΔH of peritectic fusion) can be reliably retrieved from storage. Although this diminishes some of the potential of Glauber's salt, it is of such low cost that it remains

an attractive and viable candidate even for static systems. In systems with provision for stirring, full recovery of the stored energy may be possible if the mixture always contains some undecomposed Glauber's salt: when equilibrium can be maintained between solution and both solid phases (Na_2SO_4 and $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$), then the peritectic reaction can be reversed isothermally by extracting energy from the system.

16.1.2 $\text{Na}_2\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, and $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$

The results obtained for these five hydrates are summarized in Table 16.1. All except $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ melt incongruently. $\text{Na}_2\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$, whose phase equilibrium behavior is similar to that of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, exhibited similar thermal effects: its higher peritectic temperature seems to permit more rapid reaction between anhydrate and water than is the case for $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. For $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (the latter melts almost congruently), the magnitude of ΔH of crystallization equalled ΔH of fusion. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ exhibited marked disparity between ΔH of fusion and ΔH of crystallization. The results obtained for these hydrates as well as those obtained for Glauber's salt suggest that peritectic solidification of hydrates can be viewed as a dual process: crystallization from the liquid solution and reaction of the lower hydrate (or anhydrate) with the solution; where the ΔH of crystallization appears to be less in magnitude than the ΔH of fusion, the difference can be attributed to a slower reaction rate between the solution and the lower hydrate.

1. S. Cantor and D. F. Weatherly, *Chem. Div. Anna. Prog. Rep. No. 31*, 1977, ORNL-5297, pp. 141-42.

2. S. Cantor, *Thermochim. Acta* **26**, 38, 1978.

3. D. R. Biswas, *Sol. Energy* **19**, 99 (1977).

4. J. Crank, p. 11 in *The Mathematics of Diffusion*, Clarendon Press, Oxford, 1975.

5. E. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and J. Jaffe, *Selected Values of Chemical Thermodynamic Properties*, National Bureau of Standards Circular 500, U.S. Government Printing Office, Washington, D.C., 1952.

6. We are grateful to J. Braunstein for suggesting that we estimate a diffusion coefficient and also that we examine the consequences of retrograde solubility.

Table 16.1. Summary of melting and freezing behavior observed for five salt hydrates

Salt hydrates	Results
Sodium pyrophosphate decahydrate, $\text{Na}_2\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$; melts incongruently at 79.5°C to form the anhydrous salt; above 79.5°C, anhydrous salt exhibits retrograde solubility	ΔH of fusion = 59 cal/g; ΔH of crystallization, 26–35 cal/g occurred in the range 50–66°C; on cooling scan continued, another transition appears at -10.4°C, the temperature of eutectic melting of ice and $\text{Na}_2\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$; energy-storing capacity fully recovered by overnight annealing at 65°C; test-tube samples showed crystallization first occurring at 72–73°C
Magnesium nitrate hexahydrate, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; melts congruently at 89.9°C	ΔH of fusion = 36.2 cal/g, somewhat less than the compiled value (38.2 cal/g); ΔH of solid-state transformation = 2.9 cal/g at 73°C, experimentally; ΔH of crystallization = - ΔH of fusion
Magnesium chloride hexahydrate, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$; melts incongruently at 116.7°C to form tetrahydrate, which, at 120°C, dissolves in the liquid phase	ΔH of fusion = 39.9 cal/g in good agreement with compiled value (40.3 cal/g); ΔH of crystallization = - ΔH of fusion; two-step melting (and freezing) not detected in DSC; test-tube samples showed two-step melting; on cooling the melt, virtually no supercooling occurred
Copper sulfate pentahydrate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$; melts incongruently at 95.9°C to form the trihydrate	ΔH of fusion = 32 cal/g; ΔH of crystallization = 12–19 cal/g observed at 30–60°C; test-tube experiments showed crystallization from the melt first occurring at 87°C; volume fraction occupied by melt is relatively small; $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ poor for isothermal heat storage because of supercooling and because small liquid volume will not permit much heat transfer by free convection
Sodium tetraborate decahydrate (borax), $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$; melts incongruently to either the tetrahydrate (at 58.5°C) or to the metastable pentahydrate (at 60.8°C)	ΔH of fusion = 33 cal/g at 60.8°C; crystallization detected by DSC at -10 to -15°C; borax, heated in test-tube experiments to 70°C, showed little or no melting; on cooling to 35°C showed no break in temperature-time curve

^aE. D. Rossini, D. D. Wamman, W. H. Evans, S. Levine, and L. Jaffe, *Selected Values of Chemical Thermodynamic Properties*, National Bureau of Standards Circular 500, U. S. Government Printing Office, Washington, D.C., 1952.

16.2 HEAT-STORAGE MATERIALS THAT MELT BETWEEN 90 AND 250°C

A primary application for these materials is as heat sources for absorption air conditioning and for heat-engine-driven (Rankine cycle) air conditioning systems. For both systems temperatures as high as 204°C can be used, the exact temperature depending on the details of the operating system. A second general area of application involves process heat at intermediate temperatures for industrial (food, textiles, and chemicals) use. It has been reported¹ that some 30% of industrial process heat is utilized below 300°C. In particular, several big-volume chemicals are produced catalytically in which the catalyst functions most efficiently over a narrow temperature interval; a latent-heat storage source at the required temperature could provide process control as well as aid in conserving energy resources.

16.2.1 Organic Phase-Change Materials

Preliminary screening of organic compounds and the criteria used to select candidates were

noted in the last annual report.² Although a very large number of the compounds have melting points in the desired range, very few organic chemicals are sufficiently inexpensive, hazard-free, and chemically stable toward decomposition. Using \$1.00/kg (price of the bulk chemical) as the price limitation and the *Merck Index*³ to check melting points and decomposition behavior as well as hazardous or toxic attributes, three compounds (urea, adipic acid, and phthalic anhydride) and two polymers (polyethylene and polypropylene) were selected for further consideration. For these materials, a listing as well as a brief evaluation of some properties is presented in Table 16.2.

