MASSACHUSETTS INSTITUTE OF TECHNOLOGY

Laboratory for Nuclear Science

CHEMISTRY PROGRESS REPORT

December 31, 1965

M. I. T. - 905 - 52

DISCLAIMER

MIT-905-52

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

LABORATORY FOR NUCLEAR SCIENCE

CHEMISTRY PROGRESS REPORT

December 31, 1965

M.I.T.-905-52

The work of the Chemistry Groups described in this report has been supported by and large by the Atomic Energy Commission under contract AT(30-1)-905. Support received for this work through the M.I.T. Department of Chemistry is also acknowledged.

PREFACE

It has become desirable for administrative reasons to report the progress of the Chemistry Group of the Laboratory for Nuclear Science separately and on an annual basis. This is the first report to be issued under this arrangement. It covers the period from 1 November 1964, the date of the last LNS report (MIT-2098-No. 142), to 31 December 1965.

The original letter of the sub-groups organized under this AEC contract, AT(30-1)-905, have lost some of their descriptive strength as the character of their work has changed. Consequently, new titles have been assigned to the groups in this report to better represent the areas of research effort. In addition, the work of Professor Scatchard's physical chemistry group is described in a separate section.

This is the sixty-sixth progress report of the Laboratory for Nuclear Science at the Massachusetts Institute of Techology. Progress reported covers the period for Chemistry from November 1, 1964, through December 31, 1965.

TABLE OF CONTENTS

Reprints of published papers listed herein are available in limited numbers upon request form the Laboratory for Nuclear Science Document Room.

I. Nuclear Decay-Scheme Studies

A. Decay Schemes of the ^{117}Cd Isomers

All the experimental data obtained at MIT, Amsterdam, and Oak Ridge National Laboratory on the decay of ^{117}Cd have now been analyzed. The proposed decay schemes for the two ^{117}Cd isomers are shown in Fig. 1.1.

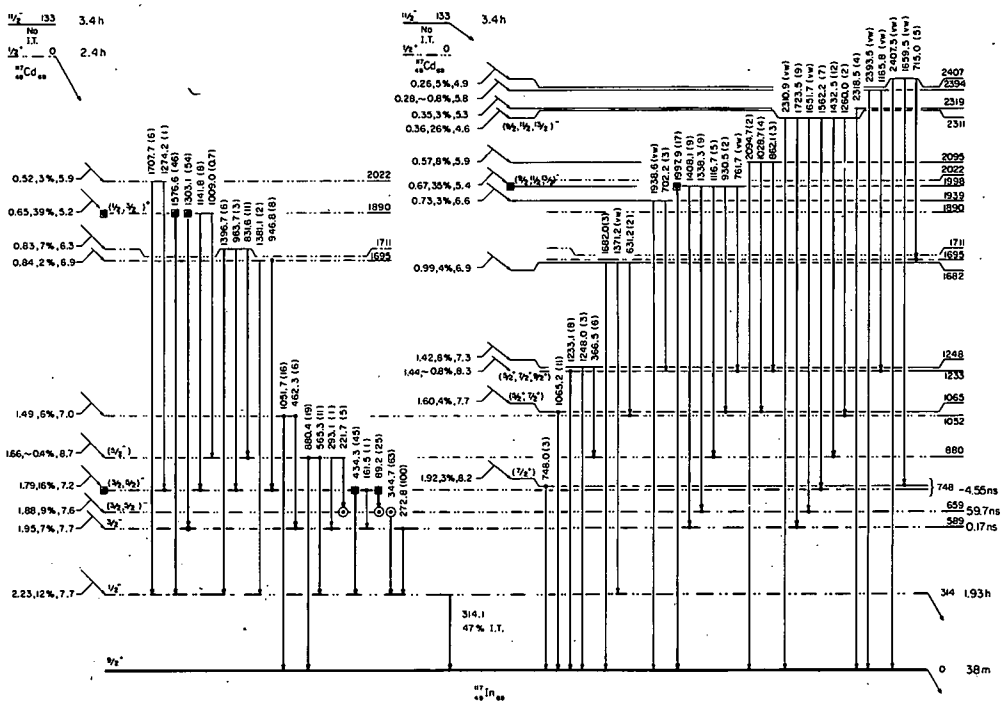


Figure 1.1

Proposed decay schemes for the ^{117}Cd isomers.

Following the convention used in the Nuclear Data Sheets, the large dots shown in the level scheme of Fig. 1.1 indicate experimentally observed coincidences. Beta- and γ-rays entering a level with dotted arrowheads are in coincidence with γ-rays leaving the same level and dotted at their origins. Introducing some new symbols, dots enclosed by squares denote specific β-γ coincidences; dots enclosed by circles signify delayed coincidences. The β-transitions are described by three numbers separated by commas. The first number indicates the maximum energy (MeV) of the β-group feeding the particular level. The second number is the percent abundance of that β-group relative to the total decay of the parent isomer, and the third number is the log ft of the transition.

The energies (in keV) of the γ-rays are shown at the origins of the arrows. The numbers enclosed in parentheses next to the energies are the intensities relative to the 273-keV γ-ray

taken as 100. Thick vertical lines show γ-rays of relative intensity 5% or higher. The γ-transitions from levels fed mainly by the low-spin 2.4-hr ^{117g}Cd (broken lines) are grouped together on the left side, and those from levels fed mainly by the high-spin 3.4-hr ^{117m}Cd (solid lines) are arranged on the right side. The purpose of this separation is to show clearly the origins of the various β- and γ-transitions with respect to the two ^{117}Cd isomers. All levels from the left side are included on the right side. Energies of the β-transitions shown were obtained by subtracting the level energies from the known energy differences between the ^{117}Cd and ^{117}In isomers (see LNS Prog. Rep., Nov. 1, 1964). The number at the right of each level gives the energy of that level in keV. Spins and parities are indicated at the left. Parentheses are used to denote inconclusive assignment of spin or parity.

The half-lives of the two ^{117}Cd isomers were measured by selectively multiscaling on particular coincident radiations. The γ-γ coincidence results were obtained from the experiments using two 3- x 3-in NaI(Tl) detectors and the 20,000-channel multiparameter pulse-height analyzer at Oak Ridge National Laboratory. Conversion-electron energies and some β-spectroscopic data were obtained at the Institute of Nuclear Physics Research in Amsterdam, using a magnetic spectrometer. Gamma-ray energies and relative intensities were determined from spectra obtained with the Ge(Li) detectors. Beta-ray intensities were calculated from the relative intensities of the γ-rays knowing the level scheme. No corrections were made for the internal conversion of the γ-rays. The log ft values were calculated using the nomograms given by Wapstra, et al. (Nuclear Spectroscopy Tables, North-Holland Publishing Co., Amsterdam, 1959). The half-lives of the three short-lived low-energy excited states of ^{117}In were measured with a time-to-amplitude converter (see Tang, Chilosi, and Van Hise, Sect. I.B). The assignments of the γ-rays to either of the ^{117}Cd isomers were based on comparative decay of the photopeak intensities of neighboring peaks in various spectra of ^{117}Cd obtained from the (d,p) or (n,γ) reaction taken at different times.

Fifty-four γ-rays were identified as due to the decay of the ^{117}Cd isomers. Of these, only 53 are accommodated in the proposed decay schemes. The single γ-ray excluded is the 1835.0 keV. It is very weak, not in coincidence with any other radiations, and it can not be attributed to any impurities in the source. The γ-rays, 493- and 528-keV, found often in the Ge(Li) spectra of ^{117}Cd, have been ascribed to the decay of 2.3-d ^{115g}Cd. Two others, 1292.6- and 1452.1-keV, have just recently been identified as originating from the decay of 43-d ^{115m}Cd (see Graeffe and Tang, Sect. I.D).

From the decay schemes constructed, it was established that 44% of the $11/2^-$ ^{117m}Cd decays to the 1.93-hr $p_1/_2$ isomer of ^{117}In and 7% of the $1/2^+$ ^{117g}Cd decays to the 38-min $9/2^+$ ground state of ^{117}In.

The data obtained in this work are generally insufficient to make unambiguous spin and parity assignments to the levels. Only for levels which are strongly fed by β-transition are the possible spins and parities indicated. The assignments are based mainly on log ft values. The log ft values of the β-transitions populating the short-lived low-lying levels of ^{117}In from the

$1/2^+$ ^{117g}Cd are consistent with their assignments as first-forbidden ($\Delta J=0, 1$, yes) or first-forbidden unique transitions ($\Delta J=2$, yes). Therefore, these levels must have low spins (1/2, 3/2, 5/2) and negative parity. The ground and 1.93-hr isomeric state of ^{117}In are known to be, respectively, $g_{9/2}$ and $p_{1/2}$ (Cameron and Summers-Gill, Can. J. Phys. 40, 104, 1962). Hence, the $1/2^-$ (intrinsic) possible assignment to the three short-lived states (589-, 659-, and 748-keV) can be eliminated.

Owing to the difficulty of generating positive-parity low-spin states, one can ignore the possibility of assigning the β-transitions to these short-lived states as ℓ-forbidden allowed transitions ($\Delta J=0, 1$, $\Delta\ell=2$, no, $\log ft > 6$). Therefore, the assignments permissible for these states are only $3/2^-$ and $5/2^-$. The $3/2^-$ state could be either a $p_{1/2}$ hole coupled to a 2^+ phonon or it could be the shell-model $p_{3/2}$ hole state. The $5/2^-$ state could be the $f_{5/2}$ shell-model state or it could be a $p_{1/2}$ hole coupled to a 2^+ phonon. The assignment of $3/2^-$ to the 589-keV level (0.17 nsec) is based mainly on consideration of transition probability of the 273-keV γ-ray (see Tang, Chilosi, and Van Hise, loc. cit.). The recently reported angular correlation between the 1303- and 273-keV γ-rays in ^{117}Cd (Mancuso and Arns, Nucl. Phys. 68, 504, 1965) seems to support this assignment.

The maximum β-energy in ^{117}Cd observed in this study is 2.2 MeV. The failure to observe a β-transition (2.67 MeV) between the $11/2^-$ isomer of ^{117}Cd and the $9/2^+$ ground state of ^{117}In is not understood. The corresponding transition in ^{115m}Cd (1.62 MeV) is very strong. Similarly, it is puzzling to note the absence of a β-transition between the $9/2^+$ ground state of ^{117}In and the 14-d $11/2^-$ isomeric state of ^{117}Sn (Lévêque, Richter, and Coryell, MIT LNS Prog. Rep., Aug. 31, 1952). (C.-W. Tang, G. Chilosi, C. D. Coryell, and A. H. Wapstra*)

B. Short-Lived Excited States in ^{117}In

The half-lives of three short-lived excited states in ^{117}In were measured with a time-to-amplitude converter at the Oak Ridge National Laboratory. The 0.17 ± 0.03 nsec half-life of the 589-keV level (see Fig. 1.1, Sect. I.A) was obtained by gating on the 1303-273 γ cascade. For the 659 keV level, the 59.7 ± 2.0 nsec half-life was obtained by gating on the 89-345 cascade. The 4.55 ± 0.32 nsec half-life for the 748-keV level was determined by gating on β-rays > 900 keV and the 434-keV γ ray. With the same gate on the β rays as above, but moving the other gate to the 89-keV γ ray gave a similar half life, suggesting that the 89- and 434-keV γ rays originate from the same level. (For a description of the experimental set-up see Oak Ridge National Laboratory, Chem. Div. Ann. Prog. Rep. ORNL-3832).

The partial half lives of the γ rays originating from the above levels were compared with the predictions of the single-particle model (Weisskopf estimates). The retardation factors show that the assignment of E1, M1, or E2 to any of the five γ transitions (273-, 345-, 89-, 162-, and 434-keV) is compatible with previously known transitions of these multipolarities. Even the

* Institute for Nuclear Physics Research, Amsterdam.

occurrence of retarded E2 transitions can not be deemed surprising, in view of the recent work of Sorensen (Phys. Rev. 133, B281, 1964) and Ikegami and Udagawa (Phys. Rev. 133, B1388, 1964) on the pairing model predicting the existence of such transitions among spherical nuclei.

From considerations of log ft values and the difficulty of generating low-spin positive-parity states (already discussed in Sect. I.A), there are, thus, only four possible states, $p_{3/2}$, $3/2^-$ ($p_{1/2} + \hbar\omega$), $5/2^-$ ($p_{1/2} + \hbar\omega$), and $f_{5/2}$, to be identified with the three short-lived levels. If one assumes that the 589-keV level is a $3/2^-$ state and that the 273-keV γ ray decaying from it is pure E2, then, from its partial half life, one should be able to tell whether this state is the phonon-coupled state. Following de Shalit (Phys. Rev. 122, 1530, 1961), the B(E2) of the 273-keV transition was compared with the B(E2) of the 0^+ to 2^+ transition of the adjacent even-even nuclide. The B(E2) of the 0^+ to 2^+ transition in ^{116}Cd is 0.58 (units of $10^{-48}e^2cm^4$) (McGowan, et al., Nucl. Phys. 66, 97, 1965) and that in ^{118}Sn is 0.23 unit (Stelson and McGowan, Phys. Rev. 110, 489, 1958). For the 273-keV transition, the B(E2) calculated (neglecting internal conversion) is 0.11 unit. Since the 2^+ phonon coupled to a $p_{1/2}$ hole or particle results in two levels, $5/2^-$ and $3/2^-$, the B(E2) of the transitions from each of the latter two levels to the $p_{1/2}$ level should be equal to half the B(E2) of the phonon transition between the 0^+ and 2^+ state. The excellent agreement between the B(E2) of the 273-keV transition and half the B(E2) of the 0^+ to 2^+ transition in ^{118}Sn suggests that the 589-keV level may be regarded as the phonon-coupled $3/2^-$ state, the $p_{1/2}$ hole coupling with the 2^+ phonon of the ^{118}Sn single-closed-shell core (cf. Silverberg's treatment of ^{115}In levels, Arkiv Fysik 20, 341 1961).

Using the same treatment as above on the 345- and 434-keV transitions indicates that neither of the two γ-rays are phonon transitions. It is clear, though, that they are either M1, or E2, or a mixture of both, but cannot be E1. (C.-W. Tang, G. Chilosi*, and J.R. Van Hise*)

C. New Value for the Fraction of I.T. in ^{117}In

The fraction of internal conversion, f, in 1.93-hr ^{117}In was determined to be 47.1 ± 2.5% in this work. This new value is in substantial disagreement with the 28 ± 3% reported by Wolfe and Hummel (J. Inorg. Nucl. Chem. 22, 7, 1961). The ^{117}In used in this work was separated from ^{117}Cd produced in the ^{116}Cd(n, γ)^{117}Cd reaction, whereas Wolfe and Hummel studied ^{117}In directly produced from the ^{121}Sb(γ, α)^{117}In reaction.

Indium-117 was separated from ^{117}Cd by ion exchange using Dowex 1 X2 resin, and eluting with 0.5 N HCl. The eluted ^{117}In was extracted into a chloroform solution of 8-hydroxyquinoline which was then evaporated on a small watch glass, leaving a small spot of ^{117}In activity on the center of the watch glass. The watch glass was mounted on a sample card 10 cm away from a 3- x 3-in NaI(Tl) detector. The watch glass serves as a partial absorber for β rays; however, additional lucite absorbers were mounted to absorb all the β rays. A number of ^{117}In samples with various growth time were prepared and γ-ray spectra of each sample were taken periodically with background subtraction.

* Oak Ridge National Laboratory.

The procedures for calculating f from the data are similar to those described by Wolfe and Hummel (loc. cit.). However, in addition to using their method for determining the intensity of the 314-keV I.T. by solving simultaneous growth-decay equations involving two spectra of the same sample taken at different times, the intensity of the 314-keV photopeak was measured directly in this work by stripping the spectrum. The γ-ray spectra used for the stripping were taken at times long after chemical separation so that the ^{117}In isomers were in transient equilibrium and any ^{117g}In formed directly from ^{117}Cd had decayed away. The 314-keV photopeak is quite prominent in all the spectra obtained in this work, so that the errors in determining its intensity are not very significant. There is negligible coincidence summing of the 554- and 158-keV γ rays in the spectra. The detector response shape for the 554-keV γ ray was obtained by γ-γ coincidence, gating on the 158-keV peak of ^{117}In, and that for the 314-keV peak was obtained by use of the single 320-keV γ ray of ^{51}Cr. Corrections for absorption and internal conversion of the 314-keV γ ray were made. The experimental α_K's of McGinnis (Phys. Rev. 97, 93, 1955) and K/L+M ratios of Chilosi (private communication) were used in the calculations. To calculate f from the present data, it was necessary to use McGinnis's value (loc. cit.) for the ratio of the intensity of the 1.772-MeV β group to that of the 1.616-MeV β group.

The value of f calculated using the two methods of determining the intensity of the 314-keV isomeric transition gave good agreement. The value of 47.1 ± 2.5% adopted here is the average of two runs using the method of stripping to obtain the 314-keV photopeak intensity. (C.-W. Tang)

D. Reinvestigation of the Decay Schemes of ^{115}Cd Isomers

The ^{115}Cd isomers have been studied earlier in many works and their decay schemes are fairly well known (see Nuclear Data Sheets for references). Because the decay schemes of the ^{117}Cd isomers are very complicated (see Tang, Chilosi, Coryell, and Wapstra, Sect. I.A), we felt it necessary to reinvestigate the decay of the ^{115}Cd isomers and see if, by using Ge(Li) detectors, we could find any transitions and levels, which were undetected in the earlier works.

1. ^{115g}Cd (2.3 day)

Cadmium-115g activity was produced at the MIT reactor by neutron activation of enriched ^{114}Cd. An ion-exchange separation was used to remove the 4.5-hr ^{115m}In daughter. A typical spectrum taken with a Ge(Li) detector is shown in Fig. 1.2. Five γ rays associated with the decay of ^{115g}Cd were found, none of which decays directly to the ^{115}In ground state. Table 1.I shows the energies and intensities of the γ rays relative to the 529-keV line obtained in the present work. Intensity values of Hans and Rao (Nucl. Phys. 44, 320, 1963) and Varma and Mandeville (Phys. Rev. 97, 977, 1955) are also shown in Table 1.I.

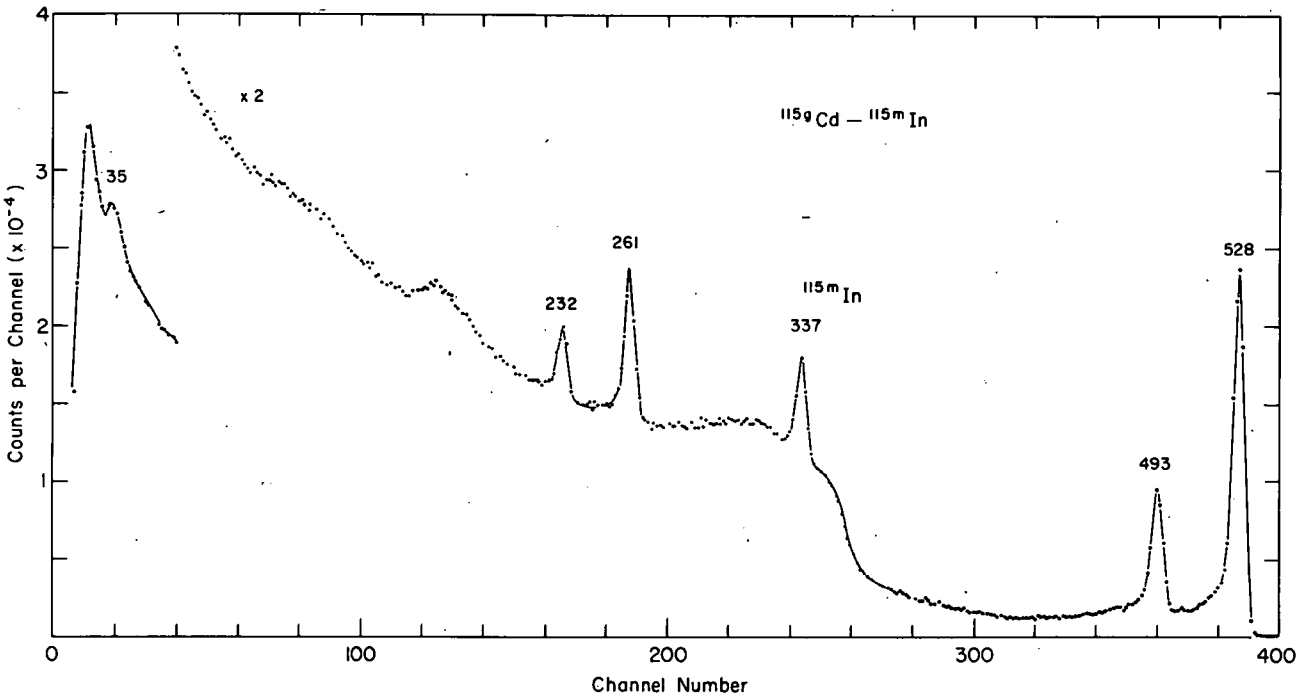


Figure 1.2

Spectrum of γ rays emitted following decay of 2.3-day ^{115g}Cd as observed with a Ge(Li) detector. Energies of the lines are given in keV. Taken using the cold-finger cryostat as the container for the Ge(Li) detector (see Graeffe, Sect. VI. C).

Table 1.I

Energies and relative intensities of γ rays following the decay of ^{115g}Cd

E_γ(keV)	Present Measurement	Hans and Rao	Varma and Mandeville
528	(100)	(100)	(100)
493	25.7	39	51
265	-	<0.2	0.7
261	6.1	7.6	7
232	1.2	1.2	1.3
35	[a]	2.0	

[a] Seen but we do not have an accurate estimate of intensity.

From log ft values, which are shown in Fig. 1.3 it appears that all β transitions are either allowed ($\Delta J = 0, 1$, no) or first forbidden ($\Delta J = 0, 1, 2$ (unique), yes). The spin and parity of the 589-keV level is very likely $3/2^-$. This is indicated by the results of neutron inelastic scattering experiments on ^{113}In (Grench, Paper C9, Conference on Bases for Nuclear Spin-Parity Assignments, Gatlinburg, Nov. 1965), and ^{115}In (Vogt, Phys. Letters 7, 61, 1963). Also the second excited level of ^{117}In seems to be $3/2^-$ (see Tang, et al., loc. cit.).

The study of the conversion-electron spectra and β-γ coincidences using Si(Li) detectors are in progress.

2. ^{115m}Cd (43 day)

Cadmium-115m activity was obtained from Oak Ridge National Laboratory. Chemical purification of the source was performed to remove 260-day ^{110}Ag contamination. We had also in our source ^{109}Cd contamination (88-keV γ ray). Fig. 1.4 shows a spectrum of ^{115m}Cd and Table 1.II gives the γ-ray intensities relative to the 935-keV γ ray. No γ rays due to ^{115m}Cd other than those shown in Table 1.II were observed in either coincidence or direct spectra. Two weak γ rays, 1421 keV and 1452 keV, were seen and assigned to the ^{115m}Cd decay. Log ft values calculated from γ-ray intensities strongly indicate that the β transitions (see Fig. 1.3) are first forbidden. The 935-keV level has been assigned as $7/2^+$ by previous investigators. Spin-parity assignments of $11/2^+$, $9/2^+$, $9/2^+$ to the 1134-, 1294, and 1421-keV levels, respectively, have been proposed by Pandharipande, et al. (Phys. Rev. 136, B346, 1964).

Conversion-electron and β-ray measurements on ^{115m}Cd decay are also in progress. (G. Graeffe and C.-W. Tang)

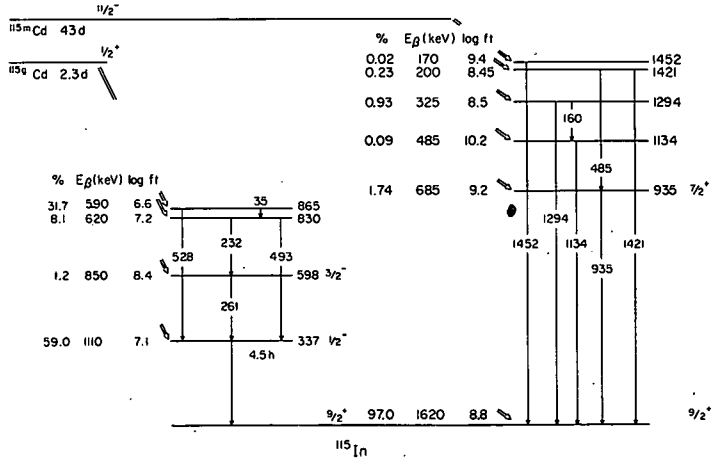


Figure 1.3
Tentative decay schemes for ^{115}Cd isomers based on present work and literature.

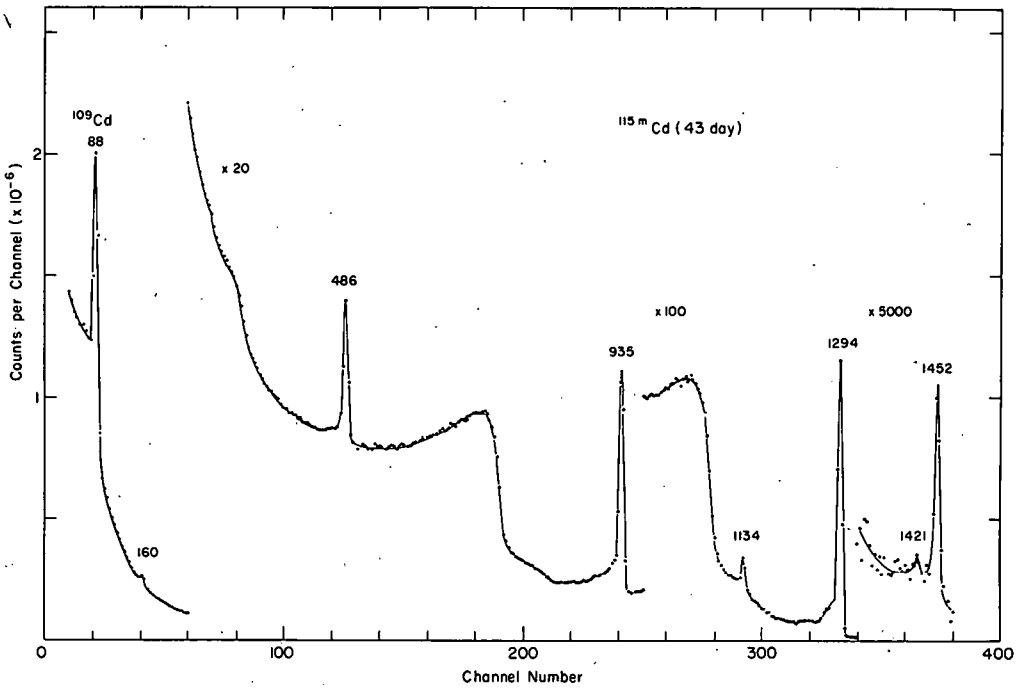


Figure 1.4

Spectrum of γ rays emitted following decay of 43-day ^{115m}Cd as observed with a Ge(Li) detector. Energies of the lines are given in keV.

Table 1.II

Energies and relative intensities of γ rays following the decay of ^{115m}Cd

E_γ(keV)	Rel. Intensity
160	1.2
486	12
935	(100)
1134	4.5
1294	49
1421	0.15
1452	0.9

E. Study of ^{115}Ag Isomers

The decay scheme of 20-min ^{115}Ag (Bahn, Pate, Fink, and Coryell, Phys. Rev. 136B, 203, 1964) is being reinvestigated with Ge(Li) detectors to obtain information on γ rays previously missed with NaI(Tl) technology. (D. J. Hnatowich and C. D. Coryell)

F. Decay-Scheme Studies on ^{127}Sb and ^{129}Sb

Investigations of the decay schemes of 3.9-day ^{127}Sb and 4.3-hr ^{129}Sb have been initiated. We wish to compare the properties of levels in ^{127}Te and ^{129}Te with those of levels known in the lower mass odd-A telluriums and with the theoretical calculations of Kisslinger and Sorensen based on the pairing model for spherical nuclei (L. S. Kisslinger and R. A. Sorensen, Rev. Mod. Phys. 35, 853, 1963). Recently published reaction data from (d,p) and (d,t) reactions on even-mass Te isotopes (R. K. Jolly, Phys. Rev. 136, B683, 1964) and data from the study of ^{125}Sb decay (Stone, Frankel, Huntzicker, and Shirley, UCRL-11828, 1964, pp. 58-62) will enable a detailed comparison to be made with the pairing-theory calculations.

Preliminary investigations of ^{129}Sb have been carried out on samples prepared via the ^{130}Te(γ,p)^{129}Sb reaction on enriched ^{130}Te samples in the photon beam of the Natick Linear Accelerator. Separation of the Sb fraction was based on the formation of Te metal by reduction of Te(IV) with hydrazine hydrochloride and subsequent precipitation of Sb_2S_3 in a 3M HCl solution (S. M. Abecasis, Radiochim. Acta 2, 103, 1963). The γ-ray spectrum of a ^{129}Sb-^{129}Te mixture obtained with a Ge(Li) detector is shown in Fig. 1.5

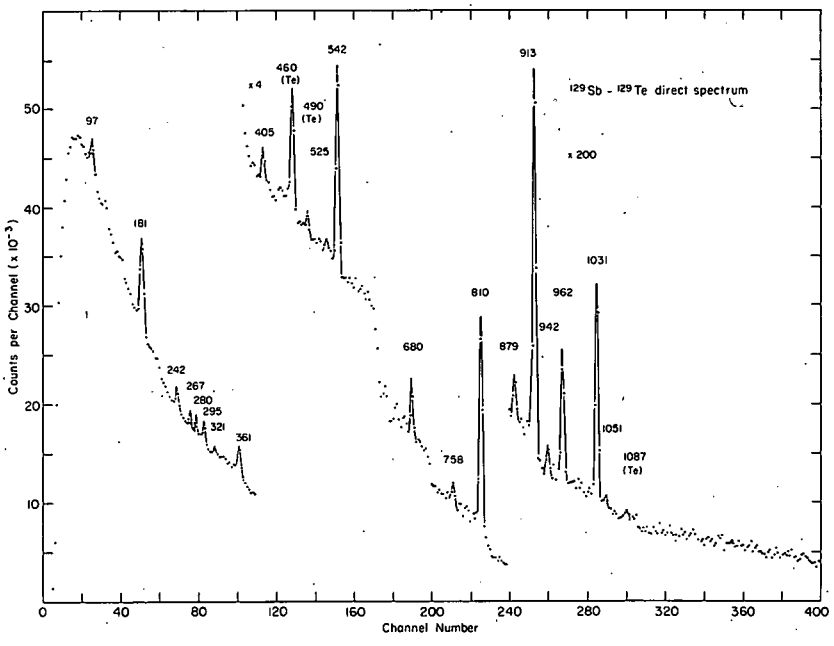


Figure 1.5

Direct γ-ray spectrum of ^{129}Sb taken with Ge(Li) detector. Energies of the peaks are given in keV.

Fission-product samples of ^{127}Sb have been prepared by thermal-neutron irradiation of several mg of ^{235}U for 8 hours. After a decay of 6 days the Sb fraction was separated using a procedure based on a stibine-generation method (K. F. Flynn, L. E. Glendenin, and E. P. Steinberg, Nucl. Sci. Series NAS-NS 3033, 1960, p.36). The Sb separation was performed by precipitation of sulfides in a 3 M HCl solution by saturation with H_2S. The precipitates were dissolved in conc. HCl, and conc. H_2SO_4, and conc. HF was added to complex Sn(IV) as $SnF_6^=$. The solution was then saturated with H_2S to precipitate the sulfides. The dissolved precipitate was reacted with a cold 2.3 M $NaBH_4$ solution to generate stibine which was caught in a trap containing 6 M HCl and several drops of liquid Br_2. One g of hydrazine-hydrochloride was added to precipitate Te metal; 1/2 g of $NaHSO_3$ was added to reduce Sb(V). Eight-hydroxyquinoline was added and the pH adjusted to 5 with conc. NH_4OH and 3 M NH_4Ac in order to precipitate Sb-8 hydroxyquinolate, which was mounted and counted.

