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MASSACHUSETTS INSTITUTE OF TECHNOLOGY

Laboratory for Nuclear Science

CHEMISTRY PROGRESS REPORT

December 31, 1966

M. I. T. - 905 - 81

RELEASED FOR ANNOUNCEMENT
IN NUCLEAR SCIENCE ABSTRACTS

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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 MIT Department of Chemistry is also acknowledged.

This is the sixty-eighth progress report of the Laboratory for Nuclear Science at the Massachusetts Institute of Technology. Progress reported covers the period for Chemistry from January 1, 1966, through December 31, 1966.

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

NUCLEAR CHEMISTRY GROUP

I. Nuclear Decay-Scheme Studies

A. Decay of ^{103}Ru

We have investigated the decay of 40-day ^{103}Ru in order better to characterize some of the transitions observed in ^{103}Rh . The levels shown in Fig. 1.1 have been established in recent studies by V. R. Potnis, E. B. Nieschmidt, C. E. Mandeville, L. D. Ellsworth, and G. P. Agin (Phys. Rev. 146, 883, 1966) and by A. Mukerji, D. N. McNelis, and J. W. Kane, Jr. (Nucl. Phys. 67, 466, 1965). The weak 117, 171, and 320-keV transitions were not reported in the earlier work. The spin assignments for the two levels at 538 and 650 keV were suggested as $5/2+$ and $7/2-$ respectively by Potnis, et al.

Figure 1.1

Decay scheme of 40-day ^{103}Ru . (Dotted lines indicate newly proposed weak transitions.)

The assignment of a spin and parity $7/2-$ to the level at 650 keV was made by Potnis, et al. on the basis of a K-conversion coefficient of 6×10^{-4} measured by B. de Raad, W. C. Middlekoop, B. van Nooijan and P. M. Endt (Physica 20, 1278, 1955). As that value of α_K indicates an E1 transition, the spin of $7/2-$ is required for the level at 650 keV. Mukerji, et al., used the $\log ft$ value of 5.7 to conclude that the β decay to the 650-keV level is allowed and thus the spin must be either $5/2+$ or $7/2+$ and obtained angular correlation data to support a spin assignment of $7/2+$.

We have remeasured the α_K for the 610-keV transition using a 2-mm Si(Li) electron detector and obtained a preliminary value of $(2.06 \pm 0.3) \times 10^{-3}$. This value is too high for an E1 transition ($\alpha_K = 1.0 \times 10^{-3}$) and too low for an M1 ($\alpha_K = 3.0 \times 10^{-3}$). It is possible that a systematic error of $\sim 10\%$ may be present as our α_K of $(4.34 \pm 0.1) \times 10^{-3}$ for the 493-keV transition is low for an M1 ($\alpha_K = 4.6 \times 10^{-3}$) or M1 + E2 transition. The nature of the 610 transition is thus still unsettled, however, if it is not M1 or M1 + E2; then it is an E1 + M2 mixture with approximately 15 percent M2 character and should have a lifetime of ≥ 4 nsec. We will therefore attempt to measure this lifetime using our TAC system (see Section V.C) and β - γ coincidence techniques. We have prepared a new source of ^{103}Ru using separated ^{102}Ru in order to obtain a higher specific activity and permit a thinner source for the conversion-electron measurements. (W. H. Zoller and W. B. Walters)

B. Decay Scheme of 22-min ^{111}gPd

We have recently begun investigation on the decay of 22-min ^{111}gPd . This nuclide is produced by short reactor irradiations of enriched ^{110}Pd and purified by eluting on a Dowex-1 anion-exchange column with 0.5 M HCl.

To date, the gamma rays associated with the decay have been determined along with several coincidence relationships. Gamma rays at 59.7, 70.3, 245.5, 290.8, 377.0, 509.3, 547.3, 580.0, 622.2, 650.4, 709.9, 836.0, 1388.4, 1458.9, and probably at 405.5, 439.7, and 1110 keV, are associated with the decay of 22-m ^{111}gPd . (D. J. Hnatowich, G. Graeffe, and C. D. Coryell)

C. Decay of 35-min ^{111}Sn

As earlier studies of the levels of ^{115}In and ^{117}In had revealed a number of interesting features, this investigation was initiated in order to extend our systematic knowledge of odd-mass In levels.

The ^{111}Sn was obtained by irradiating enriched ^{108}CdO with ^4He ions in the MIT Cyclotron. Where it was necessary to separate the ^{111}In from the CdO target, the sample was dissolved in 1 N HCl and passed through an ion-exchange column which retained the Cd and passed the In ions.

Singles coincidence spectra were taken with the 4096-channel analyzer and buffer system using Ge(Li) and NaI(Tl) detectors. Gamma rays at 373, 458, 538, 563, 762, 954, 1026, 1153, 1542, 1610, 1915, 2106, 2178, 2325, and possibly 1376 and 2213 keV were found to follow the decay of ^{111}Sn . A preliminary decay scheme is shown in Fig. 1.2. (G. Graeffe)

Figure 1.2

Proposed decay scheme of 35-min ^{111}Sn .D. Decay Scheme of 20-min ^{115}Ag

For this study, 20-min ^{115}Ag is being produced by deuteron-induced fission of natural uranium. Approximately 100 mg of natural uranium is irradiated with 14-MeV deuterons for short periods followed by a chemical separation of silver from the other fission products produced. The chemistry involves five stages: oxidation of the fission products by sodium hypochlorite, isotopic exchange of fission-product silver with silver in freshly precipitated silver chloride, iron hydroxide scavenging, silver reduction to the metal with zinc dust, and precipitation of silver chloride. Tellurium, iodine, bromine, lanthanum, molybdenum, and zirconium hold-back carriers are used at various points in the separation scheme. Experiments to determine the amount and nature of any contamination have shown that silver, completely free of all detectable contamination other than silver decay products, can be separated from fission products in good yields by the above chemistry.