16.2.2 Urea-Containing Mixtures

The observation of fairly extensive decomposition at 133°C does not necessarily preclude using urea at lower temperature in a congruently melting mixture. The urea-biuret eutectic (composition, 30 wt % biuret, reportedly melting at 111°C) was the only urea mixture checked experimentally in this study. Biuret is the principal condensed-state de-

Table 16.2. Five organic heat-storage materials

Material	Evaluation
Urea, NH_2CONH_2 ; mp, 132.7°C ; $\Delta H_{\text{fusion}} = 57.5$ cal/g; ^a cost, ^b 15¢/kg	Pure compound not usable for heat storage at its melting point because of thermal decomposition; ^c supercooling also substantial
Adipic acid, $\text{HOOC}(\text{CH}_2)_4\text{COOH}$, mp, 152°C ; $\Delta H_{\text{fusion}} = 59.6$ cal/g; ^d cost, ^b 90¢/kg	Slight thermal decomposition detected when maintained at 156°C for 25 hr; continuous cycling in range, $135\text{--}160^\circ\text{C}$, did not appear to cause thermal decomposition; ^d does not supercool; if a somewhat lower melting eutectic mixture did not decompose and if a less expensive grade was otherwise acceptable, the adipic acid would be more attractive for latent-heat storage
Phthalic anhydride, $\text{C}_6\text{H}_4(\text{CO})_2\text{O}$, mp, 131°C ; $\Delta H_{\text{fusion}} = 36.3$ cal/g; ^e cost, ^b 60¢/kg	Thermally stable ^d and does not supercool; because of relatively high price and the need for containment, this compound is not as attractive as other materials ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, form-stable polyethylene) melting at about the same temperature
Polyethylene, $(\text{CH}_2)_n$, high-density form, mp, $125\text{--}135^\circ\text{C}$; $\Delta H_{\text{fusion}} = 45$ cal/g; ^d cost, ^b 70¢/kg	Very low containment costs possible for partially cross-linked form-stable product; the material acts as its own containment; silane cross-linked pellets performed well when cycled between 105 and 145°C ; less expensive cross-linking probably available by using radiation ^f
Polypropylene, $\left(\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{C} - \text{C} \\ \quad \\ \text{H} \quad \text{CH}_3 \end{array} \right)_n$, isotactic form; mp, $155\text{--}165^\circ\text{C}$; $\Delta H_{\text{fusion}} = 44$ cal/g; ^h cost, ^b 66¢/kg	Potentially useful if form-stable product can be made cheaply

^aF. W. Miller and H. R. Dittmar, *J. Am. Chem. Soc.*, **56**, 848 (1934).^bChem. Mark. Rep. (Aug. 28, 1978).^cS. Cantor, *Thermochim. Acta* **26**, 38 (1978).^dObtained by DSC in this study.^eE. Pilla and M. Nebuloni, *J. Therm. Anal.*, **3**, 343 (1973).^fR. A. Botham et al., *Form-Stable Crystalline Polymer Pellets for Thermal Energy Storage-High Density Polyethylene Intermediate Products*, ORNL/Sub-7398/4; MRC-DA-760 (Mar. 3, 1978).^gD. H. Kaible et al., *Polym. Eng. Sci.* **15**, 673-78 (1975).^hJ. A. Curran et al., pp. 568-77 in *Analytical Calorimetry*, vol. 3, R. S. Porter and J. F. Johnson, eds., Plenum, New York, 1974.

composition product from urea; the reaction for its formation can be written:

It was reasoned that urea in an encapsulated mixture when heated to about 115°C would produce a small, but sufficient, amount of ammonia to halt the reaction from proceeding further to the right. Samples of the eutectic mixture were thermally cycled (range, $65\text{--}115^\circ\text{C}$) as well as maintained in the molten state at 114°C for several hours. Our results showed that the melting point was 104°C ,

the mixture supercooled, and the extent of decomposition was slight. These results, although mildly encouraging for the utilization of urea, should be viewed cautiously. The testing of thermal decomposition was of a preliminary nature, and, if precautions had not been taken to keep the temperature from getting too high, more decomposition might have occurred; Rollet and Cohen-Adad⁷ reported that, at 130°C and above, urea-rich mixtures became richer in biuret.

Urea forms congruently melting mixtures with several inexpensive inorganic salts, including NaCl (112°C),⁸ KCl (115°C),⁹ KBr (109°C),⁹ and K_2CO_3 (102°C). Several nitrates also form urea eutectics, but these were not considered further because of possible violent reactions. For urea mixtures to function as a latent-heat storage media, it would

be necessary to: (1) maintain NH_3 cover gas to limit thermal decomposition, (2) find a reliable means of preventing supercooling, and (3) curtail the extent of hydrolysis, should there be in-leakage of water or moisture.

16.2.3 Inorganic Phase-Change Materials

The economic and technical screening criteria identified $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and congruently melting anhydrous nitrate mixtures.

$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, although melting incongruently at 116.7°C , is completely liquefied at 120°C . This hydrate appears very favorable for heat storage at 117 – 120°C ; it costs 15¢/kg , it freezes with little or no supercooling, and it does not appear to hydrolyze at or near its melting range. A possibly unsatisfactory characteristic could be a tendency to cause stress-corrosion cracking; if this did occur with inexpensive metals of construction, protective coatings such as fluorocarbons might be applied to solve the problem.

Several relatively inexpensive congruently melting nitrate mixtures can be constituted from the components: NaNO_3 , KNO_3 , and $\text{Ca}(\text{NO}_3)_2$ (see Table 16.3). Only NaNO_3 – KNO_3 , 46–54 wt %, was evaluated by DSC in this study. ΔH of fusion was found to be 24 cal/g ; the mixture did not appear to supercool; its cost is 19¢/kg estimated from prices for NaNO_3 (7¢/lb) and KNO_3 (10¢/lb).¹ At its melting point, it should have a low decomposition vapor pressure; although the vapor is predominantly oxygen, the mixture should be compatible with mild steel because of a protective oxide coating.² NaNO_3 – KNO_3 mixtures as well as most inorganic nitrates are strong oxidizing agents. Hence, interaction of nitrates with organics

Table 16.3. Melting points of congruently melting binary nitrate mixtures

Composition	Melting point	Reference ^a
NaNO_3 – KNO_3 50–50 mol %	222°C	Fig. 1047
NaNO_3 – $\text{Ca}(\text{NO}_3)_2$ 71–29 mol %	232°C	Fig. 1050
KNO_3 – $\text{Ca}(\text{NO}_3)_2$ 66–34 mol %	146°C	Fig. 1050

^aE. M. Levin, C. R. Robbins, and H. F. McMurdie, *Phase Diagram for Ceramists*, American Ceramic Society, Columbus, Ohio, 1964.

or other reducing agents would have to be prevented; it would be inordinately risky to use a nitrate in conjunction with an organic working fluid.