The γ-ray spectrum of ^{127}Sb obtained with a Ge(Li) detector is shown in Fig. 1.6. Sum-peak spectra have been obtained with NaI(Tl) detectors and γ-γ coincidences with NaI-NaI detectors and NaI-Ge detectors. Table 1.III shows the energies of ^{127}Sb γ rays and their relative intensities. Beta-ray spectra and β-γ coincidences will be studied as soon as the experimental techniques have been developed. Upon completion of the ^{127}Sb work we plan to finish the work on ^{129}Sb which we have found to be feasible with the use of the Natick Linac. (R. C. Ragaini, G. E. Gordon, and W. B. Walters)

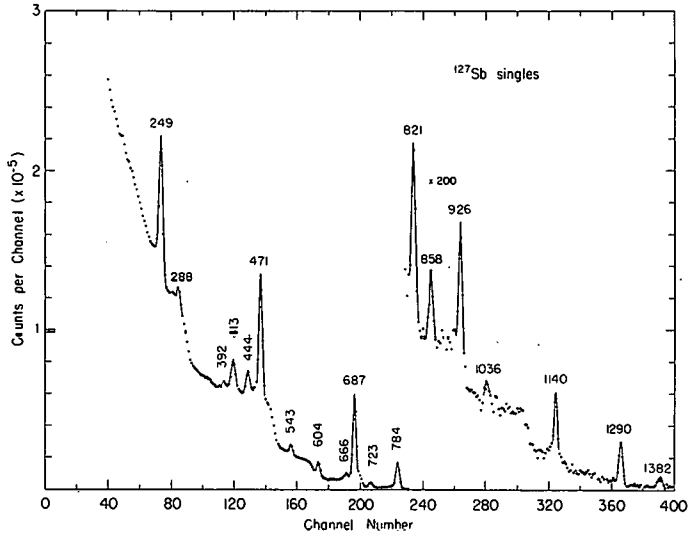


Figure 1.6

Direct γ-ray spectrum of ^{127}Sb taken with Ge(Li) detector. Energies of the peaks are given in keV.

Table 1.III

Energies and relative intensities of γ rays following decay of ^{127}Sb [a]

E_γ(keV)	Rel. Int.	E_γ(keV)	Rel. Int.
62	~15	684	(100)
253	24	720	7
291	3	782	47
394	4	818	2
413	16	858	<1
445	14	926	1
473	73	1036	<1
543	6	1141	1
603	12	1291	1
667	4	1382	<1

[a] Determined from Ge(Li) direct spectrum.

G. Decay Scheme of 25-Minute ^{131g}Te

The following is the abstract of an article published in Phys. Rev. 140, B268 (1965).

The decay of 25-min Te^{131g} produced by $Te^{130}(n, \gamma)$ has been investigated with the use of Ge(Li) and NaI(Tl) γ-ray detectors. Coincidence relationships among the γ rays were determined in γ-γ and sum-peak coincidence experiments. Because of the good resolution of the Ge(Li) detector we have been able to resolve complex γ-ray peaks observed in the ~350- and 950- to 1000-keV regions in previous studies and to observe additional γ rays. The energies (in keV) of observed γ rays and their percentage intensities relative to 150-keV (in parentheses) are: 279 (1), 343 (1.1), 384 (1.1), (453 (24.0), 493 (7.0), 544 (0.4), 603 (5.9), 654 (1.8), 695 (0.3), 727 (0.4), 842 (0.2), 898 (0.3), 933 (1.2), 948 (3.0), 952 (0.6), 997 (5.1), 1007 (1.5), 1098 (0.8), 1147 (9.4), 1295 (1.4). The main changes from previous level schemes for I^{131} are the lowering of the ~350-keV transitions to near the ground state and the addition of levels at 877, 1188, and 1445 keV. Preliminary measurements on the γ rays of 1.2-day Te^{131m} are reported. Trends of the low-lying levels of odd-A iodine isotopes from mass 127 to mass 131 are discussed. The half life of Te^{131g} was determined to be 25.0 ± 0.1 min. (W. B. Walter, C. E. Bemis, Jr., and G. E. Gordon)

H. Preliminary Investigation of the Decay Scheme of ^{131m}Te

This work was begun to determine whether or not any of the γ-ray lines observed in the 25-min ^{131g}Te spectra (see Walters, Bemis, and Gordon, Sect. II.G) could be attributed to a small amount of 30-hr ^{131m}Te that might be present in the sample.

In Fig. 1.7 is shown a γ-ray spectrum of ^{131m}Te obtained by counting several samples of irradiated ^{130}Te overnight using a Ge(Li) detector. The count was started about 15 hours after irradiation so that the ^{131g}Te produced directly by neutron capture had completely decayed leaving 30-hr ^{131m}Te, 8-day ^{131}I, and ^{131g}Te in equilibrium with ^{131m}Te. Gamma-ray peaks from all of these species are seen as well as 511-keV annihilation radiation from 12.9-hr ^{64}Cu. The lines not identified with ^{131g}Te, ^{131}I, or ^{64}Cu are presumed to accompany the β decay of ^{131m}Te. In Fig. 1.8 is shown a Ge(Li) spectrum obtained with a similar source by requiring coincidence with events in a NaI(Tl) crystal. No gate was set on the pulses from the NaI detector so that any pulse corresponding to an energy greater than 40 keV would permit the 400-ch. analyzer to accept a pulse from the Ge(Li) detector. This technique largely eliminates γ rays from ^{131}I whose decay has only one 2 γ-ray cascade and indicates roughly which ^{131m}Te lines are parts of γ-ray cascades.

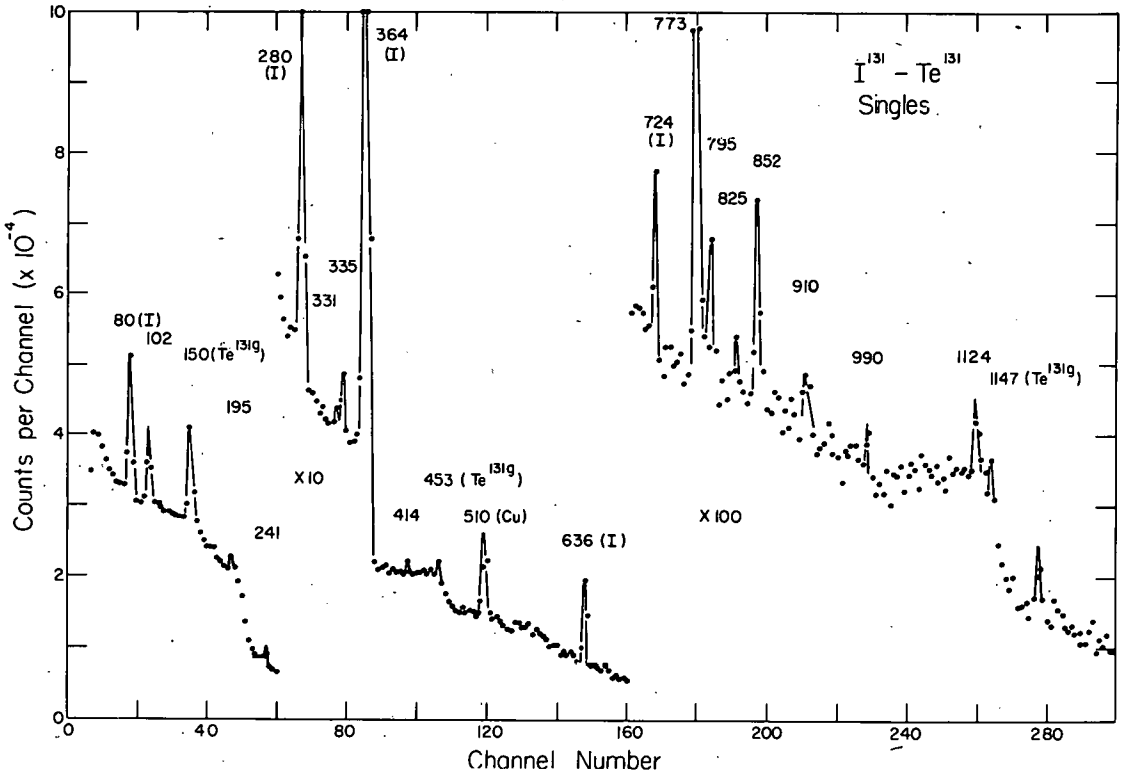


Figure 1.7

Gamma-ray spectrum of neutron-irradiated ^{130}Te samples taken 15 hours after end of irradiation with a Ge(Li) detector. Lines labelled ^{131g}Te, I and Cu are attributed to the decay of 25-min ^{131g}Te, 8-day ^{131}I, and 12.8-hr ^{64}Cu impurity, respectively; the other lines are presumed to arise in the decay of 30-hr ^{131m}Te.

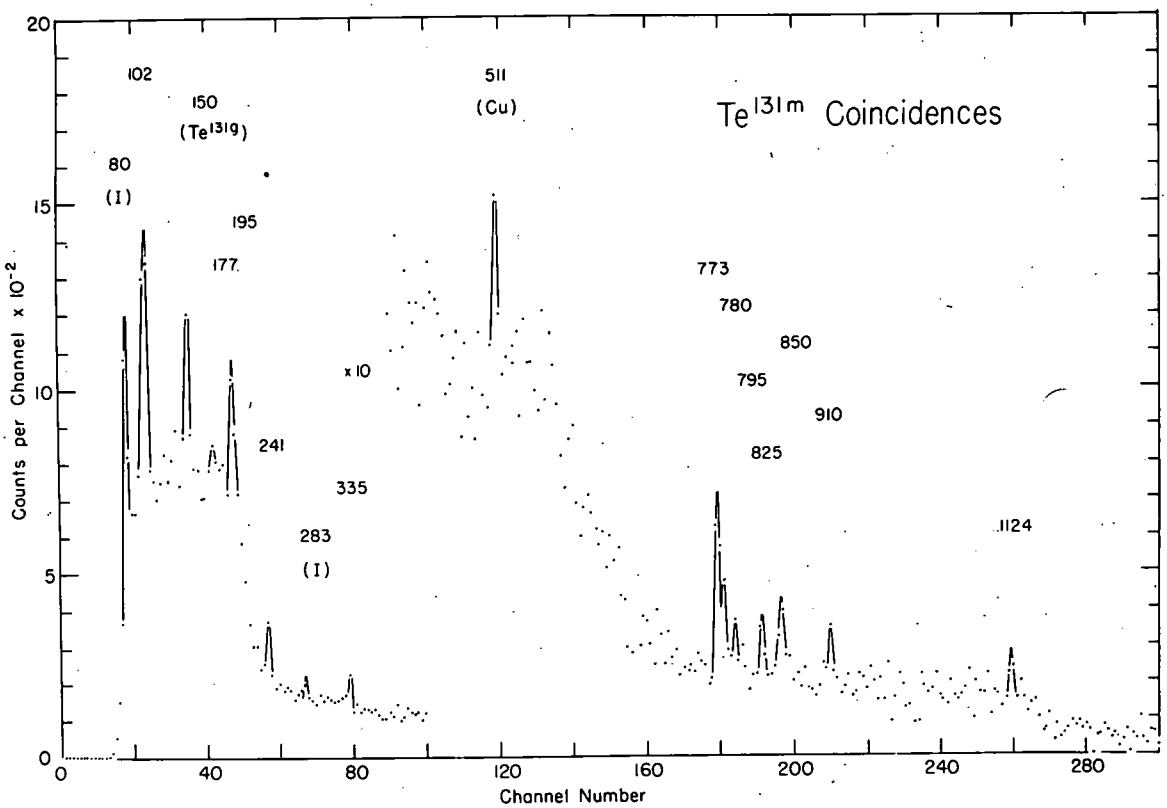


Figure 1.8

Gamma-ray spectrum observed with Ge(Li) detector, with source similar to that of Fig. 1.7, in coincidence with pulses corresponding to $E_\gamma > 40$ keV observed in NaI detector. Labelling of peaks is the same as for Fig. 1.7.

The γ rays attributed to ^{131m}Te are in reasonable agreement with the results of both Bedescu-Sigureani (Rev. Phys., Acad. Rep. Populaire Roumaine 1, 173, 1962) and Devare, Singru, and Devare (Phys. Rev. 140, B536, 1965). While the former workers were unable to construct an unambiguous decay scheme because of the inherent poor resolution of the NaI detectors used, the latter workers using both internal and external spectrometers as well as Ge(Li) detectors have arrived at a decay scheme. There are inconsistencies surrounding the levels populated by the decay of both isomers as well as a lack of information concerning a number of spin assignments. We have planned additional studies where we hope to be able to study the decay of the isomer alone by chemically removing the ^{131g}Te which is formed in about 13% of the decay of the ^{131m}Te (see Walters and Esterl, Sect. I.I). Using such a procedure would enable us to be certain of which levels populated in the decay of ^{131g}Te are also populated in the decay of ^{131m}Te.
(W. B. Walters and G. E. Gordon)

I. Preliminary Investigation of the Decay Schemes of ^{129g}Te and ^{129m}Te.

This work was initiated to determine whether any of the weaker lines observed in the decay of irradiated ^{130}Te (see Walters, Bemis, and Gordon, Sect. I.G) might be due to small amounts of ^{129g}Te produced by neutron capture on ^{128}Te in the target. This was done since our first ^{130}Te separated isotope contained nearly 3.5% ^{128}Te. (Later ^{130}Te samples were much more nearly free of other Te isotopes.) Our interest in obtaining a better understanding of the levels of ^{129}I grew as we studied the levels of ^{131}I, and found it possible to observe a number of similarities in the levels of the two nuclei.

Although the decay of ^{129}Te has been studied a number of times, our early spectra obtained with a Ge(Li) detector indicated the presence of several γ rays that had not been previously reported. The lowest two levels of ^{129}I are separated by only 27 keV and without the good resolution of the Ge(Li) detector, it had not been possible to resolve pairs of γ rays resulting from the decay of a higher level to the two lowest states. Because of the difficulty involved in obtaining coincidences with the 27-keV level, it was difficult in some cases to tell which of the two lower levels was being populated. Since the absence of a transition to a level of known spin and ratios between transition rates to other levels of known spins are important factors in the assignment of spins, it was immediately possible to propose changes of spin for some levels in the recently published decay schemes (S. H. Devare and H. G. Devare, Phys. Rev. 134, B705, 1964; A. V. Ramayya, Y. Yoshizawa, and A. C. G. Mitchell, Nucl. Phys. 56, 129, 1964).

Of the earlier investigations, only Devare and Devare had access to an irradiated sample within a short time after irradiation in order to study the decay of the 70-min ^{129g}Te. The other studies were carried out using the 33-day ^{129m}Te which decays ~33% of the time by β decay to levels in ^{129}I and by an internal transition to the 70-min isomer. As a result, there was some difficulty in determining which of the two isomers gave rise to a particular γ ray.

Recently Bornemeier, Potnis, Ellsworth, and Mandeville (Phys. Rev. 138, B525, 1965) have reported a study of the equilibrium mixture using a Ge(Li) detector. There are some serious discrepancies between their results and our own regarding the energies of several of the observed γ rays as is shown in Table 1.IV. Our results are from experiments carried out using three different Ge(Li) detectors, calibrated carefully in the region of disagreement (~300-900 keV).

In addition to the discrepancies in the γ-ray energies, there are a number of other features of the Bornemeier, et al., decay scheme that do not appear to be in agreement with the data they presented, with the work of earlier investigators, or our work. A γ-ray spectrum taken with a Ge(Li) detector is shown in Fig. 1.9. The ^{129g}Te was produced by irradiating 3 mg of ^{128}Te (>99% isotopically pure) in the MIT Reactor for 5 minutes. Because of the short irradiation time and the low cross section, it is unlikely that any interference from ^{129m}Te decay occurs.

Table 1.IV

Energies and relative intensities of γ rays from ^{129}Te decay

This work - ^{129g}Te only		Potnis, et al., - ^{129m,g}Te equilib - mixture	
E_γ(keV)	Rel. Intensity	E_γ(keV)	Rel. Intensity
208	2.2	205	1.53
251	5.0	250	0.48
278-280	9.8	277	12.10
343	0.7	340	0.74
461	100.0	455	100.00
488	20.3	482	27.20
533	2.0	523	2.65
550	0.4	550	2.61
624	1.4	630	1.01
		660	0.60
		698	83.60
		725	19.80
735	0.4		
742	0.6		
		770	3.53
		797	2.72
803	2.2	810	1.53
835	0.3	835	1.44
847	0.8		
945	0.2	945	0.62
1004	0.2		
1084	7.5	1085	9.86
1111	2.2	1112	3.03
		1222	0.60

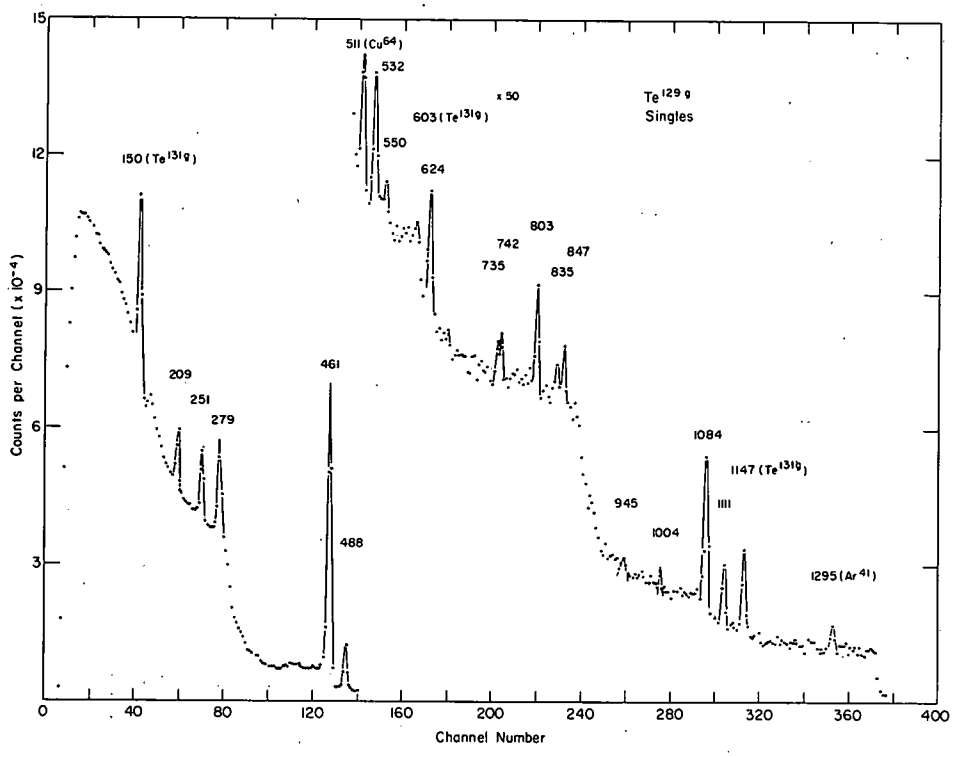


Figure 1.9

Gamma-ray spectrum of 70-min ^{129g}Te taken with a Ge(Li) detector.

With the improved γ-ray spectrometer system that we are now setting up, we expect to be able to gain a much better understanding of the decay of the ^{129g}Te by studying samples irradiated for ~5 min where there is no interference from ^{129m}Te.

Studying ^{129m}Te without interference from ^{129g}Te is a more difficult problem. It is our intention to take advantage of the observation that accompanying the internal transition from the isomeric state to the ground state there can also be a change in the chemical state of the Te atom. This was observed in 1939 by Seaborg and Kennedy (Phys. Rev. 55, 410, 1939) and recent studies indicate that nearly 100% separation is possible (R. L. Hahn, J. Chem. Phys. 41, 1986, 1964). By preparing the ^{129m}Te in solution as telluric acid, it has been observed that the ^{129g}Te formed by the internal transition is found in solution as tellurous ion and may be extracted from the solution with tributyl phosphate. By repeated extraction, it should be possible to keep the interference from the ^{129g}Te at a minimum during the study of the ^{129m}Te decay.

We show in Fig. 1.10 an incomplete decay scheme which includes some revised spin assignments obtained with the knowledge of the branching ratios and a comparison with ^{127}I levels whose spins have been assigned by angular correlation (J. S. Geiger, Phys. Letters 7, 48, 1963). The spins are not in accord, however, with the results of angular correlation studies reported by Arya and Nicholson (Bull. Am. Phys. Soc. 10, 588, 1965) whose assignments are listed in brackets. The absence of a spin 1/2 level in this region would be difficult to understand in view

of the work on ^{127}I. We have not attempted to assign log ft values for two reasons, the intensity of the 27-keV transition has yet to be measured, and until the 280 peak is resolved, it will be difficult to assign the γ intensity of transitions leading from the 560- and 278-keV levels. It is not difficult to see, however, that the 278- and 560-keV levels are not fed as intensely as the 488-keV level. This weak β-decay branching to levels suspected of being highly phonon mixed was observed in the ^{131g}Te decay and is not unexpected here. It will be important to determine the log ft's accurately in order to see how closely they compare with those in ^{131g}Te decay and to see if any differences can be accounted for theoretically. (W. B. Walters and J. Esterl)

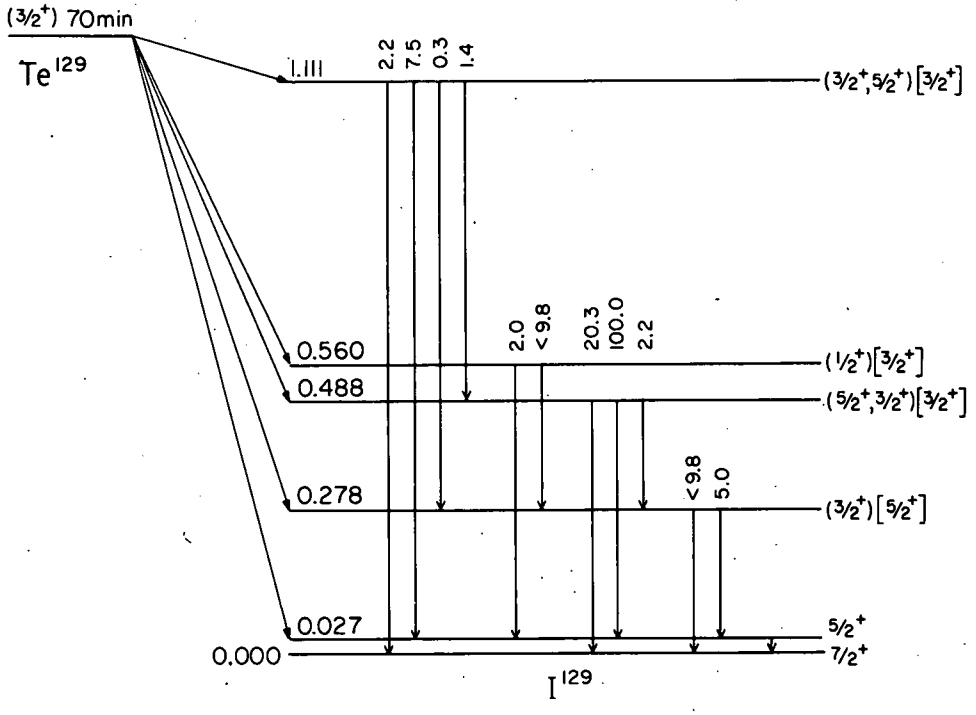


Figure 1.10

Partial decay scheme of 70-min ^{129g}Te populating levels in ^{129}I. The numbers above γ rays are relative intensities.

J. Preliminary Investigation of the Decay of ^{123}Sn

One of the interesting features of the decay of ^{131g}Te was the log ft values for β transitions from the $d_3/_2$ ground state of ^{131g}Te to levels of spins $^1/_2+$ and $^3/_2+$ in ^{131}I that are thought to be highly phonon mixed. The log ft values for these transitions are found to be higher than would be expected for allowed transitions. Though it has not been possible to calculate quantitative log ft values for similar transitions in the decay of ^{129g}Te, qualitatively the log ft values for these transitions appear to be high. Since the calculations of Kisslinger and Sorensen (Rev. Mod. Phys. 35, B53, 1963) indicated the presence of similar highly phonon-mixed levels in Sb isotopes of spins $^1/_2$ and $^3/_2+$, we have investigated the decay of ^{123}Sn to determine whether such levels are

present in ^{123}Sb and if present, how are they populated in the decay of the $d_{3/2}$ isomer of ^{123}Sn. Similar studies may be initiated on ^{125}Sn and ^{127}Sn. The most recent work on the decay of the $d_{3/2}$ isomer of ^{125}Sn (S. H. Devare and H. G. Devare, Phys. Rev. 133, B538, 1964) indicates the presence of 2 levels with high log ft values, but assigns them spins of $^1/_2$+ and $^5/_2$+ or $^7/_2$+. The assignment of the latter is somewhat questionable in view of the quoted log ft of 8.4. This is nearly 2 orders of magnitude low for a second forbidden transition required to connect states of $^3/_2$+ and $^7/_2$+.

In Fig. 1.11, we have shown the current decay scheme from the Nuclear Data Sheets. Initial γ-ray spectra taken with a Ge(Li) detector indicate the presence of 384- and 544-keV γ rays as well as the 160-keV γ ray. The 384- and 544-keV γ rays probably result from the decay of the 544-keV level seen in coulomb-excitation experiments. Another prominent γ ray is seen at 1151 keV and several questionable peaks appear in the region from 600 to 800 keV. All of the new γ rays mentioned are present in very low intensity, being only ~1/10,000 as intense as the 160-keV γ ray. There is little doubt that the log ft value for the β decay to the 544-keV level will be higher than that expected for an allowed transition. We hope to be able to obtain the complete decay scheme for the $d_{3/2}$ isomer of ^{123}Sn. (W. B. Walters)

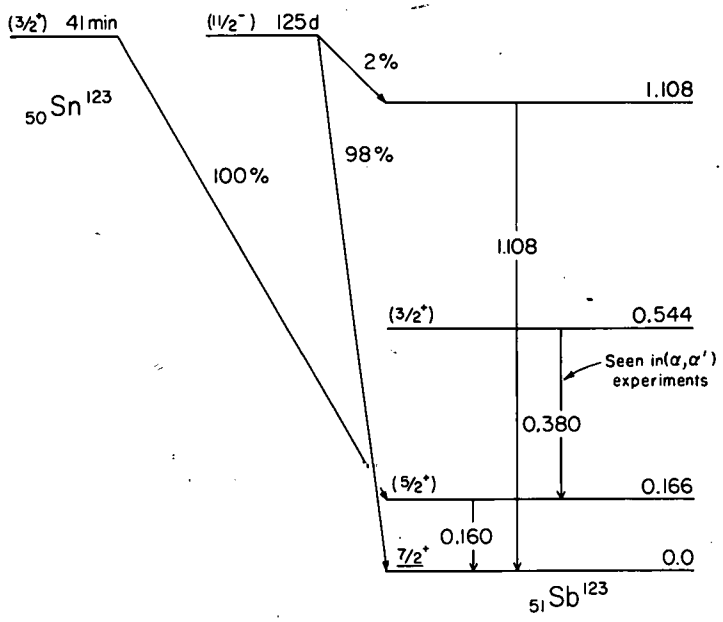


Figure 1.11
Decay scheme of ^{123}Sn isomers populating levels of ^{123}Sb.

K. Search for ^{46}K

Potassium-46, a previously unknown nuclide, and ^{46}Ca are very interesting from a shell-model viewpoint. Recently some of the levels of ^{46}K were studied by the ^{48}Ca(d, α) nuclear reaction (A. Marinov and J. R. Erskine, Phys. Letters 14, 46, 1965). The study of ^{46}K is of special interest because it decays to ^{46}Ca whose levels have not been well characterized because of its low abundance and because ^{46}Sc decays by β^- emission.

Calcium enriched to 96% in ^{48}Ca, in the form of $CaCO_3$, was wrapped in 0.15-mil Au foil and repeatedly irradiated with 15-MeV deuterons from the MIT cyclotron. Within about 2 min after each bombardment, radiations emitted by the sample were counted in an arrangement that discriminates against all radiations except β rays above about 3 MeV. An activity of half life 112 ± 12 sec. has been observed. As we have predicted the half life of ^{46}K to be in the range from a few seconds to several minutes, this could be ^{46}K. However, additional experiments are in progress to check on the possibility of its being 1.8-min ^{50}Sc (from $^{48}Ca(d, \gamma)$) or 2-min ^{15}O (from $^{16}O(d, t)$). (B. Parsa and G. E. Gordon)

L. Search for Delayed Neutrons Following Decay of 2-Sec ^{135}Sb

Since the last progress report (Bemis, Muga, Gordon, and Coryell, LNS Prog. Rep. Nov. 1964, p. 29), we have revised the chemical-separation scheme in an attempt to improve the Sb yields and decrease halogen contamination. According to the new scheme, the irradiated solution (5 mg ^{235}U in H_2O, irradiated for 30 sec) is first drawn into a flask containing 20 mg Sb(III) carrier. A stop cock is opened and the solution added fairly rapidly to 20 ml of a 20% $NaBH_4$ solution in the reaction vessel. Upon contact with the surface, SbH_3 gas is formed and drawn directly into a trap inside the neutron counter where the Sb is precipitated (as Ag_3Sb) by 1.5 M $AgNO_3$.

In Table 1.V are given the results of a least-squares computer analysis of the neutron decay curve of a sample produced with the new separation method. In this experiment, counting started 15.5 sec after the end of irradiation. The apparent chemical yields of the halogen contaminants have been reduced considerably from the yields obtained previously with the separation based on SbH_3 production from $Zn + H_2SO_4$ (see Bemis, et al., loc. cit.). If we assume that 2-sec component is associated with ^{135}Sb and that the Sb chemical yield is about 30%, which has been measured in separate tracer experiments, the neutron-branching ratio of ^{135}Sb is about 1%. This value compares well with the values of ~2% and ~5% that we have estimated from the data presented by del Marmol, de Mevergnies, and Speecke (IAEA Symp. on Physics and Chemistry of Fission, Salzburg, March 1965, paper SM-60/74) and Tomlinson (ibid., paper SM-60/62), respectively, on the assumption that all of the 2-sec component originates with ^{135}Sb. Our result, however, is subject to considerable uncertainty. Because of the complexity of the decay curve, the least-squares analysis can be performed with a wide variety of choices about the half lives of the components present. The results presented were those from the analysis giving the best values of the goodness-of-fit quantities (χ^2 and variance-of-fit). However, the results are inconsistent in that they include no 5- to 6-sec component for the 6.3-sec ^{138}I and 4.4-sec ^{89}Br that should accompany the other halogen contaminants that are clearly present.

Table 1.V

Results of least-squares fit to the neutron decay curve.

Half life (sec)	Species	Initial activity [a] (c/sec)	Apparent chem. yield (%)
56	^{87}Br	$3.91 \cdot 10^{2}$	0.11
23.5	^{137}I	$3.66 \cdot 10^{3}$	0.25
16.8	^{88}Br	$1.3 \cdot 10^{3}$	0.06
2	(^{135}Sb?)	$1.95 \cdot 10^{2}$	~30 [b]

[a] At start of counting, 15.5 sec after irradiation.

[b] Measured in separate tracer experiments.

A further source of difficulty is that As should pass through the chemical separation with a yield comparable to that of Sb. Thus, we cannot distinguish between As and Sb as the source of the 2-sec group. In the preprints of their Salzburg papers, del Marmol, et al. (loc. cit.) were unable to determine clearly whether the 2-sec group came from Sb or As, and Tomlinson (loc. cit.) found indications for both As and Sb 2-sec delayed-neutron precursors. But in the oral presentation, del Marmol reported more recent results that indicated that the 2-sec species is As.

We have decided to discontinue this project. Even with improved decontamination obtained with the new separation technique, any 2-sec Sb or As component in the decay curve is overwhelmed by the longer-lived halogen contaminants. We cannot possibly speed up the sample preparation by more than 1 or 2 sec without actually placing the reaction flask in or near the reactor. Thus, in view of the difficulties encountered by del Marmol, et al., and Tomlinson even with much quicker access to the samples, we do not feel we can perform experiments that will clearly indicate the origin of the 2-sec group.