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- P. A. Agron,* W. B. Dress,¹ and T. A. Carlson,¹ "UV-Angular Resolved Photoemission Studies of Adsorbed Species on Single Crystals." American Chemical Society, 52d Colloid and Surface Science Symposium, University of Tennessee, Knoxville, June 12-14, 1978.
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*Denotes speaker

1. Physics Division

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7. Analytical Chemistry Division

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9. Solar Energy Research Institute, Golden, Colo.

10. Battelle Institute, Frankfurt, Germany

AQUEOUS SYSTEMS AND GEOSCIENCES

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16. Solid State Division.
17. Lawrence Livermore Laboratory, Livermore, Calif.
18. IURE, Universite Paris-Sud, Orsay, France.

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Chemical Technology Division

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- W. H. Baldwin and G. W. Neal, "Colloidal Properties of Sodium Carboxylates," Symposium on Chemistry of Oil Recovery, 175th American Chemical Society National Meeting, Anaheim, Calif., March 1978.
- A. L. Compere* and W. L. Griffith, "Advanced Methods for the Treatment of Domestic Sewage," Southeastern Association of State Highway and Transportation Officials, Nashville, Tenn., Oct. 22-26, 1978.
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THEORETICAL CHEMISTRY

- E. Johnson, "A Theory for Site-Site Pair Distribution Functions of Molecular Fluids," *J. Chem. Phys.* **67**, 3194 (1977).
- E. Johnson* and R. P. Haxelme,¹ "RISM Theory Distribution Functions for Lennard-Jones Interaction Site Fluids," 5th Annual Meeting of the NOBCCHE, Boston, Mass., Apr. 26-30, 1978.
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- R. A. Marcus,*² D. W. Noid, and M. L. Koszykowski,³ "Studies in Molecular Dynamics," International Conference on Stochastic Behavior in Classic and Quantum Hamiltonian Systems, Como, Italy, June 1977.
- D. W. Noid, "Calculation of Energy Eigenvalues by Quantization of Classical Trajectories," March 1978 Meeting of the American Physics Society, *Bull. Am. Phys. Soc.* **23**, 407 (1978).
- D. W. Noid, "Classical and Semiclassical Calculation of Infrared Multiphoton Dissociation," University of Tennessee, Knoxville, Oct. 3, 1978.
- D. W. Noid, "Semiclassical Calculation of Bound States in a Multidimensional System," William and Mary University, Williamsburg, Va., December 1977.
- D. W. Noid, "Studies in Molecular Dynamics," Los Alamos Scientific Laboratory, Los Alamos, N.Mex., Jan. 23, 1978.
- D. S. Noid, M. L. Koszykowski,³ and R. A. Marcus,*² "Spectra and Other Features of Anharmonically-Coupled Molecular Vibrations," 175th American Chemical Society National Meeting, Anaheim, Calif., March 1978.

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ELECTROCHEMISTRY

- J. Braunstein, A. L. Bacarella, B. M. Benjamin, L. L. Brown, and C. A. Girard,¹ "Proton Spin Relaxation and Mobility in Hydrated Melts," *J. Electrochem. Soc.* **124**, 844 (1977).
- E. J. Kelly, "Magnetic Field Effects on Electrochemical Reactions Occurring at Metal Flowing-Electrolyte Interfaces," *J. Electrochem. Soc.* **124**, 987 (1977).
- G. E. McGuire,² A. L. Bacarella, J. C. Griess, Jr.,¹ R. E. Clausen,³ and L. D. Hulett,⁴ "Analysis of Protective Oxide Films on Copper-Nickel Alloys by Auger Spectroscopy," *J. Electrochem. Soc.* **125**, 1801 (1978).

- A. A. Palko, *The Chemical Separation of Boron Isotopes*, ORNL-5418 (June 1978).
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- F. A. Posey, A. A. Palko, and A. L. Bacarella, *Corrosivity of Geothermal Brines Progress Report for Period Ending September 1977, Final Report*, ORNL TM-6308 (March 1978).

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4. Analytical Chemistry Division.

INORGANIC CHEMISTRY OF HYDROGEN CYCLES

- C. E. Bamberger, "Chemistry of the Ce(III)-Ti Cycle," *Laboratoire des Ultra Refractaires*, Odeillo, France, Sep. 1, 1978.
- C. E. Bamberger, "Hydrogen Production from Water by Thermochemical Cycles—A 1977 Update," *Cryogenics* 18(3), 170 (1978).
- C. E. Bamberger, "Hydrogen Production Methods," *Symposium on Energy and the Development of the Americas*, Guarujá, Brazil, Mar. 12-17, 1978 (invited paper).
- C. E. Bamberger, "Inorganic Chemistry for Water Splitting," *Rheinisch-Westfälische Technische Hochschule*, Aachen, Germany, Aug. 8, 1978.
- C. E. Bamberger, "Worldwide Status of Thermochemical Hydrogen," *Kernforschungszentrum Karlsruhe*, Karlsruhe, Germany, Aug. 14, 1978.
- C. E. Bamberger, "Thermochemical Hydrogen Production from Water," *Atomic Energy Commission*, Buenos Aires, Argentina, Mar. 22, 1978.
- C. E. Bamberger, M. A. Bredig,¹ D. M. Richardson,¹ and J. B. Hendricks, III,² "Two New Copper(II) Hydroxiodides," *Inorg. Chim. Acta* 27(2), 215 (1978).
- C. E. Bamberger and J. H. DeVan,³ "Materials Problems in Large-Scale Production of Hydrogen from Water and in Hydrogen Storage," *Metall. Trans. A*, 9A, 201 (1978).
- C. E. Bamberger and D. M. Richardson,¹ "Recent Research on Thermochemical Hydrogen Production at the Oak Ridge National Laboratory," *World Hydrogen Energy Conference*, Zürich, Switzerland, Aug. 21-24, 1978.
- S. E. Beall⁴ and C. E. Bamberger, "Applications of High Temperature Solar Heat to Fuels and Chemical Manufacture," *DOE DST Advanced Thermal Power Program Review*, Golden, Colo., May 9-11, 1978.
- L. Johnson,¹ L. G. Hepler,¹ C. E. Bamberger, and D. M. Richardson,¹ "The Enthalpy of Formation of K_2CrO_4 ," *Can. J. Chem.* 56, 446 (1978).

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CHEMISTRY IN SUPPORT OF THE NUCLEAR FUEL CYCLE

- J. T. Bell and L. M. Toth, "Photo and Radiation Chemistry in Nuclear Fuel Reprocessing," *Radiochim. Acta*, in press (1978).
- M. R. Bennett and A. D. Kelmers, *The Reduction of Plutonium(IV) to Plutonium(III) in Nitric Acid by Nitric Oxide or Nitrogen Dioxide Gases*, ORNL TM-6552, in press (1978).
- G. L. Johnson¹ and L. M. Toth, *Pa(IV) and Th(IV) Hydrous Polymer Chemistry*, ORNL TM-6365 (May 1978).
- A. D. Kelmers and D. N. Browning,² *The Chloride-Catalyzed Decomposition of Ammonium Nitrate in Nitric Acid Media at 100°C*, ORNL TM-5991 (August 1977).
- A. D. Kelmers and D. N. Browning,² "Hydrazoic Acid Distribution Between TBP-Dodecane and Nitric Acid Solutions," *Inorg. Nucl. Chem. Lett.* **13**, 505-10 (1977).
- A. D. Kelmers* and D. N. Browning,² "Hydrazoic Acid Distribution Coefficients in Purex Processing," American Nuclear Society Topical Meeting on the Plutonium Fuel Cycle, Bal Harbor, Fla., May 2-4, 1977.
- A. D. Kelmers, L. Maya, D. N. Browning,² and W. Davis, Jr.,³ "The Chloride-Catalyzed Decomposition of Ammonium Nitrate in Nitric Acid Media at 100°C," submitted for publication in *J. Inorg. Nucl. Chem.*
- A. D. Kelmers and D. Y. Valentine, *Search for Alternate Holding Reductants to Stabilize Plutonium(III) Solutions*, ORNL TM-6521 (September 1978).
- J. C. Mailen³ and L. M. Toth, "Chemistry of Volatile Fission Product Elements," submitted for publication in *Light Water Nuclear Fuel Cycle*, R. G. Wymer, ed., CRC Press, Inc., 1978.
- L. Maya, "Crystalline Compounds and Glasses in the System B_2O_3 -NaF-NaBF₄," *J. Am. Ceram. Soc.* **60**, 323 (1977).
- L. Maya, "Ruthenium(IV) in Nitric Acid Media," 175th American Chemical Society National Meeting, Anaheim, Calif., Mar. 17, 1978.
- L. Maya, "Studies of Zr Complexes with Butyl Lauryl Phosphoric Acid," American Nuclear Society Topical Meeting on the Back End of the LWR Fuel Cycle, Savannah, Ga., Mar. 21, 1978.
- L. Maya and C. D. Bopp,¹ "Extraction of Zirconium from Nitric Acid Media by Butyl Lauryl Phosphoric Acid in Dodecane," *J. Inorg. Nucl. Chem.* **40**, 1147 (1978).
- L. M. Toth, J. T. Bell, and D. W. Fuller, *Chemical and Physical Behavior of Some Contaminants in the Fluorocarbon Off-Gas Process: An Interim Report*, ORNL TM-6484 (November 1978).
- L. M. Toth, H. A. Friedman, and J. T. Bell, "Photochemical Separation of Actinides in the Purex Process," American Nuclear Society National Topical Meeting on the Plutonium Fuel Cycle, Bal Harbor, Fla., May 2-4, 1977.

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THERMAL ENERGY STORAGE: PHYSICAL CHEMISTRY OF PHASE-CHANGE MATERIALS

- S. Cantor, "Application of Differential Scanning Calorimetry to the Study of Thermal Energy Storage," *Thermochim. Acta* **26**, 36 (1978).
- S. Cantor, "Thermophysical Properties and Behavioral Characteristics of Phase-Change Material," pp. 129-36 in *Proc. 2d Annual Thermal Energy Storage Contractors Information Exchange Meeting, Gatlinburg, Tenn., Sept. 29-30, 1977*; CONF-770955, Oak Ridge National Laboratory (Mar. 9, 1978).

Supplemental Activities

PROFESSIONAL AND EDUCATIONAL ACTIVITIES

- C. F. Baes, Jr. Participant, Conference on Carbon Cycle, University of California, Berkeley, May 12, 1977.
Participant, Conference on Carbon Cycle and Ocean Chemistry, Scripps Institute of Oceanography, May 13, 1977.
Attended Fifth IUPAC Conference of Chemical Thermodynamics, Ronneby, Sweden, Aug. 23-26, 1977, participated in discussion sessions on high-temperature aqueous chemistry and delivered talk entitled "The Role of Hydrolysis at Elevated Temperatures."
- C. E. Bamberger Codirector of course on molten-salt technology, Center for Professional Advancement, New Brunswick, N.J., Oct. 10-12, 1977.
- J. Braunstein Editor, *Advances in Molten Salt Chemistry*, 1970-present.
Cochairman, Second International Symposium on Molten Salts, the Electrochemical Society, October 1978.
Lecturer, University of Tennessee Oak Ridge Graduate School of Biomedical Sciences, 1971-present.
Chairman, 1979 Gordon Conference on Molten Salts and Liquid Metals.
Course Director, Molten Salt Technology, Center for Professional Advancement, New Brunswick, N.J., October 1977.
Chairman, ad hoc Committee on Molten Salts, Physical Electrochemistry Division, the Electrochemical Society, 1976-present.
- W. R. Busing Panel member, workshop on "Computational Methodology in Chemistry" sponsored by the National Resource for Computation in Chemistry.
- C. J. Collins Professor of Chemistry, part time, University of Tennessee, Knoxville, January 1964-present.
Member, Advisory Board, *Isotopes in Organic Chemistry*, Elsevier Publishing Co., Amsterdam, Netherlands.
Coholder of NATO Grant No. 814 with Prof. Michael Hanack, University of Tübingen, Germany.
- M. Conradi Recipient of Eugene Wigner Fellowship.
- S. Datz Associate Editor, *Atomic Data and Nuclear Data Tables*, 1969-present.
Chairman, XII International Conference on Physics of Electronic and Atomic Collisions.
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- R. L. Hahn Corecipient of Radiation Industry Award, American Nuclear Society, 1977.
Member, DOE Transplutonium Program Committee, 1975-present.
Secretary, Division of Nuclear Chemistry and Technology, American Chemical Society, 1978-present.
Member, Committee on Major Nuclear Facilities, Division of Nuclear Chemistry and Technology, American Chemical Society, 1976-present.
Participant, DOE Workshops on Actinides in the Environment, April 1977 and October 1978.
Guest scientist ("outside user"), SuperHILAC, Lawrence Berkeley Laboratory, Berkeley, Calif.