It should be noted that the really interesting feature of our work and of del Marmol's and Tomlinson's is the small neutron branching ratio of ^{135}Sb, at most ~5% but probably much lower. According to Seeger's mass formula (Nucl. Phys. 25, 1, 1961), Q_β of ^{135}Sb is 8.86 MeV and S_n of ^{135}Te is 2.91 MeV. With such a large Q_β-S_n, 5.95 MeV, one predicts from the Pappas-Rudstam treatment (Nucl. Phys. 21, 353, 1960) that the neutron branching ratio is 70%. Some complications may arise because of angular-momentum hindrance discussed by Sugihara (Clark Univ., Dept. of Chem., Prog. Rep., 1962). The ground-state spin of ^{135}Sb is probably $7/2^+$. Allowed β decay would give levels of spins 5/2, 7/2, and 9/2+. If neutron emission is to leave ^{134}Te in its ground state (0+), then the ℓ of the outgoing neutron would have to be 2 or more. Levels of ^{135}Te only slightly above S_n would be formed in highest probability among those from which neutron emission is possible. Neutrons emitted from those levels would have very low energies and small transmission coefficients [$T_\ell(E_n)$] for $\ell \geq 2$, thus possibly greatly hindering neutron emission relative to γ-ray emission. A certain amount of neutron emission should still be possible, in spite of this

difficulty, from levels in ^{135}Te having energies greater than $S_n + E_{2+}$, where E_{2+} is the energy of the 2+ first excited state of ^{134}Te, probably ~1 MeV. Levels of spin 5/2+ could then emit $\ell = 0$ neutrons, leaving ^{134}Te in its first excited state. Because of the high energy required of the states in ^{135}Te, they would probably not be populated very heavily in the β decay of ^{135}Sb. (D. A. Muga, G. E. Gordon, and C. D. Coryell)

II. Nuclear Fission Studies

A. Ranges of Shielded Nuclides from Thermal-Neutron Fission of ^{233}U and ^{235}U.

In this study the ranges in Al of shielded nuclides 18.7-day ^{86}Rb and 13-day ^{136}Cs are to be determined, as well as those of chain-yield species ^{89}Sr, ^{99}Mo, ^{137}Cs, and ^{140}Ba, for calibration and monitoring, and ^{111}Ag and ^{115}Cd, as typical symmetric-fission products.

As the independent yields of ^{86}Rb and ^{136}Cs are $1.5 \cdot 10^{-4}$ and 0.1% from ^{233}U fission, and $3 \cdot 10^{-5}$ and $6 \cdot 10^{-3}$% from ^{235}U fission, respectively, a procedure for separation of Rb from Cs with a decontamination factor of at least 10^5 is necessary.

An ion-exchange procedure giving a decontamination factor of greater than 10^6 has been developed. The main part of the procedure involves elution of the Rb-Cs mixture (each with about 30 mg carrier) from a 1:1 asbestos-AMP (ammonium molybdophosphate) column with NH_4NO_3-HNO_3 solution.

Because of the low ^{86}Rb activity produced in fission, it was necessary to check on the amount produced by (n, γ) reactions on any Rb impurity in the Al catcher foils. The amount produced in irradiations of Al foils was below the background level (~1-2β/min) of the low-background β proportional-counter and, thus, gives negligible contribution in the fission experiments.

Three range experiments have been performed on ^{233}U and on ^{235}U. The thin-target - thick-catcher method, as described by Aras, Menon, and Gordon (Nucl. Phys. 69, 337, 1965), was used.

The fission products of interest were separated from the Al catcher foils using the techniques discussed above and in the previous report (Amano and Nakahara, LNS Prog. Rep., Nov. 1964, p. 47). Counting of radiations from the samples was done as follows:

^{99}Mo, ^{115}Cd, and ^{140}Ba. A conventional β-proportional counter and, separately, a 256- or 400-ch. pulse-height analyzer and 3- x 3-in NaI(Tl) crystal were used for β and γ counting, respectively. Results obtained by the two different methods were compared to determine the level of contamination of samples and the effect of self-absorption and -scattering in the β measurements. Results for the two methods are listed separately in Table 1.VI.

^{89}Sr and ^{111}Ag. Only β counting was possible as neither species emits strong γ rays.

^{136}Cs and ^{137}Cs. These were determined by γ-ray spectrometry. Areas under the 0.822- and 1.04-MeV peaks were taken for ^{136}Cs and that of the 0.662-MeV peak for ^{137}Cs. After about 10 half lives of ^{136}Cs, we looked for the 0.794-MeV peak of ^{134}Cs, but it was below the limit of detection. Thus, the contribution of the 0.605-MeV line of ^{134}Cs is at most 1% in the 0.662-MeV

peak of ^{137}Cs.

^{86}Rb. A conventional β-proportional counter was used for the ^{233}U runs and the activity due to natural ^{87}Rb in the Rb carrier was subtracted after decay of the ^{86}Rb. In most cases the ^{87}Rb activity was about 10% that of ^{86}Rb in the least active foil (third catcher) and about 1% in Foils 1 and 2. In the ^{235}U runs, the ^{86}Rb and ^{87}Rb activities were comparable, so we used a 43-mg/cm^2 Al absorber and a low-background ($\sim$ 1-2 c/min) β counter.

The range values obtained from the various experiments are listed in Table 1.VI. The errors attached to the mean values are standard deviations of the mean. Ranges were calculated according to the method discussed by Aras, et al. (loc. cit.).

Table 1.VI

Tentative values of ranges in Al of fragments from thermal-neutron fission of ^{233}U and ^{235}U.

Fission product	Radiation counted	Range (mg/cm^2) ^{233}U	Range (mg/cm^2) ^{235}U
^{86}Rb	β	3.78±0.03	3.81±0.05
^{89}Sr	β	4.04±0.02	-
^{99}Mo	β	3.96±0.03	3.91±0.02
	γ	3.95±0.03	3.94±0.02
^{111}Ag	β	3.50±0.03	3.44±0.02
^{115}Cd	β	-	3.30±0.02
^{136}Cs	γ	2.79±0.01	2.80±0.01
^{137}Cs	γ	2.97±0.02	3.01±0.03
^{140}Ba	β	2.90±0.01	3.01±0.02
	γ	2.90±0.01	3.01±0.02

After completing the range measurements, we will work on conversion of ranges to corresponding kinetic energies. Also, we are calculating predictions of the kinetic-energy deficit of shielded nuclides according to the treatment of prompt-neutron emission by Gordon and Aras (IAEA Symposium on the Physics and Chemistry of Fission, Salzburg, March 1965, paper SM-60/48). (H. Nakahara, J. W. Harvey, and G. E. Gordon)

B. The Fractional Chain Yield of ^{126}Sb in Thermal-Neutron Fission of ^{235}U

The following is the abstract of a paper accepted for publication in J. Inorg. Nucl. Chem.

The fractional chain yield of 12.5-day ^{126g}Sb in thermal-neutron fission of ^{235}U has been measured by following the β decay of antimony samples separated several weeks after an irradiation. The observed ^{126g}Sb is the sum of contributions from ^{126g}Sb produced in fission and that resulting

from 19-min ^{126m}Sb, which decays 15% by isomeric transition. The ^{126m}Sb was not observed, but its independent yield relative to that of ^{126g}Sb was estimated on the basis of theoretical calculations which took into account the spins, 5+ and 8-, of the upper and lower isomers, respectively. The sum of the fractional chain yields of the ^{126}Sb isomers was determined as $(4.5 \pm 0.6) \cdot 10^{-2}$, leading to a value of most-probable charge, Z_p, for A=126 of 49.45 ± 0.05. By γ-ray spectrometry on the samples, the yield of 60.9-day ^{124g}Sb was determined relative to that of 2.78-yr ^{125}Sb. The resulting fractional chain yield for ^{124}Sb, $\leq 2.6 \cdot 10^{-3}$, gives Z_p of ≤ 48.75 for A = 124.

. . .

After submitting the paper, we received the manuscript of a paper by Strom, Grant, and Pappas, that has since been published (Can. J. Chem. 43, 2493, 1965), covering much the same kind of work. Strom, et al., were also unable to measure directly the yield of ^{126m}Sb and made a theoretical estimate of the isomer-yield ratio $Y(^{126m}Sb)/Y(^{126g}Sb)$, obtaining a value of 5.65. The value of the same quantity as calculated in our work is 4.8. Their measured yield of ^{126g}Sb is in good agreement with the value obtained in our study.

In the case of ^{124g}Sb, we have treated our measured value as an upper limit as the amount observed could have been produced entirely by ^{123}Sb(n, γ) on natural Sb contamination in the ^{235}U target if the amount of Sb present was just below our limit of detection (0.02% by weight). Consistent with this assumption, Strom, et al., obtained an ^{124g}Sb yield about a factor of 5 lower than that of ours.

A summary of our results and those of other workers is given in Table 1.VII. The fractional chain yields for ^{126}Sb and ^{124}Sb determined in our work correspond to the most-probable-charge values given above in the abstract which are in good agreement with the values obtained by Strom, et al., $Z_p(126) = 49.39 \pm 0.14$ and $Z_p(124) = 48.49 \pm 0.20$, by assumption of the empirical charge distribution

$$P(Z) = \frac{1}{\sqrt{\pi C}} \exp\left[-(Z - Z_p)^2/C\right],$$

where C = 0.94.

This work was initiated at MIT and completed in part at Oak Ridge National Laboratory, operated by the Union Carbide Corporation. (N. K. Aras and G. E. Gordon)

Table 1.VII

Fission yields of ^{124}Sb, ^{125}Sb, and ^{126}Sb

Species	Fission Yield (%)		Fractional chain Yield
	This work (rel. to ^{127}Sb=0.13)	Literature	
^{124}Sb	$\leq 4.4 \cdot 10^{-5}$	$(9.5 \pm 1.4) \cdot 10^{-6}$ [a]	
		$\leq 4.5 \cdot 10^{-5}$ [b]	
Est. ^{124}Sb	$\leq 4.8 \cdot 10^{-5}$ [c]	$(1.16 \pm 0.17) \cdot 10^{-5}$ [a]	$(6.8 \pm 1.0) \cdot 10^{-4}$ [a]
all isomers		$\leq 4.9 \cdot 10^{-5}$ [c]	$\leq 2.6 \cdot 10^{-3}$ [d]
^{125}Sb	0.021 ± 0.001	0.036 ± 0.007 [b]	
		0.21 [e]	
^{126g}Sb	$(8.5 \pm 0.5) \cdot 10^{-4}$	$(1.04 \pm 0.17) \cdot 10^{-3}$ [a]	
		$(9.0 \pm 2.0) \cdot 10^{-4}$ [b]	
		$(9.0 \pm 2.5) \cdot 10^{-4}$ [f]	
Est. ^{126}Sb	$(2.9 \pm 0.2) \cdot 10^{-3}$ [g]	$(3.7 \pm 0.6) \cdot 10^{-3}$ [a]	$(3.7 \pm 0.6) \cdot 10^{-2}$ [a]
both isomers		$(3.0 \pm 0.7) \cdot 10^{-3}$ [g,b]	$(5.2 \pm 0.3) \cdot 10^{-2}$ [h]
		$(3.0 \pm 0.8) \cdot 10^{-3}$ [g,f]	$(3.8 \pm 0.2) \cdot 10^{-2}$ [i]

[a] Strom, Grant, and Pappas, Can. J. Chem. 43, 2493 (1965). Measured relative to ^{140}Ba = 6.35%.

[b] K. Flynn and L. E. Glendenin, Argonne National Lab., private communication, 1965. Measured relative to ^{137}Cs = 6.15%.

[c] Using assumption that 10% of the upper isomers are lost by β decay of 93-sec $^{124m_1}Sb$ (J. Vanhorenbeeck, Nucl. Phys. 37, 90, 1962; G. Lange, Ph.D. thesis Univ. of Mainz, 1963).

[d] Calculated assuming chain yield of A=124 is 0.018% (S. Katcoff, Nucleonics 18, No.11, 201, 1960).

[e] Katcoff compilation (loc. cit.).

[f] G. Herrmann and G. Lange, Univ. of Mainz, private communication, 1965.

[g] Calculated from ^{126g}Sb yield using theoretical estimate of the independent isomer-yield ratio, $Y(^{126m}Sb)/Y(^{126g}Sb) = 4.8$.

[h] Calculated from fission yields of this work using the value for the ratio of chain yields 126/127 of 0.42 obtained by interpolation of Katcoff's (loc. cit.) yield-mass curve.

[i] Calculated from fission yields of this work assuming the yield-mass curve is linear between A=125 and 127.

C. Kinetic Energy Release in Photofission of ^{238}U and ^{232}Th

We are presently attempting to improve the treatment of the raw photofission kinetic-energy data prior to publication of the results. In our previous report on this work (Brenner, Cooper, and Gordon, LNS Prog. Rep., Nov. 1964, p. 41) there were some asymmetries in the final

results plotted as a function of mass of the fragments. This effect was present, for example, in Fig. 2.24 of the previous report, which showed total kinetic energy for ^{232}Th as a function of fragment mass. A curve through the points should be approximately symmetric about A ≈ 115, but is not. Similar difficulties are encountered where the experimental dispersion of kinetic energy is plotted as a function of mass number.

We believe these discrepancies arise from one or two possible sources. In the original transformation of the pulse-height - pulse-height coincidence spectra to other coordinates, the effects of the mass-dependent pulse-height defect (Schmitt, Kiker, and Williams, Phys. Rev. 137, B837, 1965) were included only in approximate form. We have now revised the transformation program to take account of the effect more accurately. The second possible source of error is the effect of absorbers upon the kinetic energy spectra. Correction of the raw kinetic energy spectra for energy degradation in the target support foils and target material was previously done simply by adding a constant ΔE to the energy value for each channel. The value of ΔE was determined by observing the spectrum of ^{252}Cf fragments directly and through the targets. The simple method of correction was used because the shifts, ΔE, were the same for the light- and heavy-mass peaks of ^{252}Cf within experimental error. We are now investigating the effects of absorbers more carefully with the use of a program we have written that includes dE/dx data for ^{127}I and ^{79,81}Br ions of typical fragment energies as measured experimentally by the Oak Ridge group (Moak and Brown, Phys. Rev. Letters 11, 284, 1963; C. D. Moak, private communication, 1965). Preliminary results of the calculation are in agreement with the experimental observation of approximately the same shift for the ^{252}Cf light- and heavy-mass peaks. (D. S. Brenner, G. E. Gordon, and R. D. Cooper (Dept. of Nucl. Eng., MIT, on leave from U. S. Army Natick Lab., Natick, Mass.))

D. Theoretical Calculations on the Fission Process

We are attempting to modify the Brunner-Paul theory of fission (see W. Brunner and H. Paul, Ann. Phys. 8, 146, 1961; also, J. B. Sykes, U.S.A.E.A. Rep. No. AERE Trans. 897, 1962). Previous modifications of the theory (J. Harvey, Ph.D. thesis, McMaster Univ., 1965) resulted in predictions of mass yields and neutron-emission probabilities that were much more reasonable than those obtained with the basic theory. According to the basic theory, yields are determined by the probabilities that the nascent fragments penetrate the barrier of the Coulomb and nuclear potential. In the present modification, we are attempting to take into account the influence of the total number of quantum states available in the fragments. We have abandoned the original assumption that fragment excitation energy is present only as surface energy of the deformed fragments. Excitation energies of the fragments above that required by their deformations are determined by the level densities of the excited fragments and the total energy available for the given mode of division. Also, the kinetic energy for a given mode is calculated from the potential at the scission point rather than being taken from experimental determinations.

Preliminary calculations with the modified treatment give good agreement with experimental charge distributions, reasonable qualitative agreement with kinetic energy distribution, but, as yet, poor agreement with yield-mass curves. (J. W. Harvey and G. E. Gordon)

E. The 145 Chain in Fission

Experiments were initiated to define the half-life and fission yield of lanthanum precursors of short-lived Ce isotopes formed in fission. The extraction of Ce(IV) nitrate from 10 M HNO_3 into hexone offers a rapid method of separation of Ce from other fission products, including La and other rare earths. This method was applied to the A = 145 chain in fission:

$$\text{short } {}^{145}\text{La} \rightarrow 3.0\text{-min } {}^{145}\text{Ce} \rightarrow 5.96\text{-hr } {}^{145}\text{Pr} \rightarrow \text{stable } {}^{145}\text{Nd}$$

After 10 sec of fission, Ce carrier was added, oxidation accomplished with $NaBiO_3$, and extractions made after delays of 0.5 to 2.0 min. Later the Ce was back-extracted into water, precipitated, and the yield of the ^{145}Ce determined by counting 5.96-hr ^{145}Pr, compared to 33-hr ^{143}Ce produced independently and by decay of 18-min ^{143}La.

The yield of the 5.96-hr activity seems to be independent of timing, which is surprising, and it was less than twice that of the 33-hr activity, which is mostly formed independently in fission in estimated fractional chain yield of 0.01 - 0.03. Further experiments are planned. (W. P. Petrick, C. D. Coryell, and W. B. Walters)

F. Intensities of the K x-Rays from a Continuous Fission Source

A 2-meter quartz bent-crystal spectrograph of the Cauchois type was used with 100-micron Ilford G-5 plates to photograph the electromagnetic radiations coming from a ^{235}U-Al plate in the thermal neutron column of the MIT reactor. Value of the observed intensities of the various x-rays and γ rays were reported previously (LNS Progress Report for Nov. 1964, p. 48).

The K x-ray spectra of the heavy fission elements come from exposure of 100 hr. in the energy region 25 - 41 keV, and a few γ rays are also seen in this energy region. The most prominent γ occurs at 30.63 keV, superposed on the $K_{\alpha 2}$ line of cesium giving a high apparent $K_{\alpha 2}/K_{\alpha 1}$ ratio. The lines seen for x-rays and γ rays are expected to come from the primary fission products after being stopped in the source ($\sim 10^{-11}$ sec), and from γ rays and their conversion associated with β decay and isomeric transition of secondary fission products.

The observed intensities of the $K_{\alpha 1}$ lines of the elements are to be corrected for self-absorption in the source, for absorption in the aluminum covering of the source, in the air gap, and in the 2-mm quartz crystal, for response of the spectrometer (E^{-2} dependence) and for response of the photographic plate (P. J. Hickson, Ph.D. thesis in Physics, MIT, June 1963). The results, shown in Table 1.VIII, supersede the values given at the April meeting of the Physical Society (Bull. Am. Phys. Soc., Ser.II, Vol. 10, 481, 1965). The first and fourth column of the table give the elements, the next columns the observed D values, and the third and sixth columns give the total yields of $K_{\alpha 1}$ lines referred to iodine as 100.

The data of Table 1.VIII are plotted in Fig. 1.12, with the upper limits for Sn and Sm given by broken lines. The predominance of yield for odd-Z elements is noteworthy. (J. E. Canty, C. D. Coryell, L. Leifer, and N. C. Rasmussen)

Table 1.VIII

Relative Intensities of K_α Lines of Heavy Fission Elements

Element	Dobs.	Yield	Element	Dobs.	Yield
Sn	<0.01	< 6.3	La	0.120	55
Sb	0.044	23	Ce	0.064	29.5
Te	0.062	30	Pr	0.140	64
I	0.216	100	Nd	0.046	27
Xe	0.066	29	Pm	0.040	20
Cs	0.199	87	Sm	<0.008	<4.2
Ba	0.071	32			

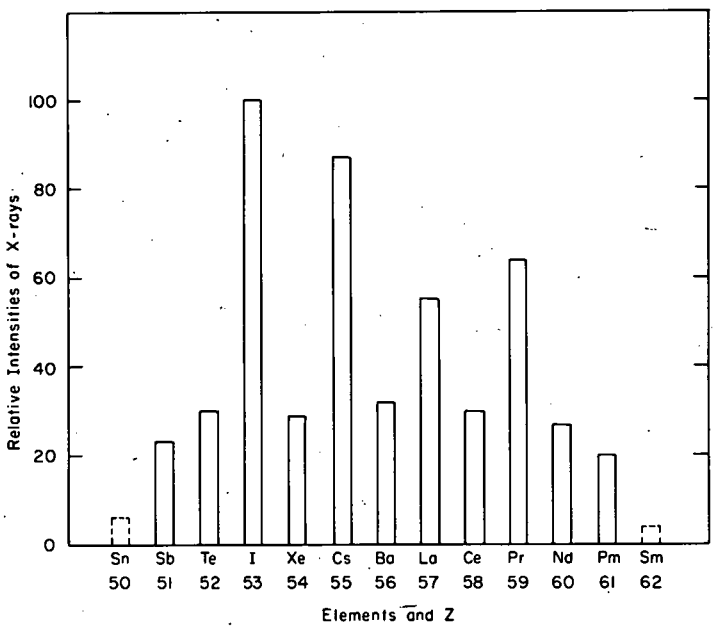


Figure 1.12

Relative intensities of K x-rays for elements in the heavy-mass peak from fission of ^{235}U with thermal neutrons.

III. Nuclear-Reaction Studies

A. Isomeric Cross Section Ratios of ^{117}Cd from the $^{116}Cd(n_{th}, \gamma)$ and $^{116}Cd(d_{14}, p)$ Reactions

With the completion of the decay schemes for the ^{117}Cd isomers (see Sec. I.A), the determination of the isomeric cross section ratios of ^{117}Cd in nuclear reactions becomes rather straightforward when Ge(Li) spectra are available. The procedures are as follow. The intensities of two prominent photopeaks, one originating from the longer-lived isomer, the other from the shorter-lived one, are determined from the Ge(Li) spectrum taken at a known time after the end

of bombardment. From the decay schemes, the fractions of total isomer decay that go through these transitions can be obtained. The intensities of the two photopeaks can then be corrected to give the total isomer activities. Through the application of the simple decay equations, the activities of the two isomers at the end of bombardment can be calculated. Finally, after corrections for the duration of bombardment, the cross section ratio of the isomers can be determined.

In this measurement, the short-lived photopeak chosen, 2.4-hr ^{117g}Cd, was the 1576-keV, and the long-lived photopeaks, 3.4-hr ^{117m}Cd, were 1432- and 1998-keV. The isomer activities calculated from the latter two photopeaks were averaged and the result used for obtaining the cross-section ratio.

The σ_m/σ_g value of ^{117}Cd from the (d,p) reaction was determined to be 1.1 ± 0.30 and that from the (n,γ) reaction to be 0.50 ± 0.20. The errors given are conservative estimates based mainly on the uncertainties in determining the photopeak intensities. The relatively high yield of the high-spin ^{117}Cd isomer is quite surprising. (C.-W. Tang and C. D. Coryell)

B. Mechanisms of Nuclear Reactions Involving High Angular Momentum

A number of calculations are in progress in an attempt to interpret the excitation functions for reactions of ^{114}Cd and ^{116}Cd bombarded with various heavy ions (R. P. Black, Ph.D. thesis, Dept. of Chemistry, MIT, May 1964; see also LNS Prog. Rep., May 1964, p. 26). The model adopted should also be capable of fitting other heavy-ion excitation functions in the same general mass region. Therefore, in addition to the Cd data, we are comparing our theoretical predictions with other results reported in the literature, e.g., reactions leading to ^{149}Dy, ^{150}Dy, and ^{151}Dy (Alexander and Simonoff, Phys. Rev. 133, B93, 1964), reactions of heavy ions with Te targets (Choppin and Klingen, Phys. Rev. 130, 1990, 1963; 1996, 1963), and reactions involved in the search for new rare-earth α emitters (Macfarlane, Phys. Rev. 137, B1448, 1965).

The basic model we are using assumes formation of a compound nucleus (CN) followed by evaporation of particles. The effect of high angular momentum is approximated by the classical assumption that the angular momentum is present entirely in the form of collective rotation and that the rotational energy, $E_{rot} = \hbar^2 I(I+1)/2J$ (where J is moment of inertia), is "unavailable" for particle emission. Thus, we calculate nuclear-reaction probabilities using a standard Monte Carlo evaporation method (Dostrovsky, Fraenkel, and Friedlander, Phys. Rev. 116, 683, 1959) using an effective excitation energy equal to the true excitation energy minus E_{rot}. It is assumed that E_{rot} is emitted in the form of γ rays after the evaporation of particles is finished.

The results of the calculations are in qualitative agreement with the experimentally observed trends: the shift of the peaks of excitation functions to higher energies with increasing angular momentum and appreciable tailing on the high-energy sides of the peaks. However, quantitatively, there are some disagreements. Our calculations, in general, give larger shifts of peaks and larger high-energy tailing than is observed experimentally. We believe that these discrepancies arise from two sources: (1) we have been using CN formation cross sections and angular-momentum distributions calculated by Thomas (Phys. Rev. 116, 703, 1959), although there is

considerable evidence that his calculations represent total reaction cross sections, including many non-CN reactions with high angular momentum and (2), in calculating E_{rot} we have been using for J the rigid-body moment of the spherical nucleus, although the equilibrium shape is predicted to be a spheroid with higher moment of inertia (J. Hiskes, UCRL-9275, 1960).

We are attempting to improve the calculations by use of an angular-momentum cutoff as obtained from the model of Kalinkin and Petkov (Acta Phys. Polonica 25, 265, 1964, available as UCRL-Trans.-1151; see also Kalinkin, Nucl. Phys. 67, 377, 1965). According to KP, before formation of a CN, the system must pass through a prolate-spheroidal transition state having a distortion determined by the classical turning point of the incoming projectile. If the derivative of total energy (surface + Coulombic + rotational) of the transition-state nucleus with increasing deformation is negative, it is assumed that the CN does not form. We are presently in the process of comparing the shapes of the transition-state nuclei with those predicted for equilibrium rotating nuclei by the Hiskes model (loc. cit.), the Beringer and Knox model (Phys. Rev. 121, 1195, 1961), and that of Cohen, Plasil, and Swiatecki (Proc. Third Conf. on Reactions between Complex Ions, U. of Calif. Press, 1963, p. 325). We also intend to use the Hiskes model to calculate the total energy not available to particle emission. For the non-spherical equilibrium nuclei, this will include both rotational and deformation energies, but the sum of these is somewhat less than E_{rot} calculated for a spherical nucleus.

We thank L. L. Altman, Lawrence Radiation Laboratory, Berkeley, for his suggestion of using the KP model and for helping us check out the program used in the calculations. (G. E. Gordon and R. P. Black)

IV. Physico-Chemical Studies

A. Considerations on the Distribution of Ions between an Organic Solution of Alkyl Ammonium Salts and an Aqueous Solution of Inorganic Salts in the Presence of Homopolymers and Heteropolymers in the Organic Phase.

The following is the abstract of a manuscript covering this work which has been submitted to J. Phys. Chem. for publication.

The distribution of a monovalent simple anion, Y^-, or of a monovalent metal complex anion, MX^-_{n+1}, between an aqueous solution of the supporting electrolyte CX and a water immiscible solution of an alkyl ammonium salt $\overline{RX}$ has been described considering the presence in the organic phase of the homopolymers $(\overline{RX})_i$, $(\overline{RY})_j$ and of the heteropolymers $[(\overline{RX})_a(\overline{RY})_b]$. A set of equations has been derived that show the dependence of the experimental distribution data on the concentration of the alkyl ammonium salt and the extracted anion.

A successful reinterpretation of the data existing in the literature on the distribution of $UO_2(NO_3)_2$ between aqueous nitrate solution and alkyl ammonium nitrate solutions has been carried out. The presence of a mixed tetramer and of monomer terms seems to fit the experimental data. (G. Scibona)

B. Distribution of Single Anions between Carbon Tetrachloride Solutions of High Molecular Tertiary Ammonium Salts and Aqueous Lithium Chloride Solutions.

The following is the abstract of a manuscript covering this work which has been submitted for publication in the J. Phys. Chem.

The distribution of ReO_4^- ions between CCl_4 solutions of tridodecylammonium salts and aqueous solutions of lithium salts has been studied as a function of the ammonium salt and perrhenate ion concentrations. The chloride, bromide, nitrate and perchlorate ammonium salts have been used. Also the distribution of Br^- ion between a CCl_4 solution of tridodecylammonium chloride and aqueous LiCl solution has been studied as a function of the ammonium salt and of the bromide ion concentrations. The deviation of the distribution of data of some of these systems from a simple mass law model has been interpreted in terms of the formation of the mixed dimer [(RX)(RY)] with X = Cl^-, Br^-, NO_3^- and Y = ReO_4^-.

The (ReO_4^*-ClO_4) and (Br^*-Cl) systems are apparently following a simple mass action law, but in the case of the (ReO_4^*-ClO_4) system, this effect may not be real. (G. Scibona, R. A. Nathan, A. S. Kertes, and J. W. Irvine, Jr.)

C. Aggregation Studies on Long Chain Alkyl-ammonium Salts in Organic Diluents. I. The Chloride, Nitrate Salts in Benzene

The following is the abstract of a manuscript covering this work which was written in cooperation with P. R. Danesi and F. Orlandini, C.N.E.N. Chemistry Division - Centro Studi Nucleari, Casaccia, Rome, Italy, and has been submitted for publication in J. Inorg. Nucl. Chem.

The aggregation equilibria of tridodecyl-ammonium chloride and tridodecyl-ammonium nitrate in benzene have been investigated by studying the vapor-pressure lowering of the solutions with matched thermistors at 25°C. For the chloride salt, measurements have also been carried out at 37°C. The existence of a monomer-dimer equilibrium for the chloride salts fits the experimental data. The equilibrium constants K_2=30±3 at 37°C, K_2=50±5 at 25°C have been calculated. The presence of dimer and trimer is necessary to explain the experimental data of the nitrate salt. K_2=65±7 and K_3=39±4 at 25°C have been calculated. (G. Scibona and S. Basol)

D. The Distribution of LiCl and Tracer LiBr between Aqueous LiCl Solution and Benzene Solution of a Quaternary Ammonium Chloride

The following is the abstract of a paper accepted by the Journal of Physical Chemistry:

The distribution of LiCl between aqueous solutions of different LiCl concentration and benzene solutions of the quaternary ammonium salt Aliquat 336 (RCl) has been studied. Thermodynamic relations have been derived for the distribution of LiCl between the two phases considering the LiCl in the organic phase either associated or dissociated. The partition of tracer Br^- between aqueous solutions of LiCl and benzene solutions of Aliquat 336 has been studied also. The distribution of LiBr between the two phases has been described, taking into account that also LiCl is present in the organic phase, by relations similar to that derived for the distribution of LiCl. If dissociated electrolytes are assumed in both phases, the ratio of the mean aqueous

activity coefficient calculated in this paper have been found, for both LiCl and LiBr, nearly independent of the aqueous concentration of LiCl. A thermodynamic equation for the dependence of the observed distribution coefficient of the LiBr, k_{LiBr}, on activity coefficients and concentrations has been derived. The deviation of k_{LiBr} from a simple mass action law can be accounted for by considering a constant ratio for either the activity coefficients of the two electrolytes in the organic phase or the activity coefficients of each electrolyte in the two phases. (G. Scibona, P. R. Danesi*, F. Orlandini*, and C. D. Coryell)

E. A Study of the Behavior of High Molecular Weight Alkylammonium Salts in Solvent Extraction Systems

The following is an abstract of the Ph.D. thesis of J. F. Byrum.

The standard free energy change was determined for the exchange of various simple anions in extraction systems containing a tetraheptylammonium salt as the extractant. The order of selectivity is found to be the same as that of anion-exchange resins: $ReO_4^- > ClO_4^- > NO_3^- > Br^- > Cl^-$.

The values determined for the enthalpy change of the exchange reaction for the different systems are 1.65 times the value for the corresponding standard free energy change.

Theoretical expressions for the free energy and enthalpy changes are derived considering only the electrostatic contributions to the free energy change that arise from the transfer of ions between media with different dielectric constants and from the formation of associated ion-pairs in the organic phase. Good agreement is obtained between the theoretical and experimental values if the water-saturated organic phase is considered a mixed-solvent system and the bulk dielectric constant is calculated from the mole fraction and dielectric constant of each component.

The presence of water in the organic phase is discussed as a possible explanation for the influence of the diluent and the supporting electrolyte on the exchange reaction.

The dependence of the extraction of Fe(III), Ga(III), In(III), and Au(III) chloro-complexes on the concentration of HCl or LiCl in the aqueous phase and the concentration of tridodecylamine hydrochloride in the organic phase was determined. The formation of mixed aggregates of the alkylammonium salt in the organic phase appears to be the cause of the inconsistent results reported in the literature for these systems.

The distribution of tetraheptylammonium salts between aqueous and organic phases and the solubility of these salts in aqueous solutions were measured. The problems in measuring the distribution of tritium-labeled tridodecylamine hydrochloride between phases are discussed. (J. F. Byrum, J. W. Irvine, Jr.)

F. Extraction of $HAuCl_4$ in the HCl-H_2O-nitrobenzene System

A number of extraction systems involving HMX_4 species have been studied in this laboratory. The solvents, bis(2-chloro-ethyl) ether and nitrobenzene, the acids HCl and HBr and the metals

* Chemistry Division of the Italian Comitato Nazionale Energia Nucleare, Casaccia, Rome, Italy.

Ga, In,and Fe have been used in various combinations. The halo-complexes of these metals are relatively unstable and the measured extraction coefficients are related to the formation constants of the tetrahedral complexes in the aqueous phase and the distribution coefficients of the complex acids.

The Au(III) complex, $AuCl_4^-$, is square planar and very stable. Its extraction from HCl into nitrobenzene has been studied and found to behave very much like the other systems. The extraction coefficient, $E=(C_M)organic/(C_M)aqueous$, shows a much smaller dependence on the aqueous HCl activity (Fig. 1.13) as would be expected from the stability of the complex and shows the same type and magnitude of dependence on metal ion concentration (Fig. 1.14) (R. H. McCorkell and J. W. Irvine, Jr.)

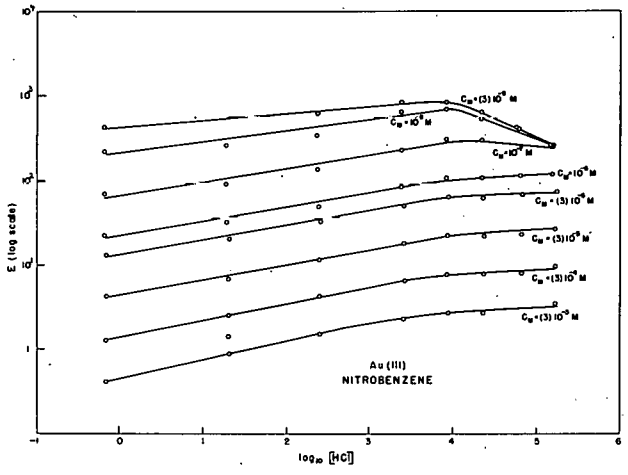


Figure 1.13

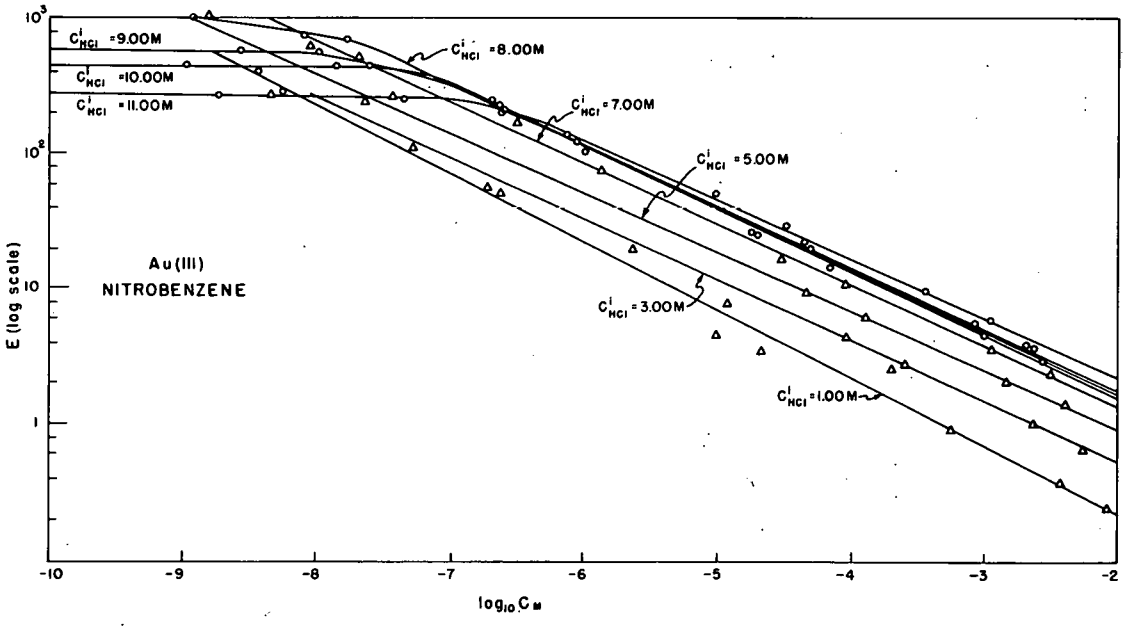


Figure 1.14

G. Extraction of $Be(SCN)_2$

Studies on the solvent extraction of $Be(SCN)_2$ and its extractive separation from Al(III) with methyl isobutyl ketone were carried out at the University of Manitoba. In order to extend the extraction of Be(II) to lower concentrations than could be measured by chemical methods, Be^7 tracer was used, covering the range of carrier-free to 10^{-3} M Be(II). In the range 10^{-1} to 10^{-3} M Be(II) the extraction coefficient increases slightly as the Be concentration decreases. Below 10^{-3} M Be(II) the extraction coefficient is independent of the Be concentration and has a value of ~0.7 at 1.5 M NH_4SCN and ~6.7 at 3 M NH_4SCN when the aqueous phase has a pH between 2 and 3. (R. H. McCorkell)

H. Polyhedral Borate Anions in Solvent Extraction Systems

The following is the abstract of the Ph.D. thesis of C. R. Schlaikjer:

The distribution of cesium and barium between nitrobenzene and aqueous solutions containing the polyhedral borate anions $B_{10}H_{10}^{--}$ and $B_{12}H_{12}^{--}$ and some of their halogenated derivatives has been studied. The extraction of the metal to the nitrobenzene was followed as a function of metal ion concentration, as a function of the concentration of the borate acid, and as a function of the aqueous phase hydronium ion concentration. It was found that for a given anion, the extraction of cesium from the aqueous phase was greater than the extraction of barium. For a given metal, the extraction was found to be greater with the increasing size of the borate anion. The distribution of the polyhedral borate acids was studied in an attempt to determine the main species present in systems containing no metal. From plots of log D vs. log concentration an attempt was made to establish from the experimental slopes the nature of the species responsible for the extraction of the metals and the acids. The data from the extraction of borate acids in the presence of hydrobromic or perchloric acid and from the extraction of cesium supported the conclusion that the borate acids, H_2L, were present in the nitrobenzene phase as HL^- over a wide concentration range. Ion pairing or association may occur in the aqueous phase between the cesium and polyhedral borate ions to form CsL^- ions. The cesium salts were probably present in the nitrobenzene phase as dissociated Cs^+ and L^{--} ions as well as CsL^- ions. The borate anions may form ion pairs in the aqueous phase with barium ions.

Alkylammonium, alkali, and alkaline earth salts of the anions $B_{10}H_{10}^{--}$ and $B_{12}H_{12}^{--}$ and of some of their halogenated derivatives were separated. Halogenations of the parent anions were carried out in methylene chloride and in aqueous solution by reaction of the triethylammonium salt or parent acid directly with elemental halogen. The sodium and potassium salts of the borate anions were found to extract quantitively into acetonitrile from aqueous solutions saturated with the corresponding alkali bicarbonate. The recrystallization of the highly water-soluble salts $K_2B_{10}Br_{10}$, $BaB_{10}Br_{10}$, and $K_2B_{10}I_9H$ was carried out from anhydrous acetonitrile and methylene chloride. The solubilities of some of the salts of the polyhedral borate anions in water and other solvents is discussed, and the solubility products of $Ag_2B_{10}H_{10}$ and $Ag_2B_{10}Br_7H_3$ in water were determined from cell measurements to be 3.65×10^{-18} and 8×10^{-12}, respectively.
(C. R. Schlaikjer, J. W. Irvine, Jr.)

I. Solvent Extraction from Molten Salts

A program has been initiated for the study of solvent extraction from the molten $LiNO_3$-KNO_3 eutectic mixture (mp 120°C) with organic phases of mixed polyphenyls and of polysiloxanes. Emphasis will be on the physico-chemical aspects of the systems and their potential application to nuclear technology. (I. Gal, J. W. Irvine, Jr.)

J. Detailed Hydration Behavior of Divalent Metal Perchlorates in Aqueous Solution

The procedures for evaluating the various hydrates of the components of electrolytes in concentrated aqueous solution have been presented (LNS Progress Report for Nov. 1, 1964, pp. 25-28). Measurements were made on the densities of $Pb(ClO_4)_2$ solutions to give the molarities M as a function of molality m . Correlation of the activities of the salts at given a_{H_2O} with the H_0 function and activities of $HClO_4$ at the same a_{H_2O} provides values of the ion activity functions $\log \varphi_0^2 a_{Pb^{2+}}$ and $\log \varphi_0^{-1} a_{ClO_4^-}$, and the ionic activity coefficient functions $\log \varphi^2 y_{Pb^{2+}}$ and $\log \varphi^{-1} y_{ClO_4^-}$ as a function of a_{H_2O}. From these, values of the hydration numbers of Pb^{2+} and ClO_4^- as a function of concentration can be evaluated. The limiting solvation for Pb^{2+} is $Pb(H_2O)_2^{2+}$, with $Pb(H_2O)_6^{2+}$ predominant at lower concentrations. The limiting solvation for ClO_4^- is $ClO_4(H_2O)^-$. Detailed concentration profiles will be presented later. Studies have also been made on the perchlorates of Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}, but the lower solubilities (less fall of a_{H_2O} for saturated solutions) make this treatment less definitive. (L. Leifer and R. H. Clarke)

K. Detailed Hydration Behavior in HCl Solutions

Following the procedures cited in the preceding section, further attention has been given to the various hydrated ions existing in HCl solutions (cf. also LNS Progress Report, Nov. 1, 1964, pp 23-25). Taking into account triply hydrated ion-pairs, $HCl(H_2O)_3$, the unhydrated ion Cl^- is the dominant chloride form above 5m, with $H(H_2O)_4^+$ as the predominant cation from 3m on, but a small amount of monohydrated proton H_3O^+ is present in solutions above 12m.

Since the values for dissociation of HCl are tentative (E. Høgfeldt, J. Inorg. Nucl. Chem. 17, 302, 1961), efforts were made to evaluate the hydration of the ions H^+ and Cl^- assuming undissociated HCl is not important except for the highest concentrations. This makes little difference in the concentration profiles of $Cl(H_2O)_4^-$ and Cl^- as a function of m, but it changes appreciably the concentration profiles of $H(H_2O)_4^+$ and H_3O^+, increasing the importance of the latter above 12m. Further analytical work is in progress. (L. Leifer and E. Ward)

V. Earth Sciences

Rare Earth Abundances in Pyromorphite and Strontianite

The following is the abstract of the S.M. thesis of A. M. Ehrlich.

Rare earth abundances have been determined in pyromorphite, $Pb_5Cl(PO_4)_3$, and strontianite, $SrCO_3$, by neutron activation analysis. The rare earths were separated by reversed-phase

chromatography on bis-(2-ethylhexyl)orthophosphoric acid adsorbed on diatomaceous silica (J. Winchester, J. Chromato. 10, 502, 1963). The data have been related to the absolute rare-earth abundances in chondrite stone meteorites (see Coryell, Chase, and Winchester, J. Geophys. Res. 68, 559, 1963).

Total rare-earth contents are 418±115 parts per million (ppm) in the pyromorphite and 395±16 ppm in the strontianite. The Eu values are, respectively, 15.5±0.3 and 18±2 ppm. The Sm values are, respectively, 38±14 and 26±3 ppm.

The ratios of actual Eu abundance to the value interpolated between Nd and Tb or Dy (on a chrondite-normalized abundance-distribution curve, see Coryell, et al., loc. cit.) are 4.8±1.7 in the pyromorphite and 2.2±0.6 in the strontianite. Samarium has an analogous value in the pyromorphite of 3.1±1.4, but there is no Sm enrichment in the strontianite.

These minerals, previously analyzed by Goldschmidt (Skrifter Norske Videnskaps Akad. i Oslo, I. Mat-Naturv. Kl. No. 4, 1937) do not show very high rare-earth contents nor the especially high Eu values reported by him. (A. M. Ehrlich and J. W. Winchester, work supported in part by ONR contract Nonr 184(74) in the Dept. of Geology and Geophysics)

VI. Instrumentation and Data Handling

A. Improvements in Instrumentation

We have made a number of improvements in instrumentation in several broad categories which concern detection of radiation, electronic handling of the signals from the detectors, and analysis of the data obtained.

Improvements in the detection of radiation have been accomplished by our use of semiconductor detectors using both Ge and Si. We have used several Ge(Li) detectors through the courtesy of Prof. N. Rasmussen, Mr. V. Orphan and Dr. J. Sovka of the MIT Department of Nuclear Engineering. Because of the necessity for maintaining these detectors in vacuum and at low temperatures we have used two operating systems that are described separately (see Graeffe, Sect. VI.C, and Parsa, Sect. VI.B). We have also obtained a small thin window NaI detector for detecting x-rays.

We have also constructed a large lead cave for the purpose of making low-background measurements.

In order to take full advantage of the high resolution obtainable with the Ge(Li) detectors, we have purchased a low-noise preamplifier and amplifier. With this system, we are able to obtain resolution of 3.8 keV FWHM for the 662-keV gamma-ray from ^{137}Cs. We have also purchased a dual-beam oscilloscope to enable us to set and adjust the various time delays in our coincidence system. This is especially important in Ge(Li)-NaI coincidence experiments where the pulses from the Ge(Li) detector are produced much faster than those from the NaI detector.

The major change in our laboratory has been the purchase of a 4096-channel multi-parameter pulse-height-analysis system from the Packard Instrument Company. The system includes two analog-to-digital converters, a 4096-channel memory, a dual live-timing unit, a fast parallel printer, and a magnetic-tape readout unit. With this system we will be able to carry out a wide range of experiments suggested in other parts of this report including high-resolution gamma ray spectroscopy, half-life studies of short-lived activities produced in fission, multiple-coincidence studies, and multiple angular-correlation studies.

With the large increase in data brought about by the 4096-channel system we have also improved our ability to analyze it using the LNS-IBM-7044 and -1401 computers. We have programs which convert the data from the readout of the 4096-channel system into a format suitable for Fortran operations, thus enabling us to analyze data in almost any way desired. We have also written a program for the PDP-1 computer to allow it to read punched-paper tape from our 400-channel analyzer and write that information on magnetic tape in a format suitable for the magnetic-tape units of the LNS Computation Center. (W. B. Walters)

B. Dewar Assembly for Ge(Li) Detectors

A dewar assembly for Ge(Li) γ-ray detectors has been developed. The main body of the dewar is of commercial manufacture (A. D. Little, Cambridge, Mass.), then it was assembled as shown in Fig. 1.15, after some minor machine work in our shop. It is made from an original design by Kraner, et al., (Kraner, Sovka, and Breckenridge, Nucl. Instr. Methods 36, 328, 1965) with some modifications:

(a) Microdot connectors were used in place of Amphenol Subminax. In this way the dewar pressure was maintained in the range of a few times 10^{-8} mm Hg.

(b) No top feedthrough was made.

(c) The position of the ion pump was changed to the top, using a Hi Seal connector.

(d) A removable bottom brass plate was used.

(e) The bottom brass plate was machined to 1/16" thickness in order to facilitate taking spectra from the bottom.

Unless otherwise specified, all Ge(Li) spectra shown in this report were taken with this assembly, or with one very similar to it. (B. Parsa)

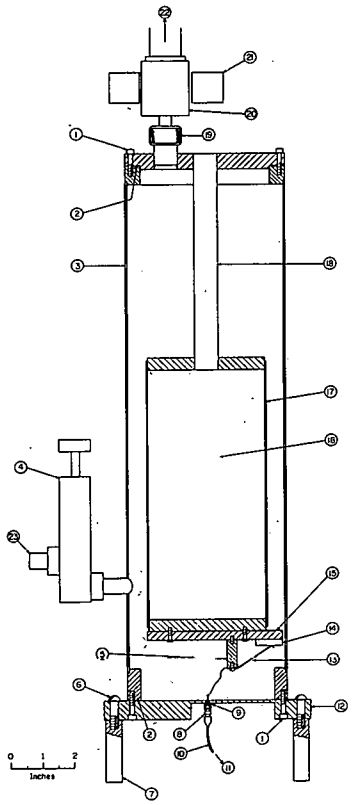


Figure 1.15

Dewar assembly for Ge(Li) detectors

1. Six #6/32 screws
2. Viton "O" ring
3. 0.035" stainless steel wall
4. High vacuum valve
5. Teflon stand-off
6. 1/4 - 20 round-head machine screws
7. Four brass legs
8. Microdot 32-21 screw-type plug
9. Microdot 51-49 hermetically sealed connector
10. Microdot 250-3819 "Mini-Noise" coaxial cable
11. To Tennelec 100C preamplifier
12. Brass plate
13. Phosphor bronze spring clip
14. Ge(Li) crystal mounted on tab of copper plate.
15. Removable copper plate held by 3 #4/40 screws
16. Liquid nitrogen reservoir
17. 0.065" stainless steel wall.
18. 0.010" stainless steel wall
19. 3/8" Quick coupling gland seal
20. Varian 913-0007 ion pump with copper tubing.
21. Varian 913-0011 permanent magnet
22. To Microperv IS-1000 ion-pump power supply.
23. To diffusion pump.

C. Cryostat for Ge(Li) Detectors

A new type of cryostat for Ge(Li) gamma-ray detectors has been designed and constructed for use in our decay-scheme studies. Often the systems used for Ge(Li) detectors are constructed so that it is impossible to measure low-energy gamma-rays with high efficiency (because of the thickness of materials that must be penetrated) and inconvenient to use the detectors in coincidence experiments. Also, to maintain the low temperatures required, one usually has to fill a liquid nitrogen reservoir quite often. The system used in most of the work reported in this report

suffers all of these disadvantages (see B. Parsa, Sect. VI.B).

The new cryostat shown in Fig. 1.16 makes use of a cold-finger as suggested to us by Prof. Nurmia (University of Helsinki, private communication, 1965). The system requires a minimum of routine maintenance, yields good counting efficiencies for low-energy gamma-rays, and is convenient for use in coincidence experiments.

The output of the detector leads, via a Kovar seal, directly to the input of the preamplifier (Tennelec 100 C) which is mounted on the chamber. All Al parts inside the chamber are polished and an Al reflector has been placed inside the brass part of the chamber to minimize heat exchange. The Ge(Li) detector is attached to a Cu plate about 5 mm from the thin Al window.

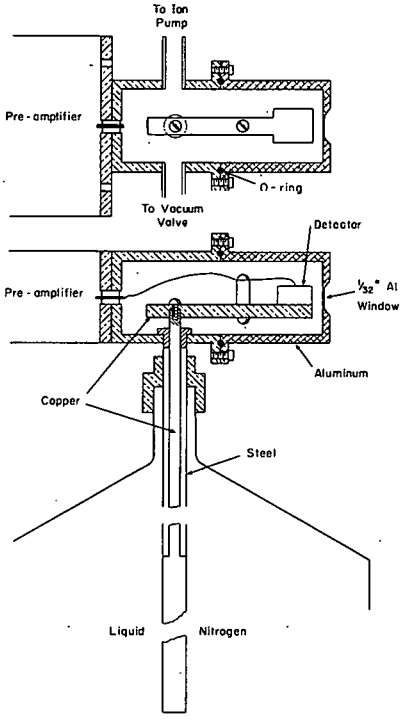


Figure 1.16
Schematic drawing of the cold-finger cryostat for Ge(Li) detectors.

The usefulness of the system for low-energy gamma-rays is shown by the spectrum of Fig. 1.2 (Sect. I.D, page 6). The 35-keV line which shows up quite clearly was impossible to observe in our older detector system. The intensity of the 35-keV line is about 2 percent that of the 528-keV line.

I wish to thank V. Orphan of the Dept. of Nuclear Engineering for his help and for supplying the Ge(Li) detector. (G. Graeffe)

D. Computer Analysis of Beta-Ray and Conversion-Electron Spectra Observed with Low-Resolution Detectors.

The following is the abstract of a paper that has been accepted for publication in Nucl. Instr. and Methods:

A computer program that permits one to resolve β-ray and conversion-electron energy spectra into their various components, taking into account experimental distortions, has been written. The program is designed to treat spectra taken with low-resolution detectors in which distortions of the true energy spectra are quite serious. Effects of the distortions upon the continuous β spectra are handled by an iterative least-squares fitting technique. An initial set of endpoint energies E_{o_i} for the various components is assumed, the true energy spectrum corresponding to the set E_{o_i} is computed from the Fermi treatment of β decay, the spectrum is distorted with the use of response functions appropriate to the detection system, and the resulting calculated spectrum is compared with the observed spectrum. Adjustments of the intensities and endpoint energies are made and a new iteration is performed. The process is continued until termination requirements are met. Output information includes the final values of the intensities and endpoint energies of the various components and uncertainties in their values, as well as statistical goodness-of-fit data. One of the main advantages of this treatment is that it retains all of the statistical information present in the observed spectrum. As written, the calculation of response functions is designed for plastic scintillators used under conditions in which scattering is a serious problem. However, the calculation of response functions is entirely contained within one subroutine which can be easily modified for use with other detection systems. (P. C. Rogers and G. E. Gordon)

E. Computer Treatment of Ge(Li) γ-Ray Spectra

It is fairly obvious that Ge(Li) detectors, which we have found very useful in nuclear decay-scheme studies, will also have wide application in the field of neutron-activation analysis (see, for example, Prussin, Harris, and Hollander, Anal. Chem. 37, 1127, 1965). The usefulness of the detectors in certain applications involving analyses of many samples of similar composition could be greatly extended if computer methods for resolving multicomponent spectra into their individual components were available. Programs designed for this application with NaI(Tl) detectors have long been in use. We are in the process of developing some simple programs of this type for use with Ge(Li) detectors. We will first test them on multicomponent spectra made up by counting γ-ray standards for various lengths of time. If successful in these tests, the programs will then be tested on some simple neutron-activation analysis problems. (M. Weisfield and G. E. Gordon)

Publications

N. K. Aras, B. Kahn, and C. D. Coryell, The Neutron Activation of the Chlorates and Perchlorates and the Preparation of $^{38}ClO_3^-$ and $^{38}ClO_4^-$, J. Inorg. Nucl. Chem. 27, 527 (1965).

N. K. Aras, M. P. Menon, and G. E. Gordon, Ranges of Fragments from Fission of U^{235} with Thermal Neutrons and the Kinetic Energy Deficit, Nucl. Phys. 69, 337 (1965).

C. E. Bemis, Jr., and J. W. Irvine, Jr., Design of Equipment for Rapid Handling of Irradiated Solutions, Nucl. Instr. Methods 34, 57 (1965).

P. R. Danesi, F. Orlandini, and G. Scibona, Uranium Nitrates and Alkyl Ammonium Nitrates. Nature of Species by Log-Log Plots, J. Inorg. Nucl. Chem. 27, 449 (1965).

G. E. Gordon, review of Friedlander, Kennedy, and Miller, Nuclear and Radiochemistry, in J. Chem. Ed. 42, 62 (1965).

G. E. Gordon and N. K. Aras, The Energy Balance in Fission and Monte Carlo Calculations on Prompt-Neutron Emission, in Physics and Chemistry of Fission (International Atomic Energy Agency, Vienna, 1965), Vol. 2, pp. 73-92.

J. W. Irvine, Jr., review of Nesmeyanov, Baranov, Zaborenko, Rudenko and Priselkov, Handbook of Radiochemical Exercises in Nuclear Applications 1, 499 (1965).

A. S. Kertes, Solubility and Activity of High-Molecular Amine Hydrochlorides in Organic Solvents, J. Inorg. Nucl. Chem. 27, 209 (1965).

M. P. Menon, N. K. Aras, and J. W. Irvine, Jr., Radiochemical Separation of Tin and Antimony by an Initial Phosphate Precipitation Step, J. Inorg. Nucl. Chem. 27, 767 (1965).

R. A. Meyer, W. B. Walters, and J. P. Hummel, Cross Sections for the $O^{16}(\gamma, \pi^+)N^{16}$ Reaction, Phys. Rev. 138, B1421 (1965).

D. G. Sarantites, G. E. Gordon, and C. D. Coryell, Ratios of Independent Yields of the Isomers $Te^{131-131m}$ and $Te^{133-133m}$ in Fission, Phys. Rev. 138, B353 (1965).

W. B. Walters, C. E. Bemis, Jr., and G. E. Gordon, Decay Scheme of 25-Minute Te^{131g}, Phys. Rev. 140, B268 (1965)

Addresses

C. E. Bemis, Jr., and G. E. Gordon, Decay of 37-min Sb^{130}, New York APS Meeting, Jan. 29, 1965.

R. P. Black and G. E. Gordon, Heavy Ion Nuclear Reactions in the Medium Mass Region, Detroit ACS Meeting, April 8, 1965.

J. E. Canty, C. D. Coryell, L. Leifer, and N.C. Rasmussen, Line X-Rays from a Continuous Fission Source, Washington APS Meeting, April 27, 1965.

G. E. Gordon, Low-Lying Levels of Antimony and Tellurium Spherical Nuclei, Department of Chemistry, Amherst College, Amherst, Mass., April 30, 1965.

G. E. Gordon, Decay Schemes of Antimony and Tellurium Spherical Nuclei, Argonne National Laboratory, August 13, 1965.

G. E. Gordon, The Use of Ge(Li) Detectors in Nuclear Decay-Scheme Studies, Graduate Faculty Lecture, Texas A and M University, College Station, Texas, November 9, 1965.

G. E. Gordon and N. K. Aras, The Energy Balance in Fission and Monte Carlo Calculations on Prompt Neutron Emission, IAEA Symposium on the Physics and Chemistry of Fission, Salzburg, Austria, March 25, 1965.

G. Scibona, Preparation of Dense Particles of Uranium and Thorium Oxide, General Atomic, San Diego, California, April 2, 1965.

G. Scibona, Relative Affinities in Amine Extractions, Gordon Conference on Ion Exchange, August 3, 1965.

C. W. Tang, C. D. Coryell and G. E. Gordon, Decay of 3.2-hr Cd^{117m} and 2.5-hr Cd^{117g}, Washington APS Meeting, April 26, 1965.

W. B. Walters, C. E. Bemis, Jr., and G. E. Gordon, Decay Scheme of Te^{131g}, Kansas City APS Meeting, March 27, 1965.

W. B. Walters and J. P. Hummel, Angular Momentum Effects in the Photoproduction of Mn^{52} Isomers, American Chemical Society National Meeting, Atlantic City, N.J., September 15, 1965.

Theses

J. F. Byrum, A Study of the Behavior of High Molecular Weight Alkylammonium Salts in Solvent Extraction Systems, Ph.D. in the Department of Chemistry, September 1965.

A. M. Ehrlich, Rare Earth Abundances in Pyromorphite and Strontianite, S.M. in the Department of Chemistry, December 1965.

W. P. Petrick, Studies on Short-Lived Lanthanum Fission-Product Nuclides, S. B. in the Department of Chemistry, June 1965.

C. R. Schlaikjer, Polyhedral Borate Anions in Solvent Extraction Systems, Ph.D. in the Dept. of Chemistry, November 1965.

C.-W. Tang, Decay Schemes of the Cadmium-117 Isomers, Ph.D. in the Department of Chemistry, December 1965.

INSTRUMENTAL CHEMISTRY GROUP

Introduction

Historically this group has evolved from one which bore the title "Chemistry of the Fission Elements". The first studies carried out by the group were investigations of the analytical chemistry and complex ion equilibria of several of the elements occurring in uranium fission. It soon became evident that problems in methodology -- that is, the separation of chemical species and the measurement of properties relevant to the determination of their concentration and structure -- were usually the major part of the undertaking. The results of the work on development of new methods, principles and techniques of analysis for application to problems in equilibrium, kinetics and structure were usually found to be of more general interest and importance than the specific problems which occasioned them. Consequently, much of the work of the group has been concerned with methodology -- particularly instrumental methodology -- of rather broad applicability, and the rest with applications of instrumental methodology to specific chemical problems. The gradual change of emphasis has made the original name of the group incongruous, and the present name is, therefore, suggested as being more descriptive of the work actually being done.

The work of the current year includes over twenty separate problems. A number of them can be grouped together under the general heading of electroanalytical chemistry and range from fundamental studies of single crystal electrodes to the development of analytical methods for trace elements in the environment. Another group of problems falls in the area of luminescence, and the remainder include such diverse subjects as plasma spectroscopy, vapor liquid equilibrium and computer methods for interpreting complex ion spectra. The principal new undertaking is the start of a program on the application of electron spectroscopy to chemical problems.

I. Electrochemistry

A. Alternating Current Polarography

Influence of High Concentrations of Supporting Electrolytes on Irreversible Alternating Current Polarographic Processes.

The effects of LiCl, $CaCl_2$, $CaBr_2$, $MgBr_2$, and NH_4NO_3 on the irreversible a.c. polarographic reduction of nickel were studied. For anion concentrations less than about seven molar, the peak current (i_s) of nickel was found to be uniformly small (~0.2 - 0.3 μa) for a nickel concentration of 10^{-3} M in all the electrolytes studied. In the case of bromide salts, however, there was an apparent exponential increase in i_s with increasing bromide concentration for anion concentration greater than 7 M. In 10 M LiBr, i_s amounted to ~20 μa, an approximately 200-fold increase over the value in the more dilute solutions.

An increase in i_s was also observed with increasing chloride concentrations, but the rate of increase was much smaller than with the bromides (i.e., for 5 M $CaCl_2$, i_s = 1 μa). No increase in peak height was observed when 12.2 M NH_4NO_3 was used as the supporting electrolyte.

Since the bromide salts showed the most pronounced effect on the nickel reduction, additional tests were run in order to try better to characterize this system. In experiments designed to show the effect of changing nickel concentration in i_s, it was found that in 4.9 M $CaBr_2$ i_s varied linearly over the concentration range studied (10^{-3} to 10^{-4} M). When HCl was added to a solution containing 10^{-3} M Ni^{++} in 4.5 M $CaBr_2$, no significant change in i_s was observed over the acid range covered (.003 to .02 M HCl). In addition, a series of experiments were run in which the effects of frequency on i_s were determined for a series of solutions of constant nickel concentration, but varying concentrations of $CaBr_2$ and LiBr.

For a reversible process, the following expression is valid:

$$i_s = \frac{N^2F^2AVC\ \omega^{1/2}D_0^{1/2}}{4\ RT}$$

where i_s = peak current

A = area of the electrode

V = amplitude of the applied voltage

C = conc. of the reduced species

$\omega = 2\pi f$

D_0 = diffusion coefficient of the active species

N, F, R, T have their normal significance.

Plots of $\sqrt{\omega}$ versus i_s yielded straight lines for the higher concentrations of supporting electrolyte, but at lower concentrations they had a smaller slope and appeared to round off at the higher frequencies. The decrease in slope suggested that the concentration of the electroactive species was decreasing as the concentration of the supporting electrolyte was decreased. The linearity of the plots at the higher concentrations of supporting electrolyte suggested that the nickel reduction had indeed become a reversible process over the frequency range studied.

From the slope of the $\sqrt{\omega}$ versus i_s plot, it is possible to obtain a value for the concentration of the reversibly reduced nickel species providing one makes certain assumptions concerning the value of D. These include assuming that D_0 for the nickel species being reversibly reduced is about the same as the value of D_0 for the simple hydrated nickel ion in a medium of the same viscosity. Thus one is able to take the value of D_0 for the simple nickel ion at infinite dilution and divide by the relative viscosity of the solution at that concentration of supporting electrolyte in order to give an approximate value for the D_0 of the electroactive nickel species. From these calculations, a value of $5\pm1 \times 10^{-4}$ M was obtained for the concentration of the reversibly reduced nickel species, indicating that it formed an appreciable part of the total nickel concentration at the higher concentrations of supporting electrolyte.