- R. G. Haere** Lecturer, Welch Foundation Lecture Series, April 1978.
ORNL Representative, International Atomic Information Exchange Committee, 1976-present.
- C. K. Johnson** President, American Crystallographic Association, 1977.
Member, ACA Council, January 1976-December 1978.
Member, U.S. National Committee for Crystallography, National Academy of Sciences National Research Council, Jan. 1, 1972-Dec. 31, 1978.
Member, Policy Board, National Resource for Computation in Chemistry, Lawrence Berkeley Laboratory, October 1977-September 1979.
Member, Advisory Committee, Chemistry and Materials Science Department, Lawrence Livermore Laboratory, June 1977-October 1978.
President, Oak Ridge Computer Association, August 1978-July 1979.
Program Chairman, Workshop on Computational Methodology in Crystallography, June 1978.
- N. R. Johnson** Member, ORIC Program Committee.
Scheduling Coordinator, ORIC.
Member, SuperHILAC Users' Executive Committee.
Mentor, HHIRF Gamma-Ray Facilities.
Vice-Chairman, 1978 Gordon Research Conference on Nuclear Chemistry.
Chairman, 1979 Gordon Research Conference on Nuclear Chemistry.
Member, Program Committee, Division of Nuclear Chemistry and Technology, American Chemical Society, 1977.
Guest scientist ("outside user"), SuperHILAC, Lawrence Berkeley Laboratory.
Chairman, Nominating Committee for members of Users' Executive Committee, HHIRF, ORNL.
Symposium Chairman, American Chemical Society Meeting, Chicago, Ill., Aug. 29, 1977.
Member, Directory Committee, Nuclear Chemistry and Technology Section, American Chemical Society, 1978-79.
- H. A. Levy** Member, Subpanel on Structures, ad hoc Panel to Carry Out a Study of Facilities and Scientific Opportunities in the Use of Low Energy Neutrons, National Academy of Sciences, Mar. 15-June 15, 1977.
Professor of Chemistry, University of Tennessee, School of Biomedical Science, Oak Ridge, Tenn., 1977-present.
Member, Doctoral Research Committee in Cryobiology, 1978.
- M. H. Lietzke** Professor of Chemistry, part time, University of Tennessee, Knoxville, 1964-present.
- R. Livingston** ORNL Liaison Officer for ORNL University of Tennessee part-time teaching program, 1968-present.
Editorial Board, *The Journal of Magnetic Resonance*, January 1971-present.
Editorial Board, *Magnetic Resonance Review*, September 1971-present.
Participant in the ERDA Workshop on the Sandia Combustion Facility, San Francisco, Calif., July 15-16, 1977.
Participant in the DOE National Bureau of Standards Workshop on High Temperature Chemical Kinetics: Applications to Combustion Research, Gaithersburg, Md., Dec. 12-13, 1977.
- W. L. Marshall** Member, National Council, American Chemical Society, 1969-74, 1976-present; Committee on Chemical Education, 1970-74, 1977-present; Subcommittee on High School Chemistry, 1971-74, 1977-present (Chairman, 1972-74, 1978-present); Steering Committee on Guidelines for Teacher Training, 1975-present; Division of Chemical Education's Committee on High School Chemistry, 1978-present.
Member, Working Groups of International Association for the Properties of Steam, 1975-present.
Participant, Visiting Scientist Program, Tennessee Academy of Science, 1975-present.
Participant, Oak Ridge Associated Universities Traveling Lecture Program, 1977-79.
- G. D. O'Kelley** Professor of Chemistry, part time, University of Tennessee, Knoxville, January 1964-present.
Alternate Councilor, Division of Nuclear Chemistry and Technology, American Chemical Society, 1977-1979.
Member, National Research Council Committee on Nuclear Science; Chairman, Subcommittee on Radiochemistry, 1974-1978.
Guest scientist ("outside user"), 88-in. Cyclotron, Lawrence Berkeley Laboratory, Berkeley, Calif.
Lecturer, ORNL-ORAU Iranian Training Program, June 1978.
Instructor, In-House Training Course on Radiochemistry, Chemistry Division, 1978.
- R. W. Stoughton** Editorial Advisory Board, *Journal of Inorganic and Nuclear Chemistry*, 1958-present.
Consulting Editor, *Inorganic and Nuclear Chemistry Letters*, 1965-present.
Organized and taught course in "Chemistry in Nuclear Technology" to visiting Iranian scientists (jointly sponsored by ORAU and ORNL).
- R. A. Strehlow** Chairman, ASTM Committee D-32.92 on Nomenclature and Definitions Associated with Catalysis.
- E. H. Taylor** Member, Committee on Chemical Sciences, National Academy of Sciences National Research Council, 1977-present.
- W. E. Thiessen** Panel Member, Workshop on Computational Methodology in Chemistry sponsored by the National Resource for Computation in Chemistry.

C. E. Vallet Abstractor for the *Molten Salts Awareness Bulletin*, Rensselaer Polytechnic Institute
 H. Zeldes Judge at Southern Appalachian Science Fair, Knoxville, Tenn., Apr. 6, 1978

COLLABORATIVE RESEARCH

Institution	Collaborator(s)	Subject	Staff Member(s)
Ames Laboratory, Iowa State University, Ames	I. Habenschuss	Structure of LaCl_3 solutions	A. H. Narten R. Trnlo
Argonne National Laboratory, Argonne, Ill.	J. M. Williams J. Schultz R. W. Mrocz	Structure of $[\text{Th}(\text{CH}_3)_2\text{C}] \text{H}(\mu\text{-H})_2 \text{C} \cdot \text{H} \cdot \text{CH}_3$	G. M. Brown
	K. L. Wolf	Spontaneous fission energetic studies	J. Halperin B. H. Ketelle G. D. O'Kelley R. W. Stoughton
Arizona State University Center for Meteorite Studies	C. B. Moore	Search for superheavy elements in nature	J. Halperin B. H. Ketelle G. D. O'Kelley R. W. Stoughton
Université Nationale du Bénin, Benin, West Africa	R. P. Hazoume	Theory of fluids	F. Johnson
The Niels Bohr Institute, Copenhagen, Denmark	O. Hansen P. R. Christensen	Heavy-ion induced reactions at Lawrence Berkeley Laboratory SuperHILAC	R. L. Ferguson
California Institute of Technology, Pasadena	R. A. Marcus	Chemical dynamics	D. W. Noid
Central College, Pella, Iowa	P. J. Ogren	Studies of elementary reactions of small free radicals in the gas phase by flash photolysis	C. J. Hochanadel I. J. Sworski
Centre College	C. A. Girard	Proton spin relaxation in hydrous melts	J. Braunstein
Centre d'Études Nucéaires, Bordeaux, France	E. Hubert	Heavy-ion transfer reactions	R. L. Hahn
Centre d'Études Nucéaires, Fontenay-aux-Roses, France	D. Damien	Transuranium element chemistry	J. H. Burns J. R. Peterson R. G. Haire
	C. Musikas	Electrochemistry of transuranium elements	J. R. Peterson R. G. Haire
Convair Aerospace Division, General Dynamics Corp., San Diego	O. E. Myers	Search for superheavy elements in nature	J. Halperin B. H. Ketelle G. D. O'Kelley R. W. Stoughton
University of Delaware, Newark, Department of Chemical Engineering	R. Agraval S. J. Sandler	The Structure of liquid bromine	A. H. Narten
Denison University, Granville, Ohio	R. R. Winters	Neutron cross sections	J. Halperin

COLLABORATIVE RESEARCH

Institution	Collaborator(s)	Subject	Staff Member(s)
Technical University of Denmark	J. H. von Barner N. J. Bierum	Coordination of transition metal ions in molten salt catalysts	G. P. Smith
Fermi National Accelerator Laboratory	D. Theriot	Search for superheavy elements in accelerator targets	J. Halperin B. H. Ketelle G. D. O'Kelley R. W. Stoughton
University of Georgia, Geochronology Laboratory	J. E. Noakes	Search for superheavy elements in nature	J. Halperin B. H. Ketelle G. D. O'Kelley R. W. Stoughton
Gesellschaft für Schwerionenforschung, Darmstadt, Germany	H. H. Guthbrod	Heavy-ion induced reactions at Lawrence Berkeley Laboratory SuperHILAC	R. L. Ferguson
Center for Astrophysics, Harvard College Observatory and Smithsonian Astrophysical Observatory, Cambridge, Mass.	E. L. Fireman	Search for superheavy elements in nature	B. H. Ketelle R. W. Stoughton
Harvard University, Cambridge, Mass.	W. N. Lipscomb F. C. Kostansek	Structures of cyclic peptides	W. E. Thiesen
University of Illinois, Urbana	J. D. McDonald	Chemical dynamics	D. W. Noid
University of Kentucky, Lexington	C. P. Brock	Structure of substituted biphenyls	H. A. Levy
University of Kentucky Purdue University	S. W. Yates P. J. Daly C. E. Dors J. Wilson	Lifetimes of high-spin states in ^{195}Pt	N. R. Johnson
Lawrence Berkeley Laboratory	R. M. Diamond	Systematic study of transition strengths in ^{152}Eu and ^{154}Gd	N. R. Johnson
University of Tennessee Texas A. & M. University	E. S. Stephens M. W. Gindry T. J. Sugihara		
Lawrence Livermore Laboratory	E. K. Hulet P. A. Rausen R. W. Lougheed J. Landrum J. Wild R. Dougan	Radiopolarography of mendelevium	G. D. O'Kelley
	E. K. Hulet R. W. Lougheed	Experimental study of spontaneous fission of ^{252}Cf [105]	C. E. Bemis R. L. Ferguson F. Plasil G. D. O'Kelley R. L. Hahn D. Hensley
	M. G. Mustafa	Theoretical studies of spontaneous fission of very heavy nuclei	R. L. Ferguson

COLLABORATIVE RESEARCH

Institution	Collaborator(s)	Subject	Staff Member(s)
Los Alamos Scientific Laboratory	H. C. Britt B. H. Erikala P. D. Goldstone R. H. Stokes	Heavy-ion induced reactions at Lawrence Berkeley Laboratory SuperHILAC	R. L. Ferguson
	G. A. Cowan J. R. Nix	Possibility of superheavy elements in nuclear explosions	J. Halperin B. H. Ketelle G. D. O'Kelley R. W. Stoughton
	G. Eller	Spectrophotometric study of uranium fluorides	J. R. Peterson J. P. Young
	J. Smith	Superconductivity of metals	R. G. Haire
	J. R. Stine	Chemical dynamics	D. W. Noid
	J. Ward	1. Heat of vaporization of metals 2. Vapor pressure of metals	R. G. Haire
	F. Willeumier	Atomic photoionization	M. O. Krause
LURE, Orsay, France			
Massachusetts Institute of Technology	S. M. Senkan	Surface properties and reactions on nickel catalysts	J. J. Fuller
Max. Planck-Institut für Kohlenforschung, Mülheim, Germany	H.-P. Hornbuen	1. Light scattering determinations of molecular weights of coal molecules 2. The Scholl reaction	C. J. Collins B. M. Benjamin B. E. Maxwell
Michigan State University	O. Gansow	Solution and solid-state studies of some lanthanide cryptate compound	J. R. Peterson
University of Southern Mississippi, University	J. W. Pinson I. L. Ingram, Jr	Structure of 1,5-bisecaborant[4]yl	G. M. Brown
NASA Johnson Space Center	E. Schonfeld	Primordial radioelements and spallogenic radionuclides in meteorites	G. D. O'Kelley
State University of New York at Albany	J. B. Garg	Neutron cross sections	J. Halperin
University of North Carolina at Charlotte	D. S. Jones	Structure of complexes of nickel, cobalt, and ruthenium	H. A. Levy
Northwestern University, Evanston, Ill.	J. M. Manriquez P. J. Fagan I. J. Marks	Structure of $[\text{Th}(\text{CH}_3)_3\text{C}][\text{B}(\mu\text{-H})_2\text{C}_2\text{H}_4\text{CH}_3]$	G. M. Brown
Institut de Physique Nucléaire, Orsay, France	Y. LeBevec H. Gauvin	Compound nucleus reactions induced by ^{36}Ar and ^{86}Kr beams	R. L. Hahn
	E. David K. Samhoun	Electrochemistry of mendelevium	R. L. Hahn G. D. O'Kelley J. R. Larrant
University of Paris-South, Orsay, France	H. Sergoile C. Roulet J. Vanhorenbeck J. Lagrange P. Colombani	Multiple coulomb excitation measurements in ^{187}W	N. R. Johnson