The above experimental data can be interpreted if one postulates the formulation of a nickel bromide complex, the reduction of which proceeds in an electrochemically reversible

manner. If one calculates the concentration of the mono bromide complex at various bromide concentrations, using published values for the formation constant,[1] it becomes readily apparent that this is not the reversibly reduced species. This is because it is present in large concentrations at sufficiently low concentrations of supporting electrolyte that it should be readily observable below 7 M bromide if it were the electroactive species. This then leaves the di-, tri-, and tetra-bromide complexes as the possible choices; work is now being directed towards obtaining UV and visible spectra of nickel in various concentrations of bromide in the hope that, from the spectrophotometric data, it will be possible to determine the identity of the nickel-bromide complex responsible for the a.c. polarographic response.

It should also be noted that, at the same bromide concentrations, solutions containing $CaBr_2$ or $MgBr_2$ yielded smaller values of i_s than did solutions containing LiBr. This is attributed to differences in the concentration of the electroactive species due to changes in the activity of water and bromide ion in going from one electrolyte to the other.

Instrumentation for A.C. Polarography

Numerous modifications were made on the a.c. polarograph in order to improve its overall performance. It had been noticed that the maximum current signal that could be applied to the a.c. polarograph without distortion produced an undesirably small response on the recorder. Therefore the sampling circuit was altered in order to allow greater signal inputs and to increase the gain of the output signal. This was accomplished by substituting a 2N389B, PNP transistor for the 2N 1308, thereby enabling the transistor to handle larger signal excursions. After this change, the current amplifier just prior to the transistor could be eliminated inasmuch as the current amplifier in the d.c. polarogrph was adjusted to provide all the gain necessary to the switch input.

Because only a small fraction of the current cycle is sampled, the output signal of the sampling circuit is small relative to the input signal. A stabilized amplifier was therefore placed at the output of the sampling circuit in order to provide sufficient voltage gain so that the 10 mv per inch recorder would be able to respond to the current signals..

In addition, it was found that a much better signal to noise ratio could be obtained by coupling the current output of the d.c. polarograph to the current input of the a.c. polarograph through an SKL Electronic Filter (Model 200). This was especially valuable when the faradaic component of the current was small. However, since the output impedance of the filter was 300 ohms, it was necessary to change the input impedance of the sampling circuit in order to obtain maximum power transfer.

Other modifications were undertaken in that part of the a.c. polarograph which produces the pulse train used to sample the alternating current. It was found that the height of the pulses was not sufficient to overcome completely the bias of the transistor switch. The height of the pulses was increased by changing some passive circuit elements in the pulse train generator, and

1. N. W. Lister, D. W. Wilson, Can. J. Chem. 39, 2606 (1961).

the variable pulse height adjustment control was removed from the front panel of the a.c. polarograph because it was deemed unnecessary. Moreover, since the a.c. polarograph is capable of operating at various frequencies, the pulse width selector was changed so that it would be possible to sample the alternating current at each of these frequencies with a constant pulse width. This entailed changing the values of the capacitors in the pulse width selector switch.

Finally, in order to reduce the effect of solution resistance, a low resistance capillary was used as the dropping mercury electrode. This reduced the effective resistance of the mercury thread in the capillary from about 50-80 ohms to about 1-2 ohms. Also, a Luggin capillary was incorporated so that the reference electrode could be positioned as close as possible to the working electrode, thereby further reducing the effect of solution resistance. (T. F. Retajczyk, D. K. Roe, D. N. Hume)

B. Experimental Evaluation of Transition Times

While chronopotentiometric measurements are easily made, the location of the transition time is ambiguous. In theory, after the transition time, potential should rise with infinite slope vs time, but the observed slope is considerably smaller because of the charging of the electrical double layer. In a previous report there was a brief discussion of an equation which gave a reasonable estimation of the current available for double layer charging. In effect, the equation was derived for the case where the constant current process was allowed to proceed to a point near the transition time, and the decay of flux with time was then noted. The difference between the applied current and the (decreasing) faradaic current is then available for double layer charging. Experimental verification for this equation has been obtained by recording chronopotentiograms to the potential of the theoretical transition time and then switching the electrode to a constant potential of the same value. The observed decay of faradaic current is then recorded oscillographically. Measurements made in this manner are valid because the flux is essentially the same in the vicinity of the potential of the transition time under conditions of controlled potential or controlled current.

In addition to the above approach to explain the shape of chronopotentiograms, attempts have recently been made to calculate the entire potential-time curve with consideration of double layer charging. The basis of the calculation is the requirement that (dE/dt) for the charging and faradaic processes must be identical. By equating the two expressions, the charging current at any time can be calculated by successive approximations. A computer program will be written to perform this calculation. (D. K. Roe)

C. Electrochemical Studies of Single Crystal Electrodes

Current-potential curves have been measured with the 111 face of single silver crystals, using operational amplifiers to generate ramp voltage scan and to amplify the resulting currents. The scan rates have been varied from 0.1 to 1 mV/sec and the overpotential range has usually been limited to ±20mV. The electrolytes consisted of 0.05M Ag^+-0.05M $HClO_4$ and 0.005M $AgClO_4$-0.095M $HClO_4$.

The results can be chronologically and logically divided into two categories: behavior of the fact and the surrounding surface in contact with the solution and behavior of the facet itself.

Initial C-V curves were obtained under conditions where the electrolyte extended beyond the periphery of the facet. These curves varied considerably among facets, although repeated cyclic scans on a given area were usually excellent. Most of the anodic curves showed a pronounced hump resembling a stripping curve, when preceded by cathodization. Very good agreement was obtained between the integrated number of coulombs deposited and the number subsequently removed. It was decided to treat the anodic curves mathmatically assuming hemispherical deposits, nernstian behavior, and inertness of substrate. The calculated stripping curves agreed fairly well with the experimental curves. Later, this model was changed to a more realistic one involving steps as were observed on metallographs. This yielded better agreement than the hemisphere model. Mathematical treatment of the cathodic curves, assuming adatom diffiusion to be rate determining, has progressed poorly partly due to the mathematical difficulties involved.

The second group of C-V curves were obtained on the facet alone. As was expected, the curves differed greatly from the previous ones where deposition occurred preferentially on the stepped regions near the edge of the facet. Notable was the lack of an anodic stripping curve, the presence of a 30-50 mV "zero" current region, and a sudden, sharp and rapid increase in the current at the cathodic end of the "zero" current region. Qualitatively, the entire curve can be explained in terms of a nucleation overpotential and nuclei formation plus subsequent epitaxial growth on a surface with relatively few growth sites.

At the cathodic end of "zero" current region, the potential scan was stopped as soon as a noticeable (10^{-10} amp) current started to flow. The resulting current time curve was recorded. This curve is indicative of nuclei growth, and is being analyzed. The current usually varied linearly with time, although deviations from this behavior were noted.

Electron micrographs, both reflection and transmissions of the facet were obtained after considerable difficulty. They served to reinforce our view of the facet as a very flat and smooth surface.

At present, double layer capacity measurements are being obtained at intervals along the zero current region, in an attempt to determine the variation in silver adatom concentration along this region. It is of great theoretical importance to know whether the adatom concentration increases with increasing cathodic potentials, or whether it remains constant. (W. M. Krebs, D. K. Roe)

D. Investigation of Trace Quantities of Heavy Metals in Natural Media

During the past year an electroanalytical technique has been developed for trace analysis of certain metals. The specific innovations are the electrode[1] and cell design. It was found that a small quantity of mercury (10^{-7} to 10^{-8} moles/cm^2) could be deposited on wax-impregnated graphite as an electrode, traces of copper, lead and other metals could be totally deposited from

1. W. R. Matson, D. K. Roe, and D. E. Carritt, Anal. Chem. 37, 1594 (1965).

solution samples and then recovered by anodic stripping. The area of the anodic current-time curve is an absolute concentration measurement. Because the metals are oxidized from an amalgam, exceptional resolution and freedom from interferences are found. The method is rapid, applicable to many natural samples without prior treatment and has shown an accuracy of 3 to 7% at concentrations as low as 10^{-10} M.

A series of lead analyses of Boston aerosols[1] was carried out in conjunction with halogen determinations by members of the Geochemistry Division of the Department of Geochemistry and Geophysics. A deficiency of bromine was found, indicating decomposition of $PbBr_2$ in the atmosphere.

A combination of this electroanalytical technique with gel filtration chromatography has been used to investigate the distribution of lead and copper in the organic material of highly colored lake water. The organic substances were separated according to molecular weight on a Sephadex G-50 column, and portions of the effluent were analyzed for the metals. Both lead and copper were found in three peaks indicating a preferential distribution with molecular weight. The largest peak for both metals occurred in organic compounds with molecular weights over 10,000. From observations at various deposition potentials and from changes in time of deposition, it was concluded that the metal-organic complexes are strongly bound and that equilibrium is attained slowly.

Samples from the Charles River and Boston Harbor have been analyzed for lead with the results showing no concentration pattern. However, comparison of lead concentrations in the surface and subsurface (ca. 5 cm. deep) layers showed an increase of from 5 to 10 times more lead in the surface samples. Such a large difference is not expected if the lead fall-out is assumed to be subject to only simple solution and diffusion processes. (W. R. Matson and D. K. Roe)

E. Galvanostatic Method for Studying Kinetics of Electrode Processes

In a previous report an experimental modification of the galvanostatic method was described and the complete overpotential-time curve was derived. The modification consisted of adding an adjustable current spike to the leading edge of the constant current step so that the double layer capacity became partially charged in a short (ca. 5×10^{-7} sec) time. The first part (ca. $< 5 \times 10^{-5}$ sec) of the overpotential-time curve then was made usable for determining exchange currents; the results obtained for the $Hg_2^{2+} + 2e^- = 2\,Hg(\ell)$ process confirmed the equations in detail.

The same modification has been used in the study of an electrode process involving a preceding chemical reaction. Matsuda, Delahay and Kleinerman[2] have derived the equations for this case; their derivation has been modified for this improved experimental method, and the

1. R. L. Lininger, R. A. Duce, J. W. Winchester, W. R. Matson, J. Geophys. Res., in press.
2. H. Matsuda, P. Delahay, P. Kleinerman, J. Am. Chem. Soc. 81, 6379 (1959).

equations have been examined in detail to locate the time intervals of kinetic importance for selected values of homogeneous and heterogeneous rate constants. The system studied was Hg(II) - ethylenediamine (en) which forms a series of complex ions.

Exchange currents were measured as a function of Hg(II) concentration to determine the transfer coefficient, which was 0.38. The order of the electrode process with respect to en was then measured and found to be -1. From the known formation constants of the various complexes, it is concluded that there is a preceding chemical reaction which is $Hg(en)_2^{2+} + OH^- = Hg(OH)(en)^+ + en$. The main participant in the charge transfer process is the hydroxy complex even though the ratio of concentration of this ion to $Hg(en)_2^{2+}$ is about 0.01. Simple charge repulsion considerations substantiate this mechanism since the mercury electrode is positively charged relative to the solution at the prevailing potentials.

The rate of the homogeneous reaction was too rapid to be measured from the slopes of the overpotential-time curves. The maximum detectable rate was estimated to be 2×10^8 ℓ/mole sec. Therefore it may be assumed that the preceding reaction is diffusion controlled. (R. L. Birke and D. K. Roe)

F. Potentiostatic Chromatography-Amalgam Electrodes

During the past two years the behavior of thin mercury-film electrodes has been investigated with the intent to determine the applicability of this type of electrode to chromatographic-type operations. The thin layer of mercury is obtained by amalgamation of a nickel wire and removing the excess mercury to leave a layer of about 10^{-4} cm. The work thus far has been concerned with the residual current and with anodic stripping voltammetry.

Although nickel has been reported to be very insoluble in mercury, a necessary requirement for these electrodes, the residual current is quite different from that of pure bulk mercury. Anodic and cathodic currents are found at potentials where formation and reduction of a surface nickel oxide would be expected. In addition, there is some evolution of hydrogen as would naturally result from the presence of nickel. The formation of small islands of nickel oxide has been visually observed on the electrodes, and the pH dependence of the current-potential curves is in agreement with qualitative predictions. Furthermore, nickel can be oxidized out of the mercury layer in a supporting electrolyte of 5 M LiCl; this measurement is in effect a direct determination of the concentration of Ni in Hg and can also be used to follow the rate of solution. It is interesting to note that the amount of nickel increased linearly with time and no saturation value was found after 15 minutes. These observations are in complete agreement with the prediction of Irvin and Russel[1], who felt that there is no single species of nickel in mercury, but that various agglomerations could form, up to macroscopic crystallites.

Anodic stripping voltammetry has been used extensively to determine if deposited metals form intermetallic compounds with nickel in the mercury layer. These measurements have been

1. N. M. Irvin, A. L. Russell, J. Chem. Soc. 891 (1932).

made on freshly prepared electrodes to avoid the obvious interference of nickel, or nickel oxide "islands", on the mercury surface. No evidence for intermetallic compounds has been noted, contrary to conclusions by other authors working with the deposition of nickel with other metals at hanging mercury drop electrodes.

In spite of the disadvantages of these electrodes due to the presence of nickel on the surface, some rather spectacular results are obtained in anodic stripping voltammetry. Clearly resolved anodic peaks are obtainable for mixtures of Pb, Tl and Cd over a potential region of 300 mV. This is a result of very rapid diffusion out of the mercury phase. By neglecting diffusion in the mercury, the mass transport equations are considerably simplified. On the basis of this model an equation for the complete anodic stripping peak has been derived for the condition of a linear potential scan. The agreement between calculated and experimental current-potential curves is very good. A complete discussion of this derivation has been published. (J. E. A. Toni, D. K. Roe)

G. Behavior of HgSe as an Indicator Electrode

Crystalline HgSe as an electrode produces a number of anodic and cathodic peaks under cyclic voltammetric conditions. The identification of the processes in neutral, unbuffered solution has been discussed in earlier reports. Most of the surface reactions involve H^+ or OH^- (such as formation of $HgSeO_3$ on the surface). Further measurements in buffers of pH = 4, 7, and 10 have confirmed the previous identifications of electrode reactions and current peaks.

After repeated cycling of the potential, the surface reactions decrease and the current is acceptably low over the voltage range from ca. +1.0 to -1.0 V vs. S.C.E. Anodic stripping voltammetry of deposited Cd, Cu, Pb and Tl has been used to determine if HgSe reacts with deposited metals, or if it is as inert as mercury. Of the four metals, only Pb gave anodic stripping peaks free of distortion from (apparen) reactions with the surface of the electrode. Treatment of the electrode by deposition of ca. 10^{-4} cm layer of mercury had no effect on the stripping peak of lead. Also the equation for anodic stripping of a metal from a thin layer of mercury (J. E. A. Toni, D. K. Roe, this report) applied reasonably well to the experimental curves. It is therefore concluded that the treatment of the electrode by repeated cycling of potential results in a surface covered with minute droplets of mercury due to gradual loss of selenium. However, reaction of some deposited metals with selenium is clearly indicated by anodic shifts of peaks from expected values, such as in the case with Cu where the shift indicates compound formation with a ΔF of -15 kcal/mole. Formation of CuSe has a ΔF of -15.2 kcal/mole. (B. F. Vickers, D. K. Roe)

H. Analysis of Surface-Adsorbed Oxygen on Solid Electrodes

For many years a dispute has raged concerning the exact chemical bonding of oxygen which has been electrochemically deposited on platinum surfaces. Some authors have supported the theory of adsorbed oxygen[1] while others have proclaimed the existence of platinum oxides[2, 3].

1. W. Bold and M. Breiter, Electrochim. Acta, 5, 145 (1961).
2. S. Feldberg, C. Enke, and C. Bricker, J. Electrochem. Soc. 110, 826 (1963).
3. F. C. Anson, and J. J. Lingane, J. Am. Chem. Soc. 79, 1015 (1957).

Although a knowledge of the chemical nature of the surface oxygen is a prerequisite to completely understanding the behavior of platinum indicator electrodes, it seems that these arguments have only led to obscuring the original interest in the adsorbed oxygen layer -- its effect on the kinetics of such systems as the Fe(II)/Fe(III) couple which becomes an increasingly irreversible system as an oxygen film is produced on the electrode surface.[1]

In potentiometry, chronopotentiometry, voltammetry, and kinetic determinations a considerable dependence on the presence of oxygen layers has been noted. In fact, to such an extent that almost all authors using such electrodes depend upon a standard anodic or cathodic pretreatment of the electrode in order to obtain reproducible results.

Since a determination of the exact bonding nature of the oxygen to the platinum surface cannot be proven electrochemically, an attempt will be made to correlate independent measurements of the amount of surface oxygen to the kinetics of certain systems at platinum indicator electrodes. This information combined with present electrochemical data should yield an elucidating picture of the surface-oxide phenomenon.

Because oxygen bound to a platinum surface, either adsorbed or as an oxide can be liberated from that surface by heating it in vacuum[2], a mass spectrometric determination of the quantity of oxygen can be made when an electrode of suitable size is employed.

The instrumentation necessary for obtaining this data is at present of primary concern: A potentiostat of the type suggested by Enke[3] has been constructed and switching characteristics have been studied to determine the most feasible galvanostat-potentiostat switching mode for pretreating the platinum indicator electrode. Further work on this aspect of the instrumental problem is necessary because the proper design and reliability of this instrument is tantamount to knowing the exact electrochemical pretreatment of the electrode. Therefore, the design of this instrument is of major importance.

In order to detect the oxygen liberated from the electrochemically pretreated electrode, an omegatron[4] will be employed. This device will be capable of quantitative measurements of oxygen at the anticipated levels. The omegatron is part of a vacuum system to which a cell with a platinum electrode can be connected.

In general, the following procedure will be utilized: The vacuum system will be pumped down to about 10^{-6} torr. Meanwhile, the cell with the platinum indicator electrode will be pretreated electrochemically, emptied, dried, and then connected to the vacuum system. Finally, the complete system will be pumped down to 10^{-6} torr; the omegatron-cell unit will be closed off from the pump system, and the amount of oxygen expelled while heating the platinum electrode will be monitored with the omegatron.

---

1. F. C. Anson, Anal. Chem. 33, 934 (1961).
2. G. Fryburg and H. Petrus, J. Electrochem. Soc. 108, 496 (1961).
3. C. G. Enke, and R. A. Barter, J. Chem. Ed. 41, 202 (1964).
4. H. Sommer, H. Thomas, and J. Hipple, Phys. Rev. 82, 697 (1951)

Preliminary calculations have shown that, for a ten square centimeter platinum indicator electrode with a monolayer of adsorbed oxygen, a partial pressure of 10^{-7} torr can be obtained inside a one liter system. This is well within the range of detectability for the omegatron, which can detect oxygen at pressures as low as 10^{-10} torr when the total pressure of the system is below 10^{-5} torr. However, due to the fact that the partial pressure of oxygen from the atmosphere will always be about 10^{-7} torr, the base oxygen signal will be of the same order of magnitude as the signal due to oxygen liberated from the electrode. Because of this possible interference, it is planned to enclose the omegatron and cell within a nitrogen-filled bag. The platinum electrode will be heated electrically with a Variac, and the temperature will be monitored by measuring the resistance of the platinum.

Once relation is established between the measured coulombs in the electrochemical oxidation of the platinum surface and the actual amount removed in the vacuum system, the procedure will be applied to systems involving an electrode-active substance in solution. (D. W. Shive and D. K. Roe)

I. Polarography of Cyclooctatetraene and its Silver Adducts

In previous reports some characteristics of the polarography of cyclooctatetraene (COT) were described. The process occurs at -1.40 to -1.55 V vs SCE, depending upon supporting electrolyte, and involves two electrons producing cyclooctatetraene after reaction with solvent. This electrode process is unusual in that the current-voltage curve can be nearly ideal. Our measurements have shown that the behavior depends strongly upon supporting electrolyte type and concentration. Using NaCl solutions, the half wave potentials vs SCE, slopes of E vs $\log(i_d - i/i)$ and electrolyte concentrations were respectively -1.506 V; 75 MV, 0.01 M; -1.467 V, 70 MV; 0.1 M; -1.417 V, 38 MV, 1 M. The shift in $E_1/_2$ is nearly the same as the change in the potential, ϕ_2, at the outer Helmholtz plane. Values of ϕ_2 are[1] -174, -119, and 166 MV at the same concentrations of Na^+. Similar results were obtained with KCl and LiCl. Using tetra-alkyl ammonium salts as the added electrolyte produced the ideal polarograms reported several times in the literature. Only a slight shift of $E_1/_2$ was found with changing concentration of type of salt which agrees with the conclusion that these cations are specifically adsorbed at low concentrations and consequently only slight changes in ϕ_2 result with increases of concentration.

The reduction of the silver adduct, $AgCOT^+$ in the presence of a slight excess of Ag^+ produces a reversible wave even in very dilute supporting electrolytes. These observations, as reported before, suggest that ion pairing may help to stabilize an intermediate, even though the ion pair is disrupted by the ultimate reduction of the Ag(I). Several attempts have been made to investigate the effect of COT on the reduction of Ag^+, but the results have been difficult to reproduce. As time permits, further attempts will be made. (P. Vouros, D. K. Roe)

---

1. C. D. Russell, J. Electroanal. Chem. 6, 486 (1963).

J. Electrochemistry of Triplet States

The purpose of this study is to determine the electrochemical behavior of the triplet state of anthracene. A solution of anthracene and a supporting electrolyte in deoxygenated tetrahydrofuran is prepared and the anthracene is excited to the triplet state using flash photolysis and the solution is rapidly scanned using a potentiostat with an oscilloscope readout.

A flash lamp circuit has been built which is capable of providing a flash of up to 50 joule total energy. Using a flashtube with a 1" arc length, this power supply-flash tube combination produces a flash with a duration (1/e) of ca. 50 μsec. The cell is a cylinder of 1" diameter with a planar face. The indicator electrode, a circular sheet of platinum foil with the back side inactivated by a coating of soft glass, faces the flash tube through the planar end. The reference electrode is a silver wire enclosed in a capillary tip which just projects over the edge of the indicator electrode between it and the front of the cell. The entire capillary is then blackened to protect the reference electrode from the light of the flash. The counter electrode is a piece of silver gauze in the rear of the cell.

The cell is filled with the proper amount of solid anthracene and tetra-n-butylammonium methane sulfonite (TBAM) to make a final solution which is ca. 0.001 M in anthracene and 0.1 M in TBAM. The entire cell is then sealed to a vacuum system in which the THF is deoxygenated by a freeze-pump-thaw technique combined with a chemical deoxygenation over NaK. When deoxygenation is complete as indicated by a blue colored solution of solvated electrons in the RHF, the THF is distilled into the cell and the cell sealed off under vacuum.

The resulting solution exhibits the typical anthracene anodic wave at +1.4V and a cathodic wave at ca. -1.9V when a current-voltage curve is obtained using a cyclic potential scan. For this system the cathodic portion of the curve is relatively reversible while the anodic wave is extremely irreversible. When the solution is excited by the flash lamp, a significant anodic current over background is observed at potentials as cathodic as -0.3 V. This is believed to be due to oxidation of the triplet state of anthracene because this anodic current is not observed when the light is blacked from the cell while the flash lamp is fired. This current is of the proper magnitude and lifetime that would be expected from our measurements of the anthracene triplet concentration and lifetime made under similar conditions.

In the next phase of the work, the measurements are to be extended to cover the entire potential range to try to find the reduction of the excited anthracene. Attempts will be made to further reduce noise pick-up in the electrochemical measuring circuit, and thereby increase the reliability of the measurements. (D. N. Bailey, D. M. Hercules, D. K. Roe)

II. Luminescence

A. Solution Electroluminescence of Aromatic Hydrocarbons

A number of experiments have been performed on light production during A.C. electrolysis of aromatic hydrocarbons. Rubrene was used as a model compound because of its high luminescence

efficiency and its desirable electrochemical properties. The solvent systems used were dimethyl-formamide (DMF) and acetonitrile (AN) with tetra n-butylammonium perchlorate as the supporting electrolyte.

It was observed that for solutions of rubrene, perylene, 9,10-diphenyl anthracene and tetraphenyl pyrene in DMF, a chemiluminescent reaction occurred when the potential range was restricted to that region where only the radical cation was produced. This behavior was not observed when AN was the solvent but did occur for AN when small concentrations of amines or DMF were added. This has been interpreted as a chemiluminescent reaction involving the radical cation and DMF or the amines. This is consistent with the electropositive character and chemical reactivity of the positive radical ion (half-life in DMF ca. 15 sec).

A number of variables affecting the rubrene reaction were studied. Oxygen was found to severely quench the light-producing reaction. Water was found to increase luminescence intensity in DMF (up to 4%) if solutions were stirred but to decrease intensity of unstirred solutions. Luminescence emitted by the positive ion reaction in DMF was found to be linear with rubrene concentration, making it unlikely that a reaction involving two rubrene molecules is responsible for light production.

The spectrum of chemiluminescence emission was measured for both the rubrene cation-anion combination reaction and the positive-ion-amine reaction. In both cases the emission was found to be identical with normal rubrene fluorescence.

The electrochemical generation of rubrene cations (R+) and anions (R^-) was found to be diffusion controlled according to the linearity of current with $t^{-1/2}$. Successive generation of first R^- and then R^+ at a platinum electrode establishes known concentrations and gradients of the two species, which then diffuse together to produce luminescence. In principle, the measurement of the light intensity-time characteristic could then be related to the rate of the chemiluminescent reaction and its efficiency. The boundary value is very complex and not solvable by conventional methods of transforms. A computer solution was obtained from Dr. Steven Feldberg at Brookhaven National Laboratories, who had already prepared a program for similar electrochemical problems.

Analysis of the data reveals that the reaction rate constant is $> 10^5 \ell$/mole sec for rubrene in DMF or AN. The efficiency of the reaction was 0.28 in DMF and 0.12 in AN. The corresponding fluorescence efficiencies in the two solvents were 0.41 and 0.31, measured by comparison with quinine sulfate using a Turner 210 absolute fluorescence spectrophotometer. Further electroluminescent experiments will be made to determine if traces of oxygen may have caused low efficiencies. (R. C. Lansbury, D. M. Hercules, D. K. Roe)

B. Chemiluminescence of Luminol

One of the most efficient and probably the best known chemiluminescent compound is luminol (5-amino2,3-dihydro-1,4-phthalazinedione, I). Light is produced when basic aqueous solutions of luminol containing oxygen are treated with an oxidizing agent such as potassium ferricyanide or hydrogen peroxide. The CL can also be observed in aprotic solvents, such as

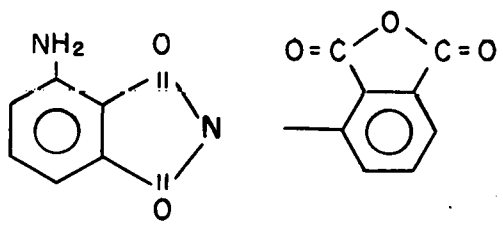
dimethyl sulfoxide (DMSO) and dimethylformamide (DMF), and in these solvents only oxygen and a base are required. The actual mechanism for the CL of luminol is not understood. However, the products of the reaction have been identified as nitrogen and sodium amino-phthalate (II). Furthermore, it has been shown that the CL spectrum of luminol is identical to the fluorescence spectrum of the 3-aminophthalate ion (3-AP), indicating that 3-AP* is the light emitting species in the CL reaction.

The purpose of the present work is to study the spectral characteristics of 3-aminophthalic acid (3-APA) and the luminol CL reaction under various conditions. This will provide some new information to aid in understanding the mechanism of the luminol CL reaction.

3-APA was purchased from Aldrich Chemical Company as the hydrochloride, and contained a yellow impurity which exhibited a bright green fluorescence. (3-APA is white and fluoresces blue.) The best method found for purifying it involved washing it with concentrated HCl, filtering, washing with tetrahydrofuran and drying. The absorption and fluorescence spectra of the resulting white crystals were identical to those of 3-APA. Neutral solutions of 3-APA were prepared and when these solutions were allowed to stand for a few days, they began to exhibit a green fluorescence. With solutions of about 10^{-2} M concentrations, it was found that after sitting for a few weeks, yellow crystals dropped out of the solution. These also showed a green fluorescence.

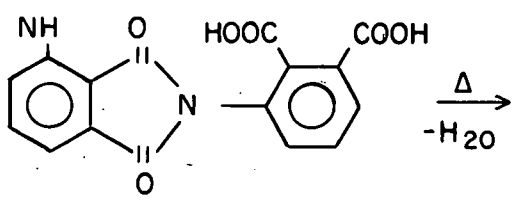
Experiments were run to determine whether the reaction was photochemical in nature, and it was found that even in the dark, neutral degassed solutions fluoresced green after a few days. This ruled out any photochemical reactions and indicated a self-decomposition of the 3-APA.

A high resolution mass spectrum was run to determine the elemental compositions corresponding to the yellow material. The computer output gave three possible elemental compositions: $C_{19}H_6N_3O_2$, $C_{21}H_8O_3$, and $C_{16}H_8N_2O_5$. The $C_{16}H_8N_2O_5$ seemed quite reasonable (3-APA: $C_8H_7NO_4$) and a tentative structure for the 308 peak is the following:



(III)

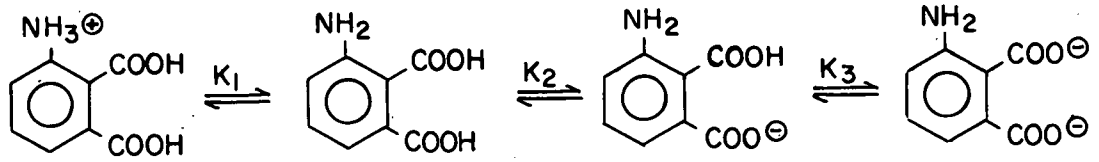
However, it is known that phthalic acid loses water and goes to phthalic anhydride in the high vacuum and high temperature of the mass spectrograph. Therefore, assuming a similar process is occurring with the "unknown", a reasonable structure for the yellow unknown would be:

IV 

(III)

The absorption and fluorescence spectra of 3-APA have been taken in the pH range 1.0-13.0. The absorption spectrum at pH = 1.0 shows a small band at 275 mμ and a larger band at 329 mμ. Upon increasing the pH, the 275 mμ band decreases and the 329 mμ band increases in intensity. At about pH = 3.0 the 329 mμ band begins to move to shorter wavelengths. When pH = 6 is reached, the band has shifted to 304 mμ and is unchanged with further increase of pH.

In order to determine the pK_a's of 3-APA, absorbance was plotted versus pH for the wavelengths: 275, 329, 321, and 304 mμ. Upon increasing the pH, the 275 mμ. The results are as follows:

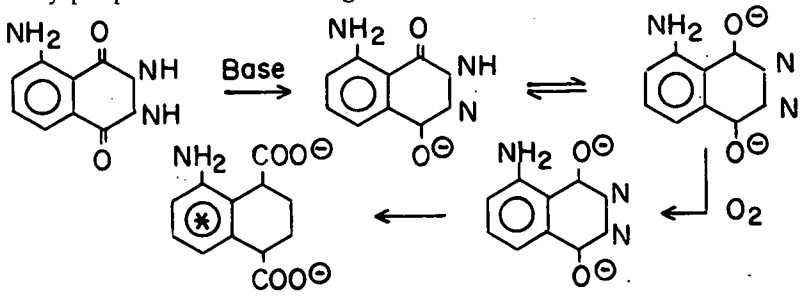


These are reasonable values to expect for 3-APA, since the pK_a's for phthalic acid are reported in the literature as 2.95 and 5.41.

The fluorescence spectra showed an increase in intensity and a shift in λ_{max} from 458 mμ to 424 mμ as the pH was increased to about pH = 6. After pH = 6, the λ_{max} remained at 424 mμ and the intensity remained constant. The λ_{max} of 424 for the fluorescence of 3-APA is in agreement with the luminol CL which is observed in basic solution. (J. D. Gorsuch and D. M. Hercules)

C. Studies on the Chemiluminescence of Luminol

Luminol (5-amino-2,3 dihydro-1,4 phthalazinedione) has long been known for its high chemiluminescence efficiency upon oxidation. In basic dimethyl-sulfoxide (DMSO) solutions luminol reacts directly with oxygen to produce light, in the absence of any other oxidizing agent. White, et al.,[1] have found the luminol reaction in DMSO to be first order with respect to luminol, oxygen and base. They proposed the following mechanism to account for the observed kinetics:



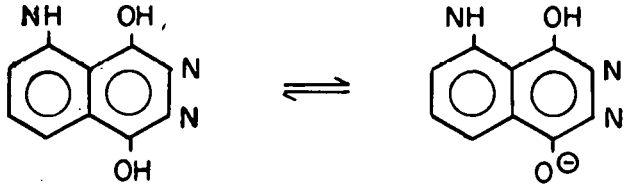
We have carried out spectrophotometric and kinetic studies which do not support the mechanism proposed by White, et al. We wish to propose a mechanism, similar to White's, but differing in several significant details.

1. E. White in Light and Life, W. D. McElroy and B. Glass, Eds., The Johns Hopkins Press, Baltimore, Maryland, 1961, p. 183; E. White, O. Zafirion, H. Kagi and J. H. M. Hill, J. Am. Chem. Soc. 86, 940 (1964); E. White and M. M. Bursey, J. Am. Chem. Soc. 86, 941 (1964).

Spectrophotometric Studies on Luminol

Before investigating the kinetics of the luminol reaction, a spectrophotometric study was carried out to determine the nature of the luminol species present in DMSO and water. First of all, both from spectrophotometric studies and from titration studies it was not possible to find evidence for existence of the dianion (III) proposed by White, et al. Even in strongly basic (potassium-t-butoxide) DMSO solutions the UV absorption spectrum matched that observed for the monoanion in DMSO.

Mixed solvent studies were performed to determine whether luminol exists in the keto form (Ia) or the enol form (Ib) in aqueous solution.



From the spectral studies (UV and IR) it is apparent that in water luminol is in form Ia and upon ionization goes to form IIa, as evidenced by the small spectral shift accompanying ionization of the molecule. Although it is not clear from the spectral studies whether form Ia or Ib exists in DMSO, the large change in ionization observed in DMSO indicates that the form is IIb. Also, in mixed solvents a 3000 cm^{-1} shift is observed in the UV spectrum of II, accompanied by significant changes in band structure. This is characteristic of a keto-enol tautomerism. The different species of luminol present in DMSO and water probably is the reason that the reaction mechanisms in these are different!

Another interesting item discovered during the spectrophotometric study was the existence of a complex formed between oxygen and DMSO. This complex absorbs in the region of 2700 A and probably is a "contact charge-transfer" complex similar to those described by Tsubomura and Mulliken[1] for a variety of solvents.

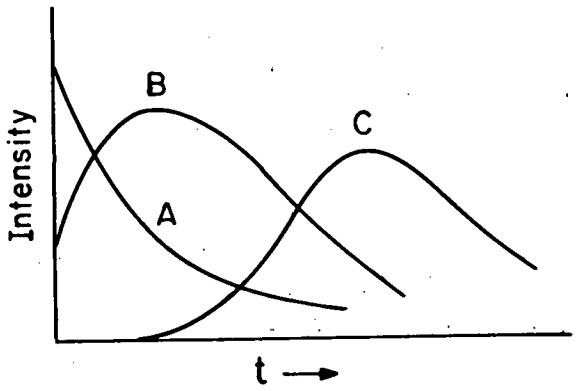
It appeared, on the basis of the kinetic studies, that the most reasonable first step would be a reaction between IIb and oxygen. Because solutions of IIb show no major change upon exposure to oxygen means that this step would have to be a reversible step, i.e., complex formation between IIb and oxygen. A slight decrease in absorbance was observed on the long wavelength bond of IIb when solutions were exposed to oxygen. Also, concentrated solutions of IIb showed a yellow color when exposed to oxygen. This would be characteristic of formation of a weak charge-transfer complex.

Kinetic Studies

Using a stopped-flow apparatus, one could obtain curves of varying form, depending upon the relative concentrations of luminol, oxygen and base.

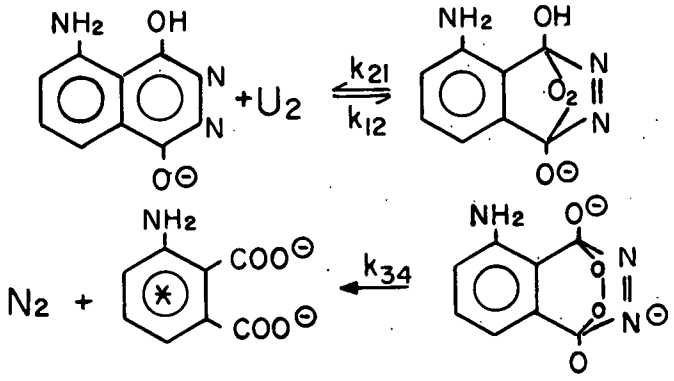
---

1. Tsubomura and R. S. Mulliken, J. Am. Chem. Soc. 82, 5966 (1960).



If the ratios of butoxide and oxygen to luminol were high, a pseudo-first order decay curve like A was observed. At intermediate ratios a curve like B was observed, and at low ratios a curve like C, showing both a maximum and an induction period were observed. These curves are typical of those obtained for an intermediate in a reaction having three or more consecutive stages.

If we assume constancy of all factors such as temperature, quantum efficiency of fluorescence, etc., then the light emission curve above represents the a rate of formation of 3-aminophthalic acid in the luminol reaction (since it is known to be the fluorescent product. This must, then, be equal to the rate of disappearance of the intermediate giving rise to 3-aminophthalic acid). Therefore, there must be <u>at least</u> three steps in the reaction which forms the excited state of aminophthalic acid. These studies led us to postulate the following mechanism for the luminol reaction:



Preliminary estimates of the rate constants are $k_{12} = 4 \times 10^3 m^{-1} sec^{-1}$, $k_{23} = 3 \times 10^3 m^{-1} sec^{-1}$, and $k_{3,4} > 5\ sec^{-1}$.

In order to decide between this mechanism and that of White, <u>et al.</u>, species IIb was equilibrated with oxygen and the decay curve obtained was compared with those obtained when IIb was not equilibrated with O_2. If White's mechanism was correct, identical curves should be obtained (under equivalent conditions of concentration) independent of oxygen equilibration. If our proposed mechanism is correct, then pre-equilibration should reduce the kinetic sequence by one

step, and the form of the curve should change. A change in the characteristic shape of the curve was observed in all cases. (G. D. Short, D. M. Hercules)

D. Excimers in Electroluminescence

Excimers, or excited state dimers, have been well established in irradiation studies of aromatic hydrocarbons. They are responsible for the appearance of a long wavelength fluorescence band in concentrated solutions of the hydrocarbons. No corresponding change is noted for the absorption spectrum of these solutions, indicating the excimers are formed only in the excited state. The excimer is described as an association between one singlet excited-state molecule and one singlet ground-state molecule.[1,2]

Birks and co-workers have made extensive kinetic studies of excimer systems.[3] Some of the compounds which they have found to exhibit excimer fluorescence are: benzene, toluene, naphthalene, 9-methylanthracene, pyrene, benzpyrene, dibenzpyrene, benzanthracene, and 2, 5 diphenyloxazole[4]. Solvent viscosity and temperature studies showed that excimer formation is diffusion-controlled and reversible.[5]

McGlynn has discussed the mechanism of excimer formation and has concluded that it is most likely due to a combination of molecular exciton splitting and charge resonance.[6]

Excimer formation and emission has been reported by Chandross, et al., via the annihilation of electrogenerated aromatic hydrocarbon radical cations and anions.[7] They studied the course of this reaction for several flat hydrocarbons unencumbered by bulky substituents and found that the path, leading to excimer formation, is a common process. Alternating current electrolysis a was used to generate the R^+ and R^- radicals of the hydrocarbons. The paths which these radicals may take are:

(a) $R^+ + R^- \rightarrow R + R^*$ (singlet or triplet)

(b) $R^+ + R^- \rightarrow (R_2)^*$ (excimer)

Some interesting contrasts with irradiation-formed excimers were apparent. The emission from perylene was mostly due to its excimer and differs sharply with the fluorescence of the same solution which has no excimer component. Even more surprising was the fact that anthracene yields mainly excimer emission by electrogeneration but no excimer emission has yet been reported for anthracene under irradiation. From fluorescence quenching experiments anthracene has been known to undergo self-quenching via the interaction of $^1R^*$ with R. The excimer of anthracene thus formed undergoes non-radiative decay to ground state molecules. Hence, it would appear that another excimer of anthracene exists from R^+, R^- annihilation and it is capable of direct fluorescent emission.

---

1. Z. Physik. Chem. N. F. 1, 19 (1954).
2. Z. Electrochem. 59, 976 (1955).
3. Proc. Roy. Soc., A 275, 575 (1963).
4. Proc. Roy. Soc., A 277, 571 (1964).
5. Proc. Roy. Soc., A 280, 289 (1964).
6. J. Chem. Phys. 41, 3131 (1964).
7. J. Am. Chem. Soc. 87, 3259 (1965).

The object of this study is to investigate contrasting excimer formation processes. Anthracene and some of its 9-substituted derivatives will be the compounds investigated. These compounds have a relatively high fluorescence efficiency and also form stable photodimers as well as excimers. The ratio of photodimer formation to excimer formation will be determined for both the electrogenerated and photolytically formed excimers. This ratio would be expected to be the same in both cases if the same process of excimer formation occurs for the two methods. Should the ratios not be identical, the mechanism of excimer formation during electrogeneration and annihilation might well be different than excimer formation in fluorescence quenching. The compound 9-methylanthroate has been prepared.[1] Attempts at purifying it and 9-methylanthracene by recrystallization have proved difficult. The purity of these compounds must be quite high for the intended study. It appears that they will have to be zone refined to guarantee the desired purity.

Solutions of 9-methylanthracene and 9-methylanthroate were made up in acetonitrile, dimethylformamide, and 1-methyl-2-pyrrolidinone. These will be used for preliminary current-voltage curves to determine the best solvent for the investigation. (T. C. Werner, D. M. Hercules)

E. Chemiluminescence from Electron Transfer Reactions

Chemiluminescence reactions are in general very complex and difficult to analyze with respect to the exact path of energy transfer and the physical and electronic nature of the emitting species. The inherent simplicity of electron-transfer reactions is attractive from the standpoint of investigating chemiluminescence mechanisms. Examples of systems meriting investigation are:

1) $e^-(\text{solvated}) + (\text{substrate})^+ \rightarrow (\text{substrate})^* \rightarrow (\text{substrate}) + h\nu$
2) $Ar\cdot^- + ML_x^{+(n+1)} \rightarrow (ML_x^{+n})^* + Ar \rightarrow ML_x^{+n} + Ar + h\nu$
3) $Ar\cdot^- + Ar\cdot^+ \rightarrow Ar^* + Ar \rightarrow 2Ar + h\nu$
4) $Ar\cdot^- + (\text{oxidant}) \rightarrow Ar^* \rightarrow Ar + h\nu$
5) $Ar\cdot^+ + (\text{reductant}) \rightarrow Ar^* \rightarrow Ar + h\nu$

The reduced form of the substrates appearing in the above reactions must be capable of fluorescence and the electron must be transfered with sufficient energy to result in production of an excited singlet state. Reactions of type (1) are valuable because the solvated electron being a very strong reducer should form a chemiluminescent reaction with most substrates that fluoresce. The aromatic negative free radical has been indicated as a useful reductant because both the source and energy of the electron are well defined. However, the production and handling of these radicals is relatively difficult.

Reactions of Type (2): Ruthenium Chelates

The first type of reaction investigated was the reduction of metal chelates. Only three basic mechanisms of fluorescence are exhibited in these complexes, the simplest being that of

1. J. Am. Chem. Soc. 76, 1088 (1954).

a fluorescent ligand such as 8-hydroxyquinoline. The lanthanide chelates of β-dikeones exhibit fluorescence created by energy transfer from the ligand pi-electron transitions to the metal ion f-electron transitions. The third mechanism of fluorescence involves a charge transfer transition from one of the ligand orbitals to a metal orbital. This can either be of a d$\leftarrow$p nature such as that exhibited by the chloride complexes of Tl(I), or of a d$\leftarrow\pi^*$ nature such as that exhibited by the tris-bipyridyl and tris-orthophenanthroline complexes of Ru(II).

Considerations of experimental problems, commercial availability, and the presence of a theoretical discussion of electronic states involved,[1] led to the investigation of the ruthenium chelates. The complexes are octahedral and the metal, when in the plus two oxidation state, has a low spin configuration (t_2^6). The absorption band occurring at 20,000 cm^{-1} is designated as $d\rightarrow\pi_1^*$, and the band at 40,000 cm as $d\rightarrow\pi_2^*$. The two remaining bands correspond to the ligand $\pi\rightarrow\pi^*$ bands. The fluorescence is very sharp, due to the lack of vibrational levels, and is designated as a $d\leftarrow\pi_1^*$ transition. It is to be noted, that the origin of the luminescence is not unambiguously determined, as Crosby, et al.,[2] have suggested that the transition is $d\leftarrow d^*$ in nature. Preliminary experiments run in this laboratory confirm the interpretation of Paris[1], and his mechanism is envoked.

Systems Demonstrating Chemiluminescence

Four different complexes have shown chemiluminescence. All have ruthenium as the metal ion and the ligands are 2,2'-bipyridyl and the 5-methyl, 5,6-dimethyl, and 3,5,6,8-tetramethyl derivatives of orthophenanthroline. It is interesting that the 5-phenyl derivative and the unsubstituted orthophenanthroline complexes have not shown chemiluminescence.

The complexes all exist in solution in the plus two oxidation state and must first be oxidized to the plus three state. So far, none of the plus three complexes have been isolated as a solid. Their stability, in this higher oxidation state is pH dependent reaching a maximum of a few hours at very high acidities. All studies have been done in aqueous solutions. The complexes are soluble in most non-aqueous polar, solvents but oxidize only with difficulty (PbO_2 or Cl_2 used as oxidizer).

Many reducers can be used but most interfere by forming insoluble reaction products or otherwise quenching. Those not showing complications are OH^- and N_2H_4.

Mechanism Studies

Because the light output from the reactions was low, a direct investigation of the chemiluminescence intensity as a function of wavelength was difficult. Using syringes and a constant flow pump, the emission spectrum of the bipyridyl complex with both hydroxide and hydrazine has been measured. It corresponded exactly to the fluorescence having a maximum at 590 mu (Ip21 photomultiplier on a modified Aminco-Bowman Spectrofluorometer) and a symmetrical peak shape of about 50 mu half width.

1. J. P. Paris, Studies on Molecular Electronic Transitions, Thesis, Purdue, 1960.
2. Crosby, G.A., et al., Luminescence from Transition-Metal Complexes: Tris (2,2'-bipyridine)- and Tris (1,10-phenenthroline) Ruthenium (II), J. Chem. Phys. 43, 1448 (1965).

The intensity of the reactions involving the orthophenanthroline derivatives was about one-tenth that of the bipyridyl complex and could not be detected with the usual instrumentation. Therefore, a chemiluminescence spectrometer was assembled. This spectrometer is essentially a photon counter that integrates the output of the reaction at a selected wavelength over a period of time. By using a flow system and manually changing the wavelength, a spectrum can be determined. However, no precaution was taken to correct for a light output varying with time. This modification is currently under construction.

Investigations into the mechanism of the reaction show that it is very fast and possibly diffusion controlled. Once an estimated value of the rate constant is obtained a detailed study of the mechanism will be undertaken with a stopped-flow spectrophotometer. (F. E. Lytle, and D. M. Hercules)

F. Chemiluminescence from Oxidation of Grignard Reagents

The reaction of certain alkyl and aryl magnesium halides with oxygen is accompanied by a green-blue luminescence, the color and intensity of which varies with the identity of the organic radical and the halogen atom. Previous investigations have failed to establish definite connections between the luminescence and

(1) the temperature of the reaction,

(2) the participation of the solvent in the reaction, and

(3) the structure of the alkyl or aryl moieties of the Grignard reagent.

Maximum luminescence intensity is obtained by rapid oxidation of aryl grignard reagents with para chloro substituents at molar concentrations in ethyl ether.

Phenyl magnesium bromide and p-chloro phenyl magnesium bromide in ethereal solution have been prepared in this laboratory, and their blue luminescence with oxygen demonstrated. The material remaining after oxidation of phenyl magnesium bromide exhibits a blue fluorescence which persists after hydrolysis in the yellow ether extract taken. This solution contains biphenyl (which is present in the original grignard solution), phenol and benzene as determined by gas chromatographic analysis. The chromatograms show the presence of several other compounds boiling above 200°C. Work is in progress to isolate these compounds and to identify the one (ones) responsible for the blue fluorescence. (R. L. Bardsley and D. M. Hercules)

III. Spectrometry

A. Spectrophotometric Determination of Stability Constants

The intent of this work is to determine the stability constants of complex compounds from spectrophotometric data. Methods are available for determining the stability constants when only one or two species are absorbing but when, for example, six complexes are formed, there may be as many as eight species absorbing, and the number of unknowns present becomes too large to handle by conventional methods. Graphical techniques exist which attempt to treat the latter

situation, but there are inherent disadvantages in these methods that one would like to avoid, i.e., they are quite subjective, they yield no dependable measure of the reliability of the values reported and they are very dependent on initial assumptions one must make as to the identity of species present at specific ligand concentrations. A recent approach to the solution of complex equilibria has been to use high-speed digital computers to perform a many-fold repetition of a low-order process, but the work in this area has been confined to data obtained from extraction, potentiometric and ion exchange studies. Spectrophotometric data have not been treated for very complex systems in this manner because in addition to the unknown concentrations of each species, there are also the unknown absorption coefficients for each species at each wavelength being studied. In this investigation, mathematical techniques in conjunction with computer techniques are to be applied to the problem of determining all of these unknown parameters.

The specific system chosen to investigate was that of the complexes of titanium (III). Titanium (III) was prepared by the reaction of HBr with TiH_2 since bromide ion was reported not to complex with Ti(III) and was, therefore, to be used to maintain a constant ionic strength. Solutions of concentration between 0.1 and 0.5 M Ti(III) were prepared from weighed amounts of TiH_2 (increasingly greater concentrations of Ti(III) required correspondingly greater concentrations of HBr to prevent hydrolysis) and the Ti(III) concentration then determined volumetrically with Fe(III). Solutions of 0.2 M Ti(III), or less concentrated, gave quantitative results corresponding to the amount of TiH_2 used. At concentrations greater than 0.3 M Ti(III), the concentration determined with Fe(III) was much lower than would correspond to the amount of TiH_2 taken. Furthermore, on addition of metallic zinc to solutions in the latter range, the absorbance at 500 mμ steadily increased, and the absorption coefficients calculated on the basis of the experimentally determined concentrations were not constant.

It has been previously reported in the literature that Ti(III) is oxidized to Ti(IV) by hydrogen ion in both HF and HCl solutions. Furthermore, a Ti(III)-Ti(IV) complex has been reported in both chloride and sulfate solutions, with an absorption maximum in the region of 480 mμ. The observed difference between the calculated and determined Ti(III) concentration could therefore be attributed to oxidation of Ti(III) to Ti(IV) in more acidic solutions, and the variation of the absorption coefficient with Ti(III) concentration could be accounted for by the presence of a complex between Ti(III) and Ti(IV), bridged by a bromide ion. Because this system was found to be more complex than anticipated and because it would be advantageous to use a well defined system for initial computations, the experimental work was discontinued and attention focussed on mathematical procedures for solving the general problem of obtaining stability constants from spectrophotometric data.

The mathematical technique of principal component analysis (eigenvector analysis) was employed to attempt to resolve a series of spectra of metal complexes at different ligand concentrations into the individual absorption spectrum of each species. A computer program was written following the general outlines of the procedure described by Simonds[1].

1. J. L. Simonds, J. Optical Soc. Am. 53, 968 (1963).

It was decided to have the computer synthesize the spectra to be evaluated in order to eliminate the experimental error which could possibly obscure the relationships between the parameters obtained as output from the program, i.e., roots, vectors, and scalar multiples and the sought for factors: number of absorbing species and concentrations and absorption coefficients at each wavelength for all the species present. Therefore, a program was written to take the absorption coefficients of nickel nitrate, copper sulfate and cobalt nitrate and combine them in various ratios so as to give absorbances to be used as input to the eigenvector program. Although these three compounds are not exactly analogous to a system containing one metal and a changing concentration of ligand, they are sufficient to determine the sought-for relationships, and at the same time they avoid a problem which may arise in the metal-ligand system, i.e., there being only n-1 independent species rather than the actual number n of absorbing species.

The number of roots determined by the program corresponded to the number of absorbing species for the synthetic system, but it was also found that the vectors, scalars and roots are all concentration dependent. In order to determine this dependency, the vectors were plotted as a function of wavelength. This procedure does not yield the original spectrum of each metal, but if the actual absorption coefficients are plotted as $a - a_v$ (a representing absorption coefficient), vector 2(V_2) resembles the spectrum for the nickel compound. If it is then assumed that the vectors are a similar function of some unknown average, i.e., $V = a - Q_{av}$, then $Q_{av} = a - V$; if we then take $a_{Ni} - V_2$ we should get Q_{av} and then $Q_{av} + V_1$ should be one of the other components and $Q_{av} + V_3$ should be the remaining component. This proves to be true only for the shape of the curve, i.e., the absolute values of the calculated and true absorption coefficients differ as do the ratios of the values. It has been concluded that one cannot separate the averaging procedure to give the absolute values of the absorption coefficients and concentrations, and that even if this were possible, these values could not be attributed to specific species present in the solution since the equation $A = a_1c_1 + a_2c_2$ can just as well be represented by $A=(a_1+a_2)c_1+a_2(c_2-c_1)$. The eigenvector program can, however, still be used to determine the total number of species contributing to the observed absorbance.

At the present time, a numerical procedure is being studied, whereby a surface is constructed from initial estimates of all the unknowns and the surface is then adjusted to give the best fit to the experimental data, i.e., absorbances at every wavelength, total metal concentration, and total ligand concentration, for each change in ligand concentration. Because of the sensitivity of such calculations to random error and noise, the elimination of as much scatter as possible in the primary data is most desirable. A smoothing program based on the least squares procedure suggested by Savitzky and Golay[1] has been written and tested on experimentally determined absorption spectra of thallium perchlorate solutions. The method appears to be very effective in eliminating noise and clarifying spectral detail and should be very useful in the analysis of complex spectra.

---

1. Savitzky, A., and Golay, M.J.E., Anal. Chem. 36, 1627 (1964).

The efficiency of a procedure for fitting stability constants and absorption coefficients to spectrophotometric data is greatly enhanced by having good initial estimates for the parameters to be evaluated. Therefore, the graphical method of Newman and Hume[1] is being modified for computer use to provide these initial estimates for the fitting procedure. (A. S. Gordon, D. N. Hume)

B. Flame Photometric Determination of Strontium and Barium in Sea Water

A procedure for the separation and determination of strontium and barium at natural levels in sea water has been developed and applied. The elements are concentrated on an ion exchange resin, selectively removed by complexation and determined flame photometrically.

A study of the removal of strontium and barium from sea water indicated that conventional organic ion exchange resins were superior for this purpose to inorganic exchangesr. A study of the optimum dilution and absorption characteristics of the elements in question revealed that maximum quantitative absorption of strontium and barium was achieved from sea water adjusted to pH 3 with hydrochloric acid using an organic ion exchanger in the calcium form. The elution characteristics showed that complexation of strontium and barium was necessary if acceptable elution volumes, predictable elution peaks and quantitative recoveries were to be obtained. It was found that 0.02 M cyclohexanedinitrilotetraacetic acid would quantitatively elute calcium and stronium from the resin at pH 5.0 and 6.5, respectively. Barium, still held in the resin, was then removed with 0.01 M EDTA in an ammonia buffer of pH 10. Radiochemical tracer studies showed that recoveries of strontium and barium were quantitative and excellent separation was achieved from other elements which might interfere in the subsequent determination.

The excitation and emission characteristics of strontium and barium in various media were studied using air-hydrogen flames. The cooler air-hydrogen flame was found to be superior to the oxy-hydrogen flame, and optimum conditions for determination at the levels obtained from sea water were worked out. Suitable sampling techniques were developed and tested. It was shown by tracer studies that the adsorption of strontium and barium from sea water was negligible on polyethylene, polypropylene, and Teflon containers when the sea water was initially adjusted to pH 3.0 with hydrochloric acid. The precision of the method was determined by replicate analysis on sea water samples, and the accuracy verified by standard addition procedures. The standard deviations of the overall separation and determination procedure were found to be 0.05 ppm for strontium and 0.6 ppb for barium.

Sea water samples taken from four ocean stations through the cooperation of the Woods Hole Oceanographic Institute have been used in a preliminary test of the method as a tool for oceanographic research. The determination of strontium and of strontium to salinity ratios as a function of depth from the surface to 2,000 meters showed very striking and reproducible profiles characterized by minima in the upper 200 meters of water. A similar pattern is observed for

1. Newman, L., and Hume, D.N., J. Am. Chem. Soc. 79, 4571 (1957)

barium. Although some suggestion of this effect might have been deduced from previously published studies, it has always been assumed that strontium to salinity ratios in particular have been constant as a function of depth because the previously available analytical methods have never had the precision to establish the existence of an effect to a sufficient degree of statistical significance. The effects here observed are much larger than the uncertainty of the analytical methods, and can be correlated with known biological activity as a function of depth. The desirability of a much more extensive oceanographic investigation is suggested. (N. R. Andersen, D. N. Hume)

C. Thallous Chloride and Perchlorate Complexes

Spectrophotometric measurements have been made of the systems $Tl^+ + Cl^- = TlCl$ and $Tl^+ + ClO_4^- = TlClO_4$ to determine formation constants. Over the range of 0.001 to 1.0 M added anion, the absorbance (A) of the aquated cation was measured with a Cary 14 Spectrophotometer. It can be easily shown that a plot of 1/A vs anion concentration times the square of the activity coefficient permits a calculation of the formation constant from the slope and intercept. There was, however, no constancy of formation constant with wavelength.

The measurements were repeated using a Turner Spectrophotofluorometer. A significant amount of fluorescence was occurring and caused an artifact in the Cary 14 measurements. The curves recorded on the Turner contain a great deal of noise and are being smoother with a computer program. When this is done, the formation constants will be calculated and interpreted. (J. R. Layton and D. K. Roe)

D. Solubility of Metallic Mercury

The purpose of this investigation was to study the solubility of mercury in aqueous electrolyte solutions as a function of applied potential. Previous studies have ignored the variable of potential. In a carefully deoxygenated pure electrolyte solution the potential of mercury is not defined, but might be presumed to be near the point of zero charge which is the point of maximum surface tension. If equilibrium exists between dissolved mercury and the bulk mercury phase, one would not expect a potential dependence of solubility. However, an equilibrium between dissolved mercury and mercury adatoms would give rise to a potential dependence since the surface concentration of the latter species is potential dependent.[1] Further considerations also point to possible difference in the rate of solution of mercury atoms with potential. Information along these lines would be useful in understanding the role of mercury electrodes in trace analysis.

Absorbance measurements were selected as the means to monitor the concentration of mercury. Bonhoeffer and Reichardt[2] have shown that the absorption maximum is at 2537A, and the molar absorptivity is 7.35×10^3. A ten-centimeter cell would show an absorbance of 0.021 if saturated with mercury.

---

1. R. J. Watts-Tobin, Phil. Mag. 6, 133 (1961).
2. K. F. Bonhoeffer, H. Reichardt, Z. Physik 67, 780 (1961).

Initial measurements were made with a combined absorbance cell-electrolytic cell. The reference electrode was Hg_2Cl_2(0.1 M KCl)/Hg. Contamination of the solution in the light path with suspended Hg_2Cl_2 occurred at an unexpected rate, and the measurements varied from reasonable to impossible values. Interferences from oxygen were also encountered. Also chloride solutions were found to have such high absorbance in the vicinity of 2537 A that the spectrophotometer gave unreliable readings.

A cell was designed to avoid the above difficulties, and the electrolyte was changed to 0.1 M Na_2SO_4 for both parts of the cell. The junction between the two electrodes was designed to further minimize diffusion. The cell was located in a nitrogen-filled box, and the absorbance cells were filled and stoppered in the inert atmosphere. Equilibration between mercury and solution was hastened by magnetic stirring. The absorbance measurements were made with a Beckman DU using scale expansion to improve accuracy.

A completely satisfactory series of measurements has not yet been made. The indications are, however, that there is a change in concentration with potential. The time-rate of change at fixed potential has not been unambiguously measured so it is not possible to decide at this time if the solutions were indeed saturated. (A. Gordon, D. K. Roe)

E. Molecular Complexes of 1, 4, 5, 8-Naphthalene Tetra-Carboxylic Acid Dianhydride (NTCADA)

We have studied the properties of NTCADA as an electron acceptor in molecular complex formation and have found it to be a strong acceptor. Naphthalene, α-methyl naphthalene, pehanthrene, pyrene, hexamethyl benzene, pentamethyl benzene, perylene, tripheylene and durene were used as donors.

The solid complexes prepared were found to be strongly fluorescent in the region 550-600 mμ. Absorption spectra were taken in a 1:1 benzene-dimethyl sulfoxide (DMSO) mixture. Molar extinction coefficients and equilibrium constants were calculated using Benesi-Hildebrand plots. (G. D. Short, T. F. Retajczyk, Jr., D. M. Hercules)

F. A Spectrophotometric Study of 8-Mercaptoquinoline

The spectra characteristics of 8-mercaptoquinoline have been studied with the aim of elucidating the nature of the electronic transitions in the molecule. Special attention was paid to the long-wavelength, visible absorption band which gives the mercaptan its intense color, since the analogous 8-hydroxyquinoline is colorless. The effects of pH, solvent, and chelation on the absorption, fluorescence, and phosphorescence of the mercaptan were studied.

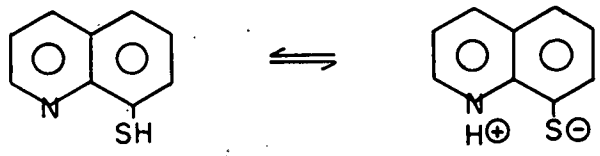
The spectra of the mercaptan were found to be directly analogous to those of 8-hydroxyquinoline, with the exception of the relative intensities of the absorption bands. The long wavelength absorption band in the mercaptan lies at 447 mμ in water, with an extinction coefficient of 1600. The analogous band in 8-hydroxyquinoline, which appears at 430 mμ, has an extinction coefficient of 64. This difference is accounted for by the change in the equilibrium constant for the following equilibrium:

Early measurements indicated that the use of the radiofrequency plasma torch resulted in elimination of the usual spectrochemical interferences. However, when minor modifications were made in the design of the confining chamber of the torch with the objective of improving stability, the interferences, e.g., aluminum depression of calcium emission, appeared in the plasma. This showed that much had still to be learned about the principles underlying the instrument in addition to simply achieving stability in spectral output. To this end, a number of carefully controlled modifications in design have been assessed. Most of the work has centered on the torch chamber itself, and variation in the confining tube diameter has been found to be particularly significant. Utilizing calcium atoms as an emitting species, it was found that emission was 20% higher from a 32 mm tube than from a 48 mm tube and that anion interferences were eliminated. Further modification included placement of an external electrode at ground potential on the outside of the tube. Aluminum has proven to be a satisfactory electrode material, its high thermal conductivity enabling it to maintain a relatively low temperature. Design of the electrode configuration required considerable experimentation. It was found necessary to position the electrode carefully so that it neither overlapped the torch tip, which caused wandering of the plasma, nor was positioned so high up the confining tube as to be ineffective. When the bottom edge of the electrode is concentric with the point of the torch tip, its effect seems to be optimized. The plasma is well centered in the tube, and very stable in appearance and spectral output.