COLLABORATIVE RESEARCH

Institution	Collaborator(s)	Subject	Staff Member(s)
University of Puerto Rico, Rio Piedras, P. R.	I. Blum	Neutron scattering from liquid water	A. H. Norton
Rice University, Houston, Department of Geology	J. A. S. Adams	Search for unknown radioactivities in nature	R. V. Gentry J. Halperin B. H. Ketelle G. D. O'Kelley R. W. Stoughton
University of Rochester	M. Blaun	Heavy-ion induced reactions at Lawrence Berkeley Laboratory SuperHIL AC	R. T. Ferguson
Sandia Laboratories, Livermore, Calif.	M. I. Koszykowski	Chemical dynamics	D. W. Nord
Science Applications Inc., Palo Alto	J. Malý	Search for superheavy elements in nature and in accelerator targets	J. Halperin B. H. Ketelle G. D. O'Kelley R. W. Stoughton
Stanford Linear Accelerator Center	D. Walz	Search for superheavy elements in accelerator targets and in nature	J. Halperin B. H. Ketelle G. D. O'Kelley R. W. Stoughton
University of Tennessee, Knoxville	M. W. Guidry R. Neese C. R. Bingham S. W. Hawkinson	Studies of the nuclear surface through coulomb-nuclear inter- ference measurements Crystal structure of trimethyl- cyclopropenium fluoborate	N. R. Johnson W. R. Busing
	P. G. Huray	Magnetic susceptibility	R. G. Haire
	G. Mamantov R. Huglen	Raman spectroscopy of molten salt catalysts	G. P. Smith G. Begun
	H. Y. McSween, Jr.	K, Th, U concentrations in achondritic meteorites	G. D. O'Kelley
	J. R. Peterson	Transuranium element chemistry	R. G. Haire J. H. Burns
	I. L. Riedinger M. W. Guidry A. C. Kahler C. R. Bingham	Studies of the backbending effect in thallium and gold nuclei	N. R. Johnson
	F. M. Schell S. W. Hawkinson	Course of photochemical cycloadditions	W. F. Thiesen
University of Tennessee	I. L. Riedinger M. W. Guidry S. W. Yates	Coulomb excitation of medium weight vibrational nuclei	N. R. Johnson
University of Kentucky University of Tennessee	I. L. Riedinger C. R. Bingham	Investigations of highly excited states in ^{171}Yb	N. R. Johnson
Washington University	D. Sarantites		
Chemical Institute, University of Tübingen, Germany	M. Hanack H. Stutz	Isotope effects in homopropargyl rearrangements	C. J. Collins R. M. Jones
Tulane University, New Orleans, La.	C. J. Fritchie P. Tsao	Structure of molybdenum enzyme analogues	H. A. Levy

COLLABORATIVE RESEARCH

Institution	Collaborator(s)	Subject	Staff Member(s)
UNISOR Consortium	L. I. Riedinger C. R. Bingham T. E. Wood R. W. Fink A. G. Schmidt L. H. Spejewski H. K. Carter P. I. Miska E. E. Zurek J. H. Hamilton	Studies of Z = 51 transitional nuclei	G. D. O'Kelley
U.S. Geological Survey	A. H. McArthur	Search for superheavy elements in nature	J. Halperin B. H. Kettle G. D. O'Kelley R. W. Stoughton
Vanderbilt University, Nashville, Tenn.	S. M. Banna	Electron spectroscopy of atomic vapors	M. O. Krause
	N. Thompson B. Ecker	Electrochemistry and corrosion of ion-implanted alloys	E. J. Kelly
Vanderbilt University	J. H. Hamilton	Combinatorial excitation, lifetime measurements, and x-ray spec-	S. R. Johnson
University of Tennessee	R. R. Rungger R. H. Cray E. E. Rostinger M. W. Gaudry A. C. Kanler	trios of high angular momentum states in ^{119}Ir	
University of Kentucky	S. W. Yates		
Lawrence Berkeley Laboratory	E. S. Stephens R. M. Diamond E. Y. Lee R. S. Simon P. A. Butler P. Colombo D. Cline		
University of Rochester	E. E. Robinson		
University of Alabama			
College of William and Mary	R. Champagnon	Collisional electron detachment from Li	S. Datz B. K. Annis

1. Physics Division

2. Department of Chemistry, University of Tennessee, Knoxville

3. Analytical Chemistry Division

VISITING SCIENTISTS

Name	Affiliation	ORNL Research Program	Sponsor
P. Allard	Chalmers University of Technology, Göteborg, Sweden	Actinide solution chemistry	Chalmers University and ORNL (G. W. Beall, B. H. Krotz, and G. D. O'Kelle)
L. Blum	University of Puerto Rico, Rio Piedras	Structure of liquids	Oak Ridge Associated Universities (A. H. Narten)
J. Bourges	Centre d'Etudes Nucléaires, Fontenay-aux-Roses, France	Transuranium element chemistry	CIA, France (R. G. Haire and G. W. Beall)
D. A. Damien	Centre d'Etudes Nucléaires, Fontenay-aux-Roses, France, and University of Tennessee, Knoxville	Transuranium element chemistry	CIA, Fontenay-aux-Roses, France (J. H. Burns, R. G. Haire, and J. R. Peterson)
F. David	Institut de Physique Nucléaire, Orsay, France	Electrochemistry of mendelevium	CNRS, France (R. L. Hahn, G. D. O'Kelle, and J. R. Tarrant)
D. D. Ensor	University of Tennessee, Knoxville	Transuranium element chemistry	University of Tennessee Research Grant (J. R. Peterson)
J. D. Frantz	Geophysical Laboratory, Carnegie Institution of Washington, Washington, D.C.	Electrical conductances of aqueous electrolyte solutions, 0-800°C, 1-4600 atm; ionization equilibria	Geophysical Laboratory and ORNL (W. L. Marshall)
T. Habenschuss	Ames Laboratory, Ames State University, Ames	Structure of LaCl_3 solutions	Oak Ridge Associated Universities (A. H. Narten)
S. W. Hawkinson	University of Tennessee, Knoxville	Structural chemistry	University of Tennessee (W. L. Marshall)
H. P. Hombach	Max-Planck-Institut für Kohlenforschung, Mulheim, Germany	Coal research	ORNL
M. Hussonois	Institut de Physique Nucléaire, Orsay, France	Transuranium element chemistry	CNRS, France (C. B. Finch and R. L. Hahn)
D. S. Jones	University of North Carolina, Charlotte	Structural chemistry	Oak Ridge Associated Universities (A. H. Narten)
C. Musikas	Centre d'Etudes Nucléaires, Fontenay-aux-Roses, France	Transuranium element chemistry	NATO Grant and CIA, France (J. R. Peterson and R. G. Haire)
S. I. Sandler	University of Delaware, Newark	X-ray diffraction studies of liquid hydrocarbons	Oak Ridge Associated Universities (A. H. Narten)
C. S. Patterson	Furman University	High temperature aqueous chemistry	R. E. Mesmer
T. T. Sugihara	Texas A. & M. University	Nuclear chemistry	ORNL and Texas A. & M. University (N. R. Johnson)
R. Triolo	University of Palermo, Italy	Neutron diffraction from aqueous solution	NATO Fellow (A. H. Narten)
S. W. Yates	University of Kentucky	Nuclear chemistry	ORNL (N. R. Johnson)

GRADUATE STUDENTS

Name	Major Professor and/or Institution	Staff Advisor	Field of Research	Sponsor
R. Agrawal	S. I. Sandler, University of Delaware, Newark		Structure of liquids	A. H. Narten
C. L. Barnes	S. W. Haskins, Jr., University of Tennessee		Structural chemistry	W. R. Busing
R. L. Cassel	S. W. Haskins, Jr., University of Tennessee		Structural chemistry	W. R. Busing
L. E. Collins, Jr.	G. D. O'Kell, Jr., University of Tennessee	G. D. O'Kell, Jr.	Nuclear spectroscopy	University of Tennessee
J. P. Filber	S. W. Haskins, Jr., University of Tennessee		Structural chemistry	W. R. Busing
W. R. Hays	M. H. Lenzke, Jr., University of Tennessee	M. H. Lenzke	Environmental chemistry	University of Tennessee
H. T. Hubert	J. R. Peterson, ¹ University of Tennessee	J. R. Peterson, ¹ J. P. Yarnall ²	Actinide spectroelectro- chemistry	University of Tennessee Research Grant
A. C. Kahler	I. R. Peterson, ¹ University of Tennessee	N. R. Johnson	Nuclear structure at high spins	University of Tennessee
I. M. Karpovich	J. R. Peterson, ¹ University of Tennessee	J. R. Peterson, ¹ G. W. Beall	Actinide environmental chemistry	University of Tennessee Teaching Assistantship
R. A. Marshall	G. D. O'Kell, Jr., University of Tennessee	G. D. O'Kell, Jr.	Nuclear geochemistry	ORAU
S. N. Nayak	P. G. Hertz, Jr., University of Tennessee	P. G. Hertz, Jr.	Magnetic susceptibilities	ORAU
R. L. Noller	M. W. Grady, Jr., University of Tennessee	N. R. Johnson	Coulomb-nuclear inter- ference effects induced by heavy ions	University of Tennessee
D. L. Rasbella	J. R. Peterson, ¹ University of Tennessee	J. R. Peterson, ¹	Actinide calorimetry	ORNL Graduate Fellowship Program
W. L. Ritz	M. H. Lenzke, Jr., University of Tennessee	M. H. Lenzke	Physical chemistry	University of Tennessee
E. M. Thomas, Jr.	University of Tennessee	E. Brannen, Jr.	Fuel cell research	E. Braunstein
M. J. Abadi	Massachusetts Institute of Technology, School of Chemical Engineering Princeton	E. E. Fisher	Structural chemistry	S. M. Siskin, Massachusetts Institute of Technology
R. N. Cason				
O. K. Chow				
J. J. Dillon				
K. E. Fallon				
T. A. Field				
C. E. Garry				
M. S. Giron				
W. J. Kausch				
M. Z. Khan				
R. J. Mattern-Alden				
L. L. Onik				
A. L. Papadopoulos				
L. L. Rios-Bayon				

GRADUATE STUDENTS

Name	Major Professor and/or Institution	Staff Advisor	Field of Research	Sponsor
D. G. Sundberg				
W. F. Song				
C. M. Talbert				
R. D. Wang				
M. F. Zimmer				

1. Department of Chemistry, University of Tennessee, Knoxville.
2. Analytical Chemistry Division.

UNDERGRADUATES STUDENTS

Name	Institution	ORNL Research Program	Sponsor
Ronald E. Hendershot	Bloomsburg State College, Bloomsburg, Pa.	X-ray and neutron diffraction	ORAU
M. L. Kiefer	Augustana College	Heavy-ion nuclear chemistry	ORAU Summer Student Trainee Program
M. J. Michalczyk	Knox College, Illinois	Coal chemistry	Great Lakes Colleges Association
Debra Schwinn	Wooster College, Wooster, Ohio	Structure of liquids	ORAU
J. R. Spears	University of the South, Sewanee, Tennessee	NMR research	Southern Colleges and Universities Union
J. M. Warakowski	Wilkes College, Wilkes-Barre, Pa.	Solubility of silica in salt solutions	ORAU Summer Student Trainee Program

DIVISIONAL PERSON-POWER AND FINANCIAL SUMMARY FY 1978

	Funding (in thousands)	Person-years
DOE PROGRAMS		
Fossil Energy	\$ 602	8
Fusion	134	2
Fission Energy ^a	50	1
Basic Energy Sciences	5,955	74
Conservation	282	3
Nuclear Physics	681	8
Geothermal	252	3
TOTAL DOE PROGRAMS	\$7,956	99
WORK FOR OTHERS PROGRAMS		
Argonne National Laboratory	\$ 225	2.5
Office of Nuclear Waste Isolation	352	4.5
Grand Junction Office	102	1.5
Miscellaneous	44	0.5
TOTAL WORK FOR OTHERS	\$ 723	9.0
TOTAL FINANCIAL PLANS	\$8,679	108.0

^a Approximately 8 persons (~640K \$) worked in this area while on loan to the Chemical Technology Division.

UNIVERSITY OF TENNESSEE
Knoxville, Tennessee

* Dual Capacity
* Also Director of Transuranic Research Laboratory
* TM, Coordinator for University of Tennessee
* Transuranic Chemistry Program
* On loan from Finance and Materials
* On loan from the Safety and Applied Health Physics
* Part-time Employee
* On-going Student
* Visiting Scientist
* Student Guide
* On loan from Physics Division

END

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12/04/79