The second area of instrumental refinements centered around the atomizer system. In addition to acquiring the more satisfactory ultrasonic transducer already described in an earlier report, the internal volume of the system has been considerably reduced. Where formerly 20 mm tubing was used, 10 mm tubing is used, giving higher flow velocity through the tubing with better mixing of the sample aerosol and plasma support gas. The sample shows only minimal heating with temperature increases of approximately 5°C per 10 minutes of atomizing. The system has been so constructed that the sample chamber may be bypassed by the plasma support gas. In this way atomizing may be interrupted, sample changed, sample chamber flushed with support gas to eliminate air, and the new sample atomized into the plasma without disturbing the balance of the plasma by introduction of foreign gases.

It was desired to measure the stability of the intensity of the spectral lines in the plasma. In order to eliminate variability due to the sample introduction system, a mixed gas was used consisting of 95% nitrogen, the usual support gas, and 5% hydrogen. The system was allowed to come to equilibrium and the 4861 A hydrogen line intensity monitored. Repeated scans across the peak gave a peak height -- using arbitrary emission units -- of 198 with a standard deviation of 3.3 units (1.6%). With the monochromator set to measure the peak intensity vs time, it was found that with a peak intensity of 120, the range of variation was 5.0 units (±2.3%).

The stability of the atomizer system was checked by atomizing sample solutions and comparing the results with those obtained above. Over a period of several minutes, using a 2.0 ppm calcium solution, for example, the average emission intensity at 4227 A was 214 and the standard deviation 10 units (4.7%). In a one-minute period the average was 220 and the standard deviation



where X = oxygen or sulfur. Because of the greater acidity of the mercapto group, the amount of the mercaptan zwitterion formed in aqueous solution is twenty-five times that of the 8-hydroxyquinoline zwitterion.

The behavior of the long-wavelength absorption band in various solvents gives conclusive evidence that it arises from an intramolecular charge transfer (from the sulfur to the ring) transition occurring in the zwitterionic form of the molecule. This band probably results from a shift of the long-wavelength absorption band in the neutral form of the molecule, which appears at about 320 mμ and has considerable charge transfer character. The shift is due to the much lower energy required to transfer an electron from a negatively charged atom to a positively charged region, compared to that required where there is no charge separation before the transfer.

The mercaptan has been found to fluoresce from the second excited singlet state of the zwitterionic form. This anomaly is due to the extremely large energy gap between the first and second excited singlet states; this situation is analogous to that encountered in azulene, which previously was the only compound known to fluoresce from the second excited singlet state in solution.

Chelation of the mercaptan precludes the formation of the zwitterionic form, and the spectral characteristics of the chelates have been found to be entirely analogous to those of the 8-hydroxyquinoline chelates. The chelates have been found to fluoresce, except where the metal ion is of such a nature that it quenches the fluorescence, as in the case of paramagnetic metal ions such as nickel.

Molecular orbital calculations were done for mercaptan. The results of the calculations lend good support to the interpretation of the experimental data. (P. D. Anderson and D. M. Hercules)

G. Plasma Emission Spectroscopy

Investigation into the properties of the radiofrequency plasma as a spectrochemical excitation source has been continued. The optimum combination of parameters for freedom from spectrochemical interferences and stabilization of spectral output has been achieved by several avenues of investigation. The modifications made have made it possible to make measurements with good reproducibility: the short term stability (1 minute) of measurements is 1.6 %, and longer term stability (5-10 minutes) about 4.7% in terms of relative standard deviation of the readings. A better understanding of the excitation mechanisms involved is being sought in order to further increase the usefulness of the technique.

3.2 units (1.5%). This indicates the magnitude of "long term" drifting of the atomizer output, and that introduction of sample into the plasma does not itself cause any instability in output.

In order better to understand the operation of the plasma source, investigations into the use of gases other than nitrogen will be made. It may be possible to improve the sensitivities already achieved through the use of mixed gases as the support medium. The easily excited elements, e.g., calcium and sodium, should be most sensitive in relatively cool plasmas. Oxide formers, e.g., aluminum and zirconium, should be most sensitive in a plasma which would also provide a reducing atmosphere. Those elements excited only with difficulty, e.g., zinc and nickel, should be most sensitive in very hot plasmas. One experiment which might test this would be to mix oxygen into the nitrogen support gas in different ratios and determine the effect on the three types of atoms. (A. L. Malenfant and D. N. Hume)

IV. Chromatography

A. Vapor Liquid Equilibrium of Aqueous Amine Solutions

The initial purpose of this investigation was the development of a technique for the study of mixed ligand complex metal ion equilibria involving volatile ligands. An examination was begun of the silver ion-pyridine-picoline system in aqueous solution by means of simultaneous EMF measurements and analysis of the vapor phase by gas chromatography. It soon became evident that the liquid-vapor equilibrium of the amine solutions was too complicated to allow direct interpretation of the metal ion-amine reactions. The gas chromatographic technique of head space analysis, however, revealed itself as a very useful means of determining vapor-liquid equilibria in otherwise difficult systems and was, therefore, developed in some detail.

The usual dynamic methods of studying vapor-liquid equilibria are slow, difficult and require large amounts of sample. The much simpler static method, which is ordinarily considered insufficiently sensitive, is made much more practical by the high sensitivity of gas chromatography. The equilibration apparatus may be very simple -- a flask closed with a serum cap -- and the method is equally applicable to binary and multicomponent systems. Solutions much more dilute than needed for conventional equilibrium stills are applicable, temperature may be varied readily, and the amount of sample actually needed for analysis is vanishingly small (approx. 10^{-9} moles). The great flexibility inherent in gas chromatography makes possible the development of a straight-forward analytical procedure for practically any mixture of compatible vapors.

To test the method, a study of the vapor pressure of amines in aqueous solutions was undertaken. The first system to be studied was pyridine in aqueous solutions containing inert electrolytes and pyridinium salts. Good agreement was obtained with studies done by previous workers using much more elaborate methods. The study showed "salting out" in the presence of salts such as potassium nitrate, potassium chloride, and sodium perchlorate, and the effect is increased by increasing the salt concentration. "Salting in" was observed in the presence of pyridinium salts. The vapor pressure of pyridine in all systems followed Henry's law until the

concentration of pyridine in solution exceeded 0.1 M.

Marked negative deviations at higher concentrations suggested a chemical effect and the possibility of a dimerization reaction was examined. If the total concentration of amine is assumed to be the sum of the concentrations of monomer and dimer, and if $C_D/C_M^2 = K_2$, the mass balance is $C_T = C_M + 2K_2C_M^2$. Assuming Henry's law to hold (as it evidently does in dilute solutions) $P_M = HC_M$, which on substitution and rearrangement gives

$$C_T/P = 1/H + (2K_2/H^2)P .$$

Experimentally, plots of C_T/P versus P were indeed found to be linear over the range of 0.1 to 0.4 M for pyridine and 0.05 M to 0.2 M for gamma-picoline. Typical results are given in Table 2.I.

Table 2.I

Evidence for Dimerization of Amines in Aqueous Solution

	Pyridine		Picoline	
Solution	H	K_2	H	K_2
Water	8.06	1.00	2.39	1.23
0.5 M KNO_3	8.55	0.90	2.48	1.07
1.0 M KNO_3	8.89	0.74	2.72	1.19
0.5 M $HPyNO_3$	5.59	0.39	2.05	0.93

The very low Henry's law constant for pyridine in pyridium nitrate (salting in) suggested another chemical effect, and the possibility of association between pyridine and pyridinium ion was examined. Assuming no other causes for the deviation from ideal behavior, the lowering of the pyridine vapor pressure was assumed to be due to the formation of $Py:H:Py^+$ ions and a formation constant calculated. Over the range of 0.04 to 0.12 M pyridine in 0.5 M pyridinium salts, excellent agreement was found with this picture, the formation constants ranging from 1.36 for chloride to 1.76 for perchlorate media. (J. N. Little and D. N. Hume)

V. Electron Spectroscopy

A. Application of Electron Spectroscopy to Chemistry

Recently it has been pointed out that electron spectroscopy offers excellent possibilities as a useful tool in analytical chemistry[1] and it should be applicable to a variety of different chemical studies. Electron spectroscopy is the analysis of the energy distribution of photoelectrons ejected from atoms when they are subjected to bombardment by x-rays. The technique is

1. S. Hagström, C. Nordling and K. Siegbahn, Phys. Letters 9, 235 (1964).

quantitative (±1% relative should be obtainable) and offers the possibility of direct determination of elemental ratios in compounds, including the C:O ratio which is generally difficult to perform. As a tool for qualitative analysis, it should be useful for determining the oxidation number (valence state) of an element and for structural analysis of organic compounds. In the latter category, it offers the kind of information obtainable for protons by NMR, but would not be limited to one or two elements as is NMR. To date, the only analytical data published by this technique are for the Si:C ratio in SiC,[1] the photoelectron lines for the sulfur atoms in $S_2O_3^{=}$[1], studies on effects of oxidation and alloying on some fifth period elements[2], and chemical shifts in Cu, Cu_2O, and CuO[3].

Instrumentation

Basically, the instrument used in electron spectroscopy (ELS) is a β-ray spectrometer, and a wide variety of such instruments have been described. This is combined with an x-ray source and a Geiger-counter detector, along with appropriate power supplies.

The photoelectrons are produced by x-ray bombardment of the material under study. Control of the x-ray intensity must be better than ±1% because this determines the maximum precision of the method. The magnetic field, B_0, causes the electrons to transcribe a circular path, with radius of curvature, ρ, and electrons having an energy equivalent of $B_0\rho$ will be focused on the detector. (Other electron energies will focus at some other point on the detector plane.) As the magnetic field is scanned (B_0 = 0 to ca. 70 gauss), an electron spectrum is produced, thus the name electron spectroscopy.

The ultimate precision with which the electron intensity can be measured is determined by the geiger detector used, and the relative precision is ca. $\sqrt{N}/N$. This means that 1% precision can be obtained by accumulating 10,000 counts. (Count rates of 10^4 cpm are not uncommon in ELS.)

The precision of locating a given electron peak depends ultimately on B_0 and ρ (as well as on slit widths and other parameters). The radius of curvature can be controlled to 0.1 mm out of 30 cm, and control of B_0 to one part in 10^5 is possible with modern electronics. Natural line widths in ELS are ca. 0.2-0.5 eV and electron energies for light elements are ca. 5 keV, so that qualitatively one can distinguish between electrons differing in energy by 1 part in 10^4.

A 255° double focusing, iron-free electron spectrometer is currently under construction at the Institute of Physics, University of Uppsala, Sweden. This instrument offers high resolution with high transmission and is stigmatic. Currently magnetic field surveys are being conducted to select a suitable location for the spectrometer when it is delivered to our laboratories (ca. July 1966). When a suitable location has been selected, construction of a set of degaussing coils will be constructed to provide the field-free region necessary for location of the spectrometer.
(D. M. Hercules)

---

1. S. Hagström, C. Nordling and K. Siegbahn, Phys. Letters 9, 235 (1964).
2. C. Nordling, Arkiv f. Fys. 15, 241 (1959).
3. C. Nordling, E. Sokolowski and K. Siegbahn, Ark. f. Fys. 13, 483 (1958).

Addresses

D. M. Hercules, "Photo-Electric Effects",
Radiation Physics Laboratory, Du Pont Experimental Station, Wilmington, Del., October 15, 1964;
University of North Carolina Faculty Seminar, Chapel Hill, N.C., March 30, 1965.
Northeastern University Faculty Seminar, Boston, Mass., April 14, 1965.

D. M. Hercules, "Luminescence of Metal Chelates", Eastern Analytical Symposium, New York, N.Y., November 13, 1964.

D. M. Hercules, "Fluorescence and Phosphorescence", University of Illinois, Urbana, Ill., Dec. 8, 10, 1964.

D. M. Hercules, "Luminescence Techniques for Trace Analysis",
Society for Applied Spectroscopy, New England Section, Boston, Mass., January 12, 1965;
Washington Section Analytical Sub-Group, American Chemical Society, Washington, D. C., January 14, 1965.

D. M. Hercules, "Electrochemically Generated Chemiluminescence", Durham International Conference on Chemiluminescence, Durham, N.C., April 2, 1965.

D. M. Hercules, Panel Discussion on Electrochemically Generated Luminescence, Electrochemical Society Meeting, San Francisco, California, May 12, 1965.

D. M. Hercules, "Why Molecules Luminesce", Mid-America Spectroscopy Symposium, Chicago, Illinois, June 14, 1965.

D. M. Hercules, "Chemiluminescence" and "Photo-Electric Effects", American Chemical Society Lecture Tours, October 15-22, 1965, and November 8-16, 1965, midwest and New York State.

D. M. Hercules, "Luminescence of Organic Molecules", Universal Oil Products Co., Des Plaines, Illinois, December 6, 1965.

D. N. Hume, "New Chemistry Curricula in the USA",
Swiss Federal Institute of Technology Colloquium, Zurich, Switzerland, Feb. 25, 1965.
University of Göteborg Colloquium, Göteborg, Sweden, March 9, 1965.
Abo Akademi Colloquium, Abo, Finland, May 18, 1965.
Institute Ruder Boskovic, Yugoslavia Atomic Energy Commission, Zagreb, Yugoslavia, June 24, 1965.

D. N. Hume, "Radio Frequency Plasma Emission Spectroscopy", University of Göteborg Colloquium, Göteborg, Sweden, March 10, 1965.

D. N. Hume, "New Approaches to the Teaching of Chemistry in the USA", Swedish Chemical Society Meeting, Stockholm, Sweden, April 1, 1965.

D. N. Hume, "The Thorium Chloranilate-Fluoride Reaction", Royal Institute of Technology, Stockholm, Sweden, April 28, 1965.

D. N. Hume, "Plasma Emission Spectroscopy," Analytical Group, Northeastern Section, American Chemical Society, Cambridge, Mass., Nov. 30, 1965.

W. E. Ohnesorge, "Analytical Applications of Metal Chelate Luminescence", Western New York Section, American Chemical Society, Buffalo, N.Y., December 8, 1964.

W. E. Ohnesorge, "Fluorescence and Phosphorescence of Metal Chelates", Lehigh University Faculty Seminar, Bethlehem, Pa., April 13, 1965.

D. K. Roe, "A Mechanism of the Galvanostatic Voltage Oscillations during Formic Acid Oxidation", Electrochemical Society Meeting, San Francisco, Calif., May 13, 1965.

D. K. Roe, "Potentiostatic Chromatography with Thin Film Mercury Electrodes", Union Oil Co., Brea, Calif., May 14, 1965.

D. K. Roe, "Cathodic and Anodic Processes of Silver Single Crystal Electrodes", Shell Development Co., Emeryville, Calif., May 17, 1965.

D. K. Roe, "Anodic Stripping Voltammetry with Thin Film Mercury Electrodes"
Leeds and Northrup Co., North Wales, Pa., May 19, 1965 (also "The Determination of Transition Times from Chronopotentiometric Curves".
North American Philips Co., Briarcliff Manor, N.Y., May 20, 1965.

D. K. Roe, "Anodic Stripping Voltammetry with Amalgamated Nickel Electrodes", Pennsylvania State University, Department of Chemistry Seminar, July 29, 1965.

D. K. Roe, "Solution to Two Diffusion Problems in Electrochemistry", Northeastern University Department of Chemistry Seminar, October 21, 1965.

D. K. Roe, "Electrode Reaction Kinetics - Methodology and Interpretation", Florida State University Department of Chemistry, Seminar, November 5, 1965.

G. D. Short, "Electroluminescence of Organic Compounds: The Role of Gaseous Discharge in the Excitation Process", American Chemical Society National Meeting, Detroit, Michigan, April 5, 1965.

Publications

D. N. Bailey and D. M. Hercules, "Flash Photolysis - A Technique for Studying Fast Reactions", J. Chem. Ed. 42, A83 (1965).

R. L. Birke and D. K. Roe, "Galvanostatic Method for Measuring Rates of Fast Electrode Reactions, I. Reconsideration of the Single Pulse Method", Anal. Chem. 37, 450 (1965).

R. L. Birke and D. K. Roe, "Galvanostatic Method for Measuring Rates of Fast Electrode Reactions, II. Modified Method with Precharging of the Double Layer", Anal. Chem. 37, 455 (1965).

W. R. Matson, D. K. Roe, and D. E. Carritt, "Composite Graphite-Mercury Electrode for Anodic Stripping Voltammetry", Anal. Chem. 37, 1594 (1965).

O. Popovych and L. B. Rogers, "Effects of Steric Hindrance and of Bond Type on Electronic Absorption Spectra of Certain 8-Quinolinolates", Spectrochim. Acta 21, 1229 (1965).

D. K. Roe and J. E. A. Toni, "An Equation for Anodic Stripping Curves of Thin Mercury-Film Electrodes", Anal. Chem. 37, 1480 (1965).

G. D. Short and D. M. Hercules, "Electroluminescence of Organic Compounds: The Role of Gaseous Discharge in the Excitation Process", J. Am. Chem. Soc. 87, 1439 (1965).

A. L. Van Geet and D. N. Hume, "Measurement of Proton Relaxation Times with a High Resolution Nuclear Magnetic Resonance Spectrometer: Progressive Saturation Method", Anal. Chem. 37, 979 (1965).

A. L. Van Geet and D. N. Hume, "Measurement of Proton Relaxation Times with a High Resolution Nuclear Magnetic Resonance Spectrometer: Direct Method", Anal. Chem. 37 983 (1965).

J. T. Watson, D. K. Roe, and H. A. Selenkow, "Iodine-129 as a 'Nonradioactive' Tracer", Radiation Research 26, 159 (1965).

Theses

N. R. Andersen, "Flame Photometric Determination of Strontium and Barium in Sea Water", Ph.D., September 1965.

P. D. Anderson, "A Spectrophotometric Study of 8-Mercaptoquinoline", Ph.D., December 1965 (to be awarded Feb. 1966).

R. L. Birke, "A Study of Galvanostatic Analysis for the Investigation of Fast Electrode Processes", Ph.D., September 1965.

Barbara Vickers, "Anodic Stripping Voltammetry using a HgSe Indicator Electrode", B.S. (Chemistry) June 1965.

ORGANIC ISOTOPE APPLICATIONS GROUP

Summary

Chlorine (Cl^{35}/Cl^{37}) isotope effects, coupled with kinetic order and substituent effects, show that reactions of triphenylmethyl chloride in benzene at 25° proceed by entirely different mechanisms depending on the nucleophile. The first-order reaction with quaternary ammonium carbonate or fluoride (or with radio-chloride or azide at low concentrations) is zero order in salt and has a large chlorine isotope effect (1.9%), evidently involving formation of a triphenylcarbonium salt intermediate in the rate-determining step. The second-order reaction with 0.1 M. azide is much faster, and has an even larger chlorine isotope effect (2.0%), which is invariant with substituents. This requires the ionic carbonium chloride to be formed in a fast first step, followed by a rate-determining reaction of this carbonium salt with the azide salt. The third-order reaction with 0.1 M. methanol is very slow, and has small chlorine isotope effects highly variable with substituents. This is incompatible with any carbonium ion mechanism, but consistent with a cyclic front-side displacement yielding ether in one step. The major new discovery revealed by the chlorine isotope effects is the second order carbonium ion mechanism for the azide reaction. The second-order kinetics seems incompatible with front-side attack by the quaternary ammonium azide, but consistent with back-side attack. This mechanistic diversity, all with one alkyl halide, solvent and temperature, seems quite remarkable.

The Grunwald-Winstein solvent polarity (Y value) of tetra-n-hexyl-ammonium benzoate (a liquid salt at 25°) is -0.37, close to that of the reference solvent mixture, 80% ethanol - 20% water.

The largest hydrogen isotope effects ever measured in a single-step reaction have been observed in the enolization of sodium d-p-(α-isobutylphenacyl)-benzenesulfonate, the rate determining step in the racemization of this optically active ketone in aqueous solution at 25°. These primary kinetic tritium (k_H/k_T) isotope effects are 16.7, 19.5 and 24.9 for attack by hydroxide, 2, 2, 2-trifluoro-

ethoxide and phenoxide ions. Comparison with Brönsted catalysis law slopes and secondary solvent isotope effects obtained previously indicate an unexpectedly thin barrier and high coupling force constant between reacting O-H and H-C bonds at the transition state.

The decomposition of benzenediazonium ion in neutral or acidic solvents is an authentic unimolecular decomposition. The N^{14}/N^{15} isotope effect for the carbon-bound nitrogen in the decomposition of benzenediazonium fluoborate in 1.0 M. sulfuric acid at 25° is 1.0207 ± 0.0016, incompatible with a concerted displacement mechanism but consistent with one proceeding through the very unstable phenyl cation as an intermediate. The k_H/k_D ortho-hydrogen effects are also very large, 1.53 ± 0.03, indicating that the transition state has considerable positive charge delocalized onto these hydrogens (as in a protonated benzyne). The para-hydrogen effect is small, 1.03, showing that the charge is not distributed this far.

t-Butyltrimethylammonium ion solvolyzes in 84-95% sulfuric acid at 176° at a rate independent of water and bisulfate ion concentrations, confirming that trimethylcarbonium ion (and not t-butyloxonium ion or t-butylsulfuric acid) is forming in the rate-determining step.

The k_{16}/k_{18} solvent water isotope effect in solvolysis of benzoyl chloride is 1.0078 ± 0.0026 in 50% water - 50% dioxane at 25°, but 0.9966 ± 0.0028 in 20% water - 80% dioxane, suggesting an ionization mechanism in 50% water but mainly a concerted or addition-elimination reaction in 20% water.

The variation of activity coefficient with % sulfuric acid in sulfuric acid-water mixtures up to 70% sulfuric is remarkably constant for six carbonium, quaternary ammonium and phosphonium, and tertiary oxonium and sulfonium salts, each of which either has its central atom well shielded by organic groups or else has a highly delocalized positive charge. Different behavior is observed for diphenylhalogenonium ions, primary, secondary, tertiary and less shielded quaternary ammonium ions, and alkali metal ions. A major revision of the H_R acidity scale may be required above 50% sulfuric acid by evidence that substantial fractions of the cations from nitro-substituted triarylcarbinols exist as colorless

oxonium ions at acidities just below those which yield predominantly carbonium ions. (C. G. Swain)

Structure-reactivity relationships in free radical reactions are under investigation in a variety of atom transfer reactions of carbon radicals (9-decalyl, 8-hydrindyl, 4-t-butyl-1-methylcyclohexyl), a termination reaction (cage recombination of alpha-phenylethyl radicals), and oxidative cyclization reactions (conversion of erythro-5-deutero-2-hexanol to cis- and trans-2,5-dimethyltetrahydrofuran by lead tetraacetate and via the hypochlorite). The 9-decalyl radical has been examined by means of the chain decomposition of cis- and trans-9-decalylcarbinyl hypochlorite. The ratio of trans to cis-9-decalyl chloride is dependent on initial hypochlorite concentration in the cis series but not in the trans series. Two types of 9-decalcyl radicals must be involved; the radical from the cis series may be converted to that from the trans series but the reverse change does not occur. Examination of cis- and trans-dimethyl(1,3)-dimethylcyclobutyl)carbinyl hypochlorite indicates that the same 1,3-dimethyl-1-cyclobutyl radical is formed in both series.

The previously developed method of electrolytic generation of radical ions in situ has been applied to investigation of the mode of decomposition of nitroalkane radical anions. Continued difficulty has been encountered in efforts to produce radical anions of saturated hydrocarbons. Radical anions of o, m, and p-deuteroanisole have been prepared and employed in studies of coupling to form biphenyl. (F. D. Greene)

I. Mechanisms of Reaction of Triphenylmethyl Chloride in Benzene

Chlorine isotope effects have finally settled the mechanisms by which triphenylmethyl (trityl) chloride reacts in benzene solution at 25° with different nucleophiles such as quaternary ammonium carbonate, azide (0.1 M.) or methanol. It is now evident that three quite distinct mechanisms are involved with these three nucleophiles.

II. The Ionizing Power of Tetra-n-hexylammonium Benzoate

Tetra-n-hexylammonium benzoate is a viscous oil at 25°. Hence, by using this salt as a solvent, one can study organic reactions in fused salts at relatively low temperatures. One might expect high polarity for this solvent because it is a salt. On the other hand, the large alkyl groups might so shield the ammonium and benzoate groups that it would more closely resemble a hydrocarbon.

A measure of solvent polarity is the Y value of Grunwald and Winstein, defined as the common logarithm of the ratio of first order rate constants for solvolysis of t-butyl chloride in a given solvent and in 80% ethanol - 20% water as a standard.

We have now determined that the Y value is -0.37 for this solvent. Thus it is, in fact, of intermediate polarity, nearly the same as 80% ethanol, as judged by its ability to promote solvolysis of t-butyl chloride. (A. Ohno)

III. Enolization of Ketones by Bases

The structure of the transition state in the base-catalyzed enolization ketones is being studied by observing effects on rate and equilibrium in the enolization of sodium p-(α-isobutylphenacyl) benzenesulfonate, an optically active ketone with only one α-hydrogen, caused by variations in base, ketone, solvent, inert salts and temperature. Our previous work on this problem by Dr. M. F. Grundon was concerned especially with the dependence of rate on base strength and with secondary solvent isotope effects. With different alkoxide, phenoxide and carboxylate anions in water at 25°, the Brönsted catalysis law plot is a smooth curve with slope varying from 0.25 for hydroxide to 0.8 for trimethylacetate, indicating that as the basicity of the oxygen anion decreases there is a progressive variation in the structure of the transition state from one close to reactants to one close to products with respect to bond order of the $\overset{-}{O}$---H bond which is forming. The secondary isotope effect from comparison of DO^- and HO^- as bases (in D_2O and H_2O respectively) affords another criterion of the degree of formation of the O---H bond at the

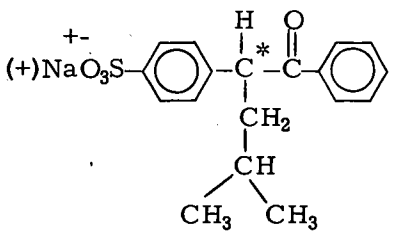
The simplest of these is the one for carbonate (0-0.05 M.), fluoride (0-0.02 M.), radiochloride below 0.007 M., and azide below 0.05 M. For these the rate is first order in trityl chloride, zero order in salt. The salts used are usually tetrabutylammonium or tetrahexylammonium salts. The chlorine isotope effect is 1.0191 ± .0001.

The second-order reaction with 0.05-0.1 M. azide has a rate over forty times faster than the preceding reaction. The chlorine isotope effects are even slightly larger than before, and invariant with different substituents: 1.0197 ± 0.0004 for p-methyl, 1.0196 ± 0.0001 for unsubstituted, 1.201 ± 0.0001 for p-chloro, 1.0997 ± 0.0001 for m-chloro and 1.0197 ± 0.0001 for p-nitro. This constant maximum value indicates a two-step mechanism with ionization of the chloride, assisted by azide, completed in the first step, but with the second step, covalent bond formation between carbonium salt and azide, the rate determining one. In order for it to be rate determining, the reaction of carbonium salt with azide must be slower than the reaction with chloride represented by reversal of the first step. This seems possible only if the azide is on the backside. Then the second step results in quaternary ammonium and chloride ions separated by trityl azide, which is electrostatically less advantageous than reversal, because reversal results in no separation of the components of an ion pair.

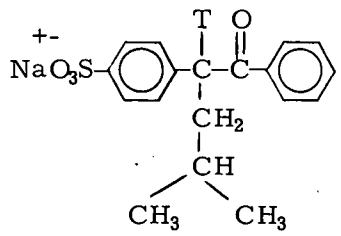
Most complex is the relatively very slow third-order reaction with methanol. This has been discussed in earlier reports, but an important additional chlorine isotope effect has now been determined for the p-nitro substituent. The combined isotope effects are 1.0102 ± 0.0006 for di-p-methyl, 1.0089 ± 0.0003 for p-methyl, 1.0064 ± 0.0006 for unsubstituted, 1.0052 ± 0.0002 for p-chloro, and 1.0026 ± 0.0001 for p-nitro. Thus they are generally less than half of the maximum effect of 2.0%, but highly dependent on substituent. This is incompatible with a carbonium ion mechanism of any kind, but fully consistent with the front-side cyclic mechanism involving two methanol molecules (or one at lower concentrations) as proposed earlier. (A. Ohno, Joanne W. Mitchell)

transition state. This ratio is 1.23. Since the maximum effect is the equilibrium constant for the reaction $DO^- + 1/2\ H_2O \rightleftharpoons HO^- + 1/2\ D_2O$, for which recent values range from 2.0 to 2.2, this corresponds to log 1.23/log K or 26-30%, in satisfactory agreement with the value of 25% derived from the slope of the Brönsted catalysis law plot in the region of catalysis by strong bases.

Primary hydrogen isotope effects (α-H vs. α-T in the ketone) are now being measured. Although most current theories predict a maximum for about half transfer, in fact no system is known in which an experimental primary isotope effect first rises and then unambiguously falls with a systematic monotonic change of structure. The present system must give this result if these theories are correct because the transfer ranges from 0.25 complete for hydroxide ion to 0.8 complete for trimethylacetate ion, with seven bases in between. The maximum primary isotope effect is predicted for 0.40 transfer. Table 3.1 summarizes initial kinetic results on racemization of IA and exchange of IB. The kinetic H-T isotope effect increases



IA



IB (racemic)

Table 3.1

Primary kinetic isotope effects in enolization of ketones at 25.0° C.

Base RO^-	$[RO^-]$, M.	[ROH], M.	$[OH^-]$, M.	$10^4 k_H$, $M.^{-1}sec.^{-1}$	$10^4 k_T$, $M.^{-1}sec.^{-1}$	k_H/k_T	pK_B
HO^-	0.0501	55.5	0.0501	118	7.05	16.7	0.00
$CF_3CH_2O^-$	0.0889	0.186	0.0111	69.4	3.55	19.5	3.37
$C_6H_5O^-$	0.0998	0.0204	0.0004	7.74	0.311	24.9	5.76

with increasing basicity of the attacking nucleophile. It is not known yet whether the isotope effect will, in fact, go through a maximum. The isotope effect for m-nitro phenoxide ion (pK_B = 7.36) is now under study. If the isotope effect does

go through a maximum it would appear from the present data that it will be a broad one. This suggests that the frequency for crossing the potential barrier separating reactants and products ($i\nu^{\ddagger}$) is large and, accordingly, tunnelling (non-classical barrier penetration) should be important. These predictions are subject to experimental verification and work along these lines will continue. (V. P. Vitullo)

IV. Mechanism of Decomposition of Benzenediazonium Ion

The major products of decomposition of benzenediazonium fluoborate, BF, in both protic and aprotic solvents of widely varying nucleophilicity, are derived from attack on the solvent, even when nucleophiles such as chloride or bromide are present. When 0.03-0.05 M. BF is decomposed in 1.00 M. hydrochloric or hydrobromic acid, yields of 0.8-1.4% fluorobenzene and 8% chlorobenzene or 13% bromobenzene are obtained. The yields of halobenzene are decreased by adding up to 10 M. sulfuric acid or by increasing the temperature to 50-60°. Decomposition of 10^{-3} M. BF at 25° in acetic acid containing 0-1.00 M. lithium chloride produces 70-80% phenyl acetate and no more than 28% chlorobenzene. Decomposition of 0.100 M. BF in acetone or 3-methylsulfolane at 25° produces 87% or 54% phenol respectively, but only 13% or 17% fluorobenzene.

The insensitivity to solvent nucleophilicity is shown also by the constancy of the rate constant $k = 2.14 \pm 0.03 \times 10^{-5}$ sec.$^{-1}$ in the range from 75 to 105% sulfuric acid and its near equality in 3-methylsulfolane. $1.31 \pm 0.033 \times 10^{-5}$, methylene chloride, $2.20 \pm 0.05 \times 10^{-5}$, water, $4.59 \pm 0.03 \times 10^{-5}$ and methanol, $9.80 \pm 0.042 \times 10^{-5}$. The solvent isotope effect is $k_{H_2O}/k_{D_2O} = 1.00 \pm 0.03$. The absence of a correlation of either rate constants or yields of products with nucleophilicity of the attacking species rules out a concerted mechanism.

When 0.1 M. BF is decomposed in 75% aqueous acetic acid containing 0.20-0.25 M. sulfuric acid and 0.44-4.0 M. bromine, the maximum total yield of bromobenzene and p-dibromobenzene is only 28%. Benzene, the product resulting from abstraction of hydrogen by phenyl radicals formed in less than 5% yield in all solutions studied. The low yields of benzene and bromobenzene therefore rule out radical intermediates.

The kinetic nitrogen isotope effect k_{14}/k_{15} for decomposition of BF in 1.00 M. sulfuric acid is 1.0207 ± 0.0016, in agreement with published data within experimental error. The nitrogen isotope effect calculated from the Bigeleisen equation for a two-fragment model with 75% breakage of a bond between a benzene ring with mass 77 and a nitrogen molecule with mass 28 or 29 at the transition state in 1.0200.

Since a phenyl cation might be expected to gain some stability by overlapping its empty orbital with the carbon-hydrogen bond on an ortho carbon to form a structure similar to benzyne, diazonium salts labeled with deuterium in ortho and para positions have been decomposed in order to determine whether the carbon-hydrogen bonds were altered in the transition state. The results in Table 3.2 were obtained.

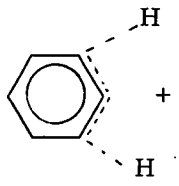
Table 3.2

Deuterium isotope effects

Compound	Solvent	Temperature	$k_H \times 10^5$	$k_D \times 10^5$	k_H/k_D
2,4,6-trideuterobenzenediazonium fluoborate	0.1 M. H_2SO_4	25.10°	4.62	3.10	1.49
	1 M. H_2SO_4	25.20°	4.42	2.92	1.52
	1 M. H_2SO_4	25.00°	4.16	2.70	1.54
	CH_2Cl_2	25.20°	2.24	1.42	1.58
p-deuterobenzenediazonium fluoborate	1 M. H_2SO_4	25.00°	4.16	4.05	1.03

Since the isotope effect in most aromatic reactions is small and inverse, the value k_H/k_D of 1.49-1.58 is quite unusual. Since the value for deuterium in the p-position is so small, and may indeed be within experimental error, it is evident that only the hydrogens on the ortho positions are affecting the rate. Formation of a benzyne intermediate would require the formation of large amounts of product in which the entering nucleophile adds ortho to the original position. Products of this kind have not been reported but may be present to the extent of a few per cent, since

most of the product studies for this reaction have been done before gas chromatography was available. It is more likely, however, that the bonds should be represented as shown. The overlap of the empty orbital and the C-H bonds can be on



both sides simultaneously.

All of the experimental data are consistent with an elimination-addition mechanism with rate-determining formation of phenyl cation. (J. E. Sheats)

V. The State of Solvation of t-Butyl Cation

To determine if carbonium-ion intermediates are involved in reactions of t-butyl and other tertiary aliphatic halides, esters and "onium ions", even in very polar solvents like 80-100% sulfuric acid, we undertook to measure rates of solvolysis of t-butyl compounds in these media to see whether the rate parallels the water concentration (implying bimolecular nucleophilic attack by water), or bisulfate ion concentration (ester formation rate determining) or is independent of both (ionization to carbonium ion rate determining). Our previous work on rate of enolization of a ketone in these solvents showed it to parallel water concentration very precisely (nucleophilic attack by water only). Therefore it seemed possible that the t-butyl group, like the proton, might be merely transferred bimolecularly, without ever being set free.

t-Butyloxonium ions were studied using t-butyl alcohol and t-butylmethyl ether. The n.m.r. spectral absorption at 92.5 c.p.s. was used to obtain the rate constants in Table 3.3 for t-butyl alcohol solvolysis.

Table 3.3

Solvolysis of t-butyl alcohol in sulfuric acid at 55°

[t-BuOH], M.	Acid, %	$k_1 \times 10^4$, sec.$^{-1}$
0.27	95.2	> 100. at 25°
0.10	85.0	2.5 = 0.8
0.10	74.4	2.1 = 0.6
0.02	74.4	0.9 = 0.3

A similar study was done using t-butylmethyl ether. Since both compounds are more than 99% protonated in the acid region studied, the increase of rate of solvolysis with increasing acid concentration is interpreted as a reaction with sulfur trioxide.

Table 3.4 summarizes data obtained using t-butyltrimethylammonium bisulfate.

Table 3.4

Solvolysis of t-butyltrimethylammonium bisulfate in concentrated sulfuric acid at elevated temperatures

Temp., °C	Conc. of Acid, %	Conc. of Salt, m.	Rate Constant $k_1 \times 10^5$, sec.$^{-1}$
185.	84.98	0.1255	5.62
185.	84.98	0.1200	5.56
185.	94.82	0.1215	5.92
175.84	84.86	0.0130	2.98 ± 0.17
175.84	87.80	0.0106	3.04 ± 0.24
175.84	95.19	0.0106	3.10 ± 0.17

These rate constants were obtained from the decrease of t-butyl n.m.r. absorption relative to an internal standard. These results are interpreted as supporting an S_N1 mechanism for the solvolysis of this compound, i.e., the formation of the t-butyl cation does not require a water molecule or bisulfate ion to stabilize it at 176-185°.

The required temperatures are so extreme with this quaternary ammonium salt that we cannot be sure that the same mechanism operates at 25°. Currently work is in progress on the t-butyldimethylsulfonium perchlorate system which has a rate constant of 3.81×10^{-7} sec.$^{-1}$ for solvolysis at 75.2° in 87.5% sulfuric acid, and work is continuing on the t-butyloxonium ions, which react at reasonable rates even at 25°, to see if the same mechanism holds over the whole range. (T. J. Lynch)

VI. Oxygen Isotope Effects in the Hydrolysis of Benzoyl Chloride

The water-oxygen isotope effect in the hydrolysis of benzoyl chloride in dioxane-water mixtures at 25° is given for three mixtures in Table 3.5. These

Table 3.5

Oxygen isotope effects in the hydrolysis of benzoyl chloride

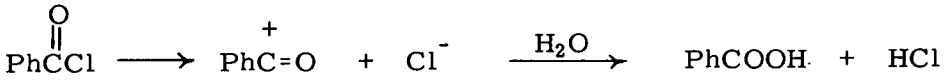
Solvent Vol. Percent Water	$\frac{k_{16}}{k_{18}}$
50	1.0078 ± 0.0026
20	0.9966 ± 0.0028
5	0.9990 ± 0.0030

oxygen isotope effects were obtained by comparison of the oxygen-18 abundances of two samples of benzoic acid: the first from hydrolysis of benzoyl chloride with an exactly equivalent amount of water, the second from hydrolysis of benzoyl chloride in dilute solution. Both benzoic acid samples were converted to carbon dioxide by pyrolysis at 550°, and the carbon dioxide analyzed using a mass spectrometer.

The oxygen isotope effect is the same in 20% water as in 5% water within experimental error. However, the isotope effect in 50% water is significantly different from the other two. It is unlikely that a variation of this magnitude represents merely a solvent effect - two distinct mechanisms must be involved in these two cases. This conclusion is consistent with a considerable amount of data previously reported. Particularly convincing is the change in slope of the Hammett

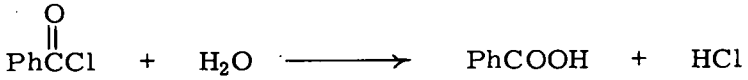
plot for solvolysis of substituted benzoyl chlorides. In nonpolar solvents a good Hammett plot is obtained, with slope about +2. In solvents of intermediate polarity the plot is parabolic, and in very polar solvents the plot is again a straight line, but with a slope of about -4.

The isotope effect in 50% water is most consistent with an ionization mechanism. This mechanism has been postulated many times, and is well-

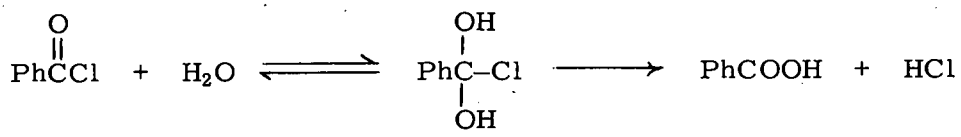


established in the case of mesitoyl chloride.

It is not yet possible on the basis of the present data to distinguish between a concerted hydrolysis



and a stepwise hydrolysis involving a tetrahedral intermediate in less polar sol-



vents, but work in progress on oxygen exchange should soon differentiate between these possibilities. (M. H. O'Leary)

VII. Activity Coefficients of Cations in Sulfuric Acid-Water Mixtures

The activity coefficients of a number of cations are being determined by measurement of the solubilities of their salts in aqueous sulfuric acid. Comparison of the activity coefficient behavior of triarylcarbonium ions is being used to check the validity of the H_R acidity function. The data will be used also to choose one cation as a standard ion for comparison of activity coefficient behavior of other cations.

The 1-benzenesulfonyl-1, 2, 3, 3-tetracyanopropenide (BSTCP) salts of a number of cations were prepared and their solubilities in a number of concentrations of sulfuric acid between 0 and 70% were measured. As a simple, single parameter to characterize the solubility behavior of the salts, the logarithm of the ratio of the solubility in 70% sulfuric acid to the solubility in 40% sulfuric acid has been chosen arbitrarily. Table 3.6 shows the value of this parameter for the salts whose solubilities were measured during 1965. Table 3.7 shows some data obtained previously and data obtained by Deno.

Table 3.6

Solubility behavior of BSTCP salts measured in 1965

Cation	Log. solubility ratio[a]
Triphenyloxonium	1.779
Triphenylcyclopropenium	1.811
Diphenyliodonium	1.309
Diphenylbromonium	1.463
Tetraethylammonium[b]	0.483

a. Log (solubility in 70% H_2SO_4/solubility in 40% H_2SO_4)

b. Invalid because of formation of a liquid phase at the higher acidities.

Table 3.7

Solubilities of BSTCP salts measured previously

Cation	Log. solubility ratio[a]
Triphenylsulfonium	1.802
Triphenylcyclopropenium[b]	1.811
Trianisylcarbonium[c]	1.815
Tetraphenylphosphonium[c, d]	1.803
Tetrabutylammonium[c, d]	1.736
Potassium[c, d]	0.566

a. Log (solubility in 70% H_2SO_4/solubility in 40% H_2SO_4).

b. Standard ion. Solubility ratio for perchlorate salt is 1.172.

c. Calculated from the solubility ratio of the perchlorate.

d. Calculated from data of Deno.

As can be seen from these data, a number of cations have similar activity coefficients, namely those whose central atom is shielded by three or four organic groups or those possessing extensive delocalization of the positive charge. The cations which possess differing activity coefficients are the poorly shielded diphenylhalogenonium ions, potassium ion and the tetraalkylammonium ions. It has been previously observed by Deno and Boyd that ammonium ions possessing one or more protons on the nitrogen and the tetraalkylammonium ions differ markedly in activity coefficient behavior both from other cations and among themselves. The behavior of the activity coefficients of the tetraalkylammonium ions seems to approach that of the triphenyl'onium ions as the length of the alkyl group is increased.

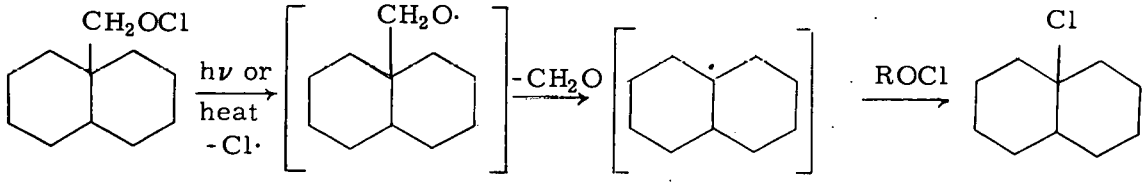
It was found that in the case of tetraethylammonium and trimethylsulfonium BSTCP salts at certain concentrations of sulfuric acid the phase in equilibrium with the acid was not the pure salt, but a salt-rich liquid phase. A similar behavior has been observed by Deno for tetrabutylammonium perchlorate above 70% sulfuric acid. It is interesting that none of these compounds forms a hydrate below 98% relative humidity. A benzene solvate of tetrabutylammonium perchlorate is known.

In another aspect of this problem, the distribution coefficients of p-nitrophenyldiphenylmethanol (NPDPM) were measured between heptane and 0-62% sulfuric acid. It was found that the distribution coefficient of uncolored species (carbinol plus oxonium ion) increases by a factor of four between 40 and 62% sulfuric acid. In this region, simple aromatic compounds such as benzene or diphenylmethane have essentially invariant solubilities. Nitrobenzene increases in solubility above 30% sulfuric acid. The solubility behavior of nitrobenzene is similar to that of NPDPM up to ca. 52% sulfuric acid, but increases much less rapidly at higher concentrations of acid. This indicates that the formation of oxonium ion from NPDPM is important in the acidity range in which its ionization has been measured and suggests that the H_R acidity function may be invalid in the region above 50% sulfuric acid. (K. Harbison)

VIII. Selectivity in Free Radical Reactions

Studies of selectivity in atom transfer reactions to the 9-decalyl radical have been completed. The principal results and conclusions are summarized in the abstract of the thesis of N. N. Lowry.

The 9-decalyl radical has been examined by the free radical chain decomposition of cis- and trans-9-decalylcarbinyl hypochlorites in fluorotrichloromethane. The major products of the reaction are formaldehyde and cis- and trans-9-decalyl



chlorides. The ratio of trans to cis chloride is dependent on the stereochemistry of the starting hypochlorite. Decomposition of trans-9-decalylcarbinyl hypochlorite affords trans- to cis-9-decalyl chloride in a ratio of 15 (0°) and 30 (-40°); the ratio of chlorides is independent of initial hypochlorite concentration. Decomposition of cis-9-decalylcarbinyl hypochlorite (initial concentration, 0.4 M) yields the chlorides in a ratio (trans/cis) of 6.1 (0°) and 3.8 (-40°). The ratios are dependent on initial concentration and vary from 1.1 (3 M, -40°) to 30 (0.008 M, -40°). Chain length studies indicate both cis- and trans-9-decalylcarbinyl hypochlorites decompose with chain lengths greater than 1000. The results indicate the occurrence of two different 9-decalyl radicals, in which the radical initially formed from the cis-hypochlorite either reacts with hypochlorite to give decalyl chloride or isomerizes to the radical derived from the trans-hypochlorite; this radical does not convert back to the radical initially formed from the cis-hypochlorite. The relevance of these results to questions of the conformation of the decalyl system and to radical geometry are discussed.

cis- and trans-9-Chlorodecalin have been reduced with tri-n-butyltin hydride at 130°, 60°, and 0°. The same ratio of cis- and trans-decalin was obtained at each

$$RCl + R'_xSnH_{4-x} \longrightarrow RH + R'_xSnH_{3-x}Cl$$

temperature (cis/trans = 1/11 at 0°) regardless of the stereochemistry of the starting chloride. Use of triphenyltin hydride or di-n-butyltin dihydride gave ratios of decalin products similar to those obtained with tri-n-butyltin hydride.

Photochemical chlorination of decalin in carbon disulfide, attempted formation of cis-9-decalylcarbinyl hypochlorite, and the reaction between 1-methylcyclohexyl formate and t-butyl hypochlorite were briefly studied as potential means of forming tertiary radicals; these reactions did not give meaningful results concerning the stereochemistry of carbon radicals. (N. N. Lowry)

In order to ascertain whether the two decalyl radicals, required by the results of N. N. Lowry (above), differ in geometry at the angular position (cis vs. trans radicals) or in conformations of the rings, an investigation of the 8-hydrindyl radical has been undertaken. The starting materials and products needed for this study, cis and trans-8-chlorohydrindane, and the 1-8 and 4-8 hydrindenes have been prepared. Experiments to establish stereochemistry are complete, and will be followed by detailed examination of decomposition of cis and trans-8-hydrindylcarbinyl hypochlorite.

Decomposition of either cis- or trans-dimethyl(1, 3-dimethyl-1-cyclobutyl) carbinyl hypochlorite in $CFCl_3$ at -80° affords the same mixture 45/55 of cis- and trans-1-chloro-1, 3-dimethylcyclobutane. These results indicate that the strained 1, 3-dimethyl-1-cyclobutyl radical either is planar or has a low barrier to interconversion of pyramidal forms. (J. P. Engstrom)

The 4-t-butyl-1-methylcyclohexyl radical, generated by the free radical chain reduction of either the cis or trans-1-chloro derivative by tri-n-butyltin hydride, undergoes hydrogen atom transfer with the tin hydride to afford 4-t-butyl-1-methylcyclohexane with appreciable selectivity (trans/cis = 18/1 at 0°). Data on selectivity in halogen atom transfer to this radical by R-O-Cl, a "hotter" atom transfer agent than R_3SnH, are needed and are being sought by decomposition of

cis- and trans-4-t-butyl-1-methylcyclohexylcarbinyl hypochlorites. (A. Fang)

Isotope effects and selectivity in intramolecular hydrogen abstraction have been examined in the oxidative conversion of erythro-5-deutero-2-hexanol (prepared by a stereospecific synthesis) to cis- and trans-2,5-dimethyltetrahydrofuran by means of lead tetraacetate and hypochlorous acid. The cyclic ethers were separated by vapor phase chromatography, and deuterium content was established by mass spectral data. The results are summarized in Table 3.8.

Table 3.8

Oxidative cyclization of erythro-5-deutero-2-hexanol in chlorobenzene

Reagent	Temp.	Cyclic ether % cis	Cyclic ether % trans	%D in ether cis	%D in ether trans	k_M/k_D
$Pb(OAc)_4$	83°	35	65	85	85	5.8
HOCl[a]	-78°	52	48	91.7	92	12.5
HOCl[a]	80°	51	49	81	(81)	4.5

a. $ROH + HOCl \longrightarrow R\text{-}O\text{-}Cl \longrightarrow CH_3CHClCH_2CH_2CHOHCH_3 \xrightarrow[\Delta]{NaH}$ 2,5-dimethyltetrahydrofuran.

It is clear that both the lead tetraacetate oxidation and the hypochlorite decomposition proceed via intermediates which lose geometrical integrity at the 5-position. (M. J. Rafuse)

Previous results of these laboratories have indicated no stereospecificity in the termination reaction of statiscally distributed α-phenylethyl radicals. This serves as a clear point of reference from which to examine the time scale for radical recombination within a "solvent cage". Optically active azo-α-phenylethane has been prepared and experiments are in progress to effect decomposition under conditions in which all non-cage α-phenylethyl radicals are irreversibly scavenged and from which cage products (meso and dl-2,3-diphenylbutane) may be obtained for stereochemical and optical analysis. (M. A. Berwick)

IX. Radical Ions

Studies of generation of radical ions by sodium potassium alloy and by in situ electrolytic reduction are described in the thesis of G. J. Nolfi, Jr. of which the abstract is given here.

The scope of the electrolytic method of in situ generation of radical ions for ESR study has been investigated with respect to a variety of compounds, temperatures, solvents, and supporting electrolytes. A new variable temperature cell has been employed. New supporting electrolytes for use in non-aqueous media have been developed. These include tetra-n-butylammonium methanesulfonate, trifluoromethanesulfonate, and n-butanesulfonate. The use of the low melting tetra-n-butylammonium n-butanesulfonate as a molten salt medium for electrogeneration of radical ions has been explored in a preliminary fashion. Chemical reactions resulting from the electroreduction of anthracene in dimethylformamide and dimethoxyethane at higher voltages have been studied. A detailed comparison has been made of the electrolytic and alkali metal methods of generating radical anions of organic compounds for ESR study.

ESR spectra have been obtained for anisole and a variety of substituted anisoles and related compounds. The cleavage-coupling reaction of anisole to biphenyl, induced by sodium/potassium alloy in 2:1 (v/v) tetrahydrofuran: dimethoxyethane has been investigated by measurement of anisole consumption, and by use of the three monodeuteroanisoles, 4,4'-dideuterobiphenyl, and the three monomethoxybiphenyls. Other types of cleavage reactions have been found in substituted anisoles and related compounds. Quantitative measurements of the concentrations of anisole and biphenyl radical anions have been made. (G. J. Nolfi, Jr.)

The electrolytic method has made possible preparation of radical ions at temperatures as low as -100°; this technique has permitted examination by electron spin resonance spectroscopy of species such as the nitromethane radical anion which are not observable at higher temperatures. A series of radical anions of aliphatic nitro compounds has been examined in this way. Previous studies [A. K. Hoffmann et al., J. Am. Chem. Soc., 86, 631, 639 (1964)] of a few tertiary

nitroalkanes indicated that radical anion decomposed to nitrite ion and alkyl radical. The possibility of fragmentation, ($RNO_2^{\cdot -} \rightarrow R\cdot + NO_2^-$), has been examined as a potential method for investigation of structure-reactivity relationships in radical anion and radical reactions. The experiments involve electrolytic generation of a steady state concentration of radical anion, cut-off of current, followed by measurement of rate of decay of paramagnetic signal. Decay rates were first order throughout the series. The results are summarized in Table 3.9. No nitroxide

Table 3.9

ESR study of rate of decay of radical anions of nitroalkanes in dimethylformamide at -50°

R	1-Propyl	2-Propyl	Cyclopentyl	t-Butyl	1-Norbornyl	1-Adamantyl
$k \times 10^2$, $sec.^{-1}$	4.8	3.4	4.0	2.2	1.3	2.8

was observed in any of these cases. The small variation in rate over the large structural variations of alkyl moiety of primary to tertiary to bridgehead is strongly indicative that fragmentation is not the primary decay process under these conditions. Studies to ascertain the mode of decay (e.g. hydrogen abstraction from solvent) are under investigation. (J. Crosthwaite)

Attempts have been made to obtain radical anions of the following compounds: adamantane, 1-methoxyadamantane, 1-ethoxyadamantane, 2,4,10-trioxaadamantane, hexamethylenetetramine, congressane, cyclopropane, and nortricyclene. The procedure was that used previously by K. W. Bowers. In no case was a paramagnetic resonance signal definitely attributable to one of the desired radical ions observed. Adamantane samples frequently gave spectra consisting of five-line patterns, approximately 3.8 g. separation, but these signals were not significantly different from the spectrum of benzene radical anion, and in cases of particularly intense signals two additional lines could be detected. Blank samples of solvents and sodium-potassium also frequently gave similar signals; it is not clear whether

these signals arise from impurities present in the solvents alone or in both solvents and adamantane. 1-Ethoxyadamantane and 1-methoxyadamantane gave spectra of seven lines, a ≐ 3.8 g. with additional lines superimposed; no interpretation of these spectra in terms of expected radical ions could be made. 2, 4, 10-Trioxaadamantane and congressane have signals indistinguishable from those obtained from solvent blanks; hexamethylenetetramine gave on one occasion seven lines, a = 3.8 g. and superimposed nine lines of unequal spacing and on another occasion only a single weak line. Cyclopropane generally gave no signal, but occasionally gave a broad single line. Nortricyclene gave only a very weak signal. Also in contrast to earlier results, cyclopropane and nortricyclene samples in dimethoxyethane - tetrahydrofuran with Na/K were stable when stored for several days in liquid nitrogen. The basis for the difference between these results and those obtained earlier by K. W. Bowers is not known, but may be due to differences in alloy composition and/or surface. (T. H. Lowry)

PUBLICATIONS

C. G. Swain, D. A. Kuhn and R. L. Schowen, "Effect of Structural Changes in Reactants on the Position of Hydrogen-Bonding Hydrogens and Solvating Molecules in Transition States. The Mechanism of Tetrahydrofuran Formation from 4-Chloroethanol, J. Am. Chem. Soc., 87, 1553 (1965).

C. G. Swain and R. L. Schowen, "A Free-Electron Model for Kinetic Substituent Effects", J. Org. Chem., 30, 615 (1965).

C. G. Swain and J. C. Worosz, "Mechanism of General Acid Catalysis of Addition of Amines to Carbonyl Groups," Tetrahedron Letters, No. 36, 3199 (1965).

ADDRESSES

C. G. Swain, "Solvent Isotope Effects for Study of Organic Reaction Mechanisms", Moelwyn-Hughes Symposium on Solvation, University of Arkansas, Fayetteville, Arkansas, April 23, 1965.

C. G. Swain, "Use of Hydrogen Isotope Effects for the Study of Reaction Mechanisms", 150th A.C.S. Meeting, Norris Award Symposium, Atlantic City, N.J., September 14, 1965.

C. G. Swain, "Use of Hydrogen Isotope Effects for the Study of Reaction Mechanisms", Jackson Laboratory Seminars, DuPont Company, Penns Grove, N.J., October 28, 1965.

F. D. Greene, "Stereospecificity in Free Radical Reactions", Symposium on Free Radical Reactions, 149th A.C.S. Meeting, Detroit, Michigan, April 7, 1965.

F. D. Greene, "Mechanisms of Decomposition of Diacyl Peroxides", Columbia University, New York City, February, 1965.

F. D. Greene, "Mechanisms of Decomposition of Peroxygen Compounds", Research Laboratories, American Cyanamid, Stamford, Connecticut, March 29, 1965.

F. D. Greene, "Mechanisms of Decomposition of Diacyl Peroxides", Sprague Electric Company, North Adams, Massachusetts, April 30, 1965.

F. D. Greene, "Stereospecificity in Free Radical Reactions", Iowa State University, Ames, Iowa, June 23, 1965.

F. D. Greene, "Stereospecificity in Free Radical Reactions", Union Carbide Plastics Division, Bound Brook, New Jersey, October 20, 1965.

THESES

John E. Sheats, "Mechanism of Decomposition of Benzenediazonium Ion", Ph.D. thesis, December, 1965.

Nancy N. Lowry, "Studies on the 9-Decalyl Radical," Ph.D. thesis, August, 1965.

George J. Nolfi, Jr., "Electron Spin Resonance Studies of Organic Free Radical Species", Ph.D. thesis, October, 1965.

PHYSICAL CHEMISTRY GROUP

A. Determination of Vapor-Liquid Equilibrium from Measurements of the Equilibrium Temperature. Total Volume, and Over-all Composition.

This project has been slowed by difficulties with bath liquids, with stirring and with temperature control and measurement. We believe that these difficulties have all been overcome. We have attained a temperature control to ±0.001°, which is the most we have hoped for. This precision should fix the osmotic coefficient of sodium chloride to 0.001 from 1 to 6 molal, and from 25° to 100°. A first run with about 5 molal sodium chloride before some of the difficulties were overcome did not quite achieve this.

We have recalculated the freezing point measurements of Scatchard and Prentiss (J. Am. Chem. Soc. 55, 4355 (1933)) with up-to-date freezing point and Debye-Hückel constants. This decreases the MIT values of the osmotic coefficients at 25° below 1 m by about 0.001, and gives almost perfect agreement with the values of Robinson and Stokes. We hope to resolve the much larger discrepancies at higher concentrations at 25°, and to give a better standard for isotonic (isopiestic) measurements at high temperatures. (R. A. Rousseau, H. F. Gibbard, Jr., and G. Scatchard)

B. The Electromotive Forces of NH_4Br and KBr Concentration Cells. Are the Abnormalities in the Freezing Points of Ammonium Salts Due to Surface Effects?

A paper with this title, based on the S.B. thesis of W. H. Orttung, Department of Chemistry, 1956, has been accepted for publication in the Journal of Colloid Chemistry. The abstract follows:

Measurements of the electromotive force of concentration cells with silver-silver bromide electrodes, with or without cation exchanger electrodes, show differences between NH_4Br and KBr about one fifth those calculated from freezing points. This is taken as proof that the abnormalities in the freezing points of ammonium salts do not arise in the water phase. It is extremely improbable that they arise in the ice, and the most probable cause is the surface electrical potential due to the great difference in solubilities of the ions in ice. Whether they arise in the ice or in the surface they lead to uncertainty in the osmotic coefficients for water activity and in the mean activity coefficients of ammonium salts determined from freezing points. (G. Scatchard and W. H. Orttung)

C. Diffusion and the Bi-ionic Potential with an Ion Exchanger Membrane

A paper with this title, based on the S.B. thesis of W. H. Orttung, Department of Chemistry, 1956, has been accepted for publication in the Journal of Colloid Chemistry. The abstract follows:

The potential between two silver-silver bromide electrodes in 0.1 m HBr and NaBr separated by a cation exchanger membrane was studied for several hundred hours. After

stirring there was a rapid decrease to a minimum at 20 minutes, then a rise to a maximum at 400 minutes, followed by a slow almost linear decrease which extrapolated at zero time to only 1 MV lower than the value with solutions flowing. This decrease is probably caused by the activity gradients shifting from the membrane to the liquid solutions. It is suggested that the earlier changes may be explained by gradients shifting from the transition layer, and that the more transient effects which are some times observed may be explained by lags in the dissipation of heat. (G. Scatchard and W. H. Orttung)

Address

G. Scatchard, "Water", Seminars in Biophysics and Physical Chemistry of Connective Tissue, Stowe, Vermont, October 11, 1965.

Publications

D. H. Freeman and G. Scatchard, "Volumetric Studies of Ion-Exchange Resin Particles using Microscopy", J. Phys. Chem. 69, 70 (1965).

G. Scatchard, "The Computation of the Activity Coefficients of Small Ions from the Loeb, Overbeek and Wiersema Tables", Zeitschr. f. physikalische Chemie 228, 354 (1965).

LIST OF RESEARCH PERSONNEL

Nuclear Chemistry Group

Research Staff

Prof. C. D. Coryell
Prof. G. E. Gordon
Prof. J. W. Irvine, Jr.
Prof. W. B. Walters
*Dr. G. Chilosi
Dr. I. Gal
Dr. G. Graeffe
Dr. J. W. Harvey
*Dr. R. H. McCorkell
*Dr. G. Scibona

Guests

*Dr. H. Amano
Division of Radio Isotope Production
Tokai Research Establishment
Japan Atomic Energy Research Inst.
Takai-Mura, Japan
Prof. L. Leifer
Department of Chemistry
Boston College
Chestnut Hill, Mass.

Graduate Students

*S. Basol
*J. F. Byrum
*J. E. Canty
A. M. Ehrlich
J. L. Fasching
D. J. Hnatowich
M. A. Kay
H. Nakahara
D. Muga
B. Parsa (J. F. Norris Fellow)
R. C. Ragaini (MMM Fellow)
J. D. Ramshaw (AEC Fellow)
*D. Schlaikjer
C. H. Tan
C.-W. Tang
J. F. Wild

Undergraduate Students

J. E. Esterl
*W. P. Petrick
M. W. Weisfield

Instrumental Chemistry Group

Research Staff

Prof. D. N. Hume
Prof. D. M. Hercules
*Prof. W. E. Ohnesorge
Prof. D. K. Roe
Dr. R. L. Bardsley
*Dr. R. C. Lansbury
Dr. O. Nudelman
*Dr. G. D. Short
*Dr. J. E. A. Toni

Guest

Dr. E. Bickerdike

Graduate Students

S. R. Abbott
*N. R. Andersen
*P. D. Anderson
D. N. Bailey
*R. C. Berlo
*R. L. Birke
Adrienne Gordon
J. D. Gorsuch
W. M. Krebs
J. R. Layton
K. D. Legg
J. N. Little
F. E. Lytel
A. L. Malenfant
W. R. Matson
T. F. Retajczyk
D. W. Shive
*P. Vouros
T. C. Werner

Undergraduate Students

*Barbara T. Vickers

*Terminated

List of Research Personnel

Organic Isotope Applications Group

Research Staff

Prof. F. D. Greene, II
Prof. C. G. Swain
*Dr. K. W. Bowers
Dr. A. L. Powell
*Dr. J. C. Crosthwaite
Dr. Nancy N. Lowry
Dr. T. H. Lowry
*Dr. C. R. Morgan
*Dr. A. Ohno
Dr. V. P. Vitullo

Graduate Students

M. A. Berwick
*R. V. Cartwright
R. D. Cramer
J. A. Eckert
J. P. Engstrom
Anna Fang
*Mrs. Judith A. (Mullikin) Harbison
K. G. Harbison
T. J. Lynch
Joanne (Worosz) Mitchell
*G. J. Nolfi, Jr.
E. A. Nordstrom
Marion H. O'Leary
*J. Pazos
Mrs. Mary Jane Rafuse
*J. E. Sheats
*H. Stein
J. T. Viola

Undergraduate Students

*E. C. Lupton, Jr.

Physical Chemistry Group

Research Staff

Prof. G. Scatchard
*Dr. R. A. Rousseau

Graduate Student

H. F. Gibbard, Jr.

*Terminated