A total of 47 γ rays have been assigned to 20-min ^{115}Ag . They are listed in Table 1.I along with their intensities relative to the 229.2 keV γ ray. In addition, several γ - γ coincidence experiments have been performed using NaI(Tl) and Ge(Li) detectors. A partial decay scheme for 20-min ^{115}Ag has been constructed using the results of the above experiments and is presented in Figure 1.3. The intensities of the transitions are given in parentheses after the transition

energy. Solid dots on the arrows representing γ transitions show the observed coincidence relationships. Dotted transitions imply a large uncertainty.

Table 1.I

Energies and Relative Intensities of γ Rays Following Decay of 20-min ^{115}Ag (D. E. = double escape of annihilation photons).

$E_\gamma(\text{keV})$	Rel.Int.	$E_\gamma(\text{keV})$	Rel.Int.	$E_\gamma(\text{keV})$	Rel. Int.
131.5	12	510	5 ?	1467.8 D. E.	3
213.0	25	547.8	<1	1508.0	9
229.2	100	583.4	1	1608.6	2
236.4	6	649.2	17	1644.5 D. E.	3
243.6	2	697.0	11	1795.8	2
303.1	5	775.9	3	1841.8	12
326.2	11	821.2 D. E.	3	1884.5 D. E.	3
331 ?	<1	906.2 D. E.	2	1927.5	8
340.0	<1	931.3	<1	2114.1	6
361.3	2	963.3	3	2156.6	16
372.7	10	1092.0 D. E.	8	2385.3	1
389.2	3	1133.2 D. E.	19	2489.8	1
405.3	<1	1182.5 ?	1	2529.7	<1
417.1	2	1363.3 D. E.	3	2666.5	<1
473.1	18	1378.9	3	2906.5	1
507	5?	1410.1	1		

Figure 1.3

Tentative decay scheme of 20-min ^{115}Ag .

Upon completion of the investigation of 20-min ^{115}Ag , work will begin on a study of the 50-sec ^{115}Ag . The MIT Reactor, with its rapid sample transferring facilities, along with rapid chemical separations, will be used. (D. H. Hnatowich and C. D. Coryell)

E. Decay of 43-Day $^{115\text{m}}\text{Cd}$ and 2.3-Day $^{115\text{g}}\text{Cd}$

The following paragraph is the abstract of an article that appeared in The Physical Review (Phys. Rev. 149, 884 (1966)).

Abstract: The decay schemes of 43-day $^{115\text{m}}\text{Cd}$ and 2.3-day $^{115\text{g}}\text{Cd}$ were studied using Ge(Li) γ -ray detectors and coincidence techniques. Gamma rays of the following energies (in keV) and relative intensities (in parentheses) were observed in the decay of $^{115\text{g}}\text{Cd}$: 35(1.4), 232 (2.4), 261 (6.5), 267 (0.13), 336 (178, $^{115\text{m}}\text{In}$ I. T.), 493(26), and 528(100). The energies and relative intensities of γ rays observed in the decay of $^{115\text{m}}\text{Cd}$ are: 106 (0.45), 158 (0.9), 336 (0.25, $^{115\text{m}}\text{In}$ I. T.), 485 (13.6), 493 (0.45), 934 (100), 1133 (4.2), 1291 (46), 1419 (0.11), and 1450 (0.85). Upper limits of 0.03 and 0.10 are placed on the relative intensities of 130- and 292-keV γ rays, respectively, that have previously been reported for $^{115\text{m}}\text{Cd}$ decay. The 106-, 336-, 493-, and 1450-keV γ rays have not been previously observed in $^{115\text{m}}\text{Cd}$ decay, although the 336- ($^{115\text{m}}\text{In}$ I. T.) and 493-keV γ rays are well known to occur in the decay of $^{115\text{g}}\text{Cd}$. Excited states in ^{115}In are established at 336 (4.4-h $^{115\text{m}}\text{In}$), 597, 829, 864, 934, 1078 (from previous electromagnetic excitation studies), 1133, 1291, 1419, and 1450 keV. The first four of these levels are fed directly by β decay of $^{115\text{g}}\text{Cd}$ and the ground state plus levels at 934, 1133, 1291, 1419, and 1450 by that of $^{115\text{m}}\text{Cd}$. We have found that $^{115\text{m}}\text{In}$ is formed in about 0.009% of the $^{115\text{m}}\text{Cd}$ decays as a result of the 106-keV γ transition from the 934-keV level to that at 829 keV, followed by the 493-keV γ transition to $^{115\text{m}}\text{In}$. The conversion coefficient α_K of the 35-keV transition was measured as 9.6 ± 1.2 . For the 336-keV $^{115\text{m}}\text{In}$ I. T. we found $\alpha_K = 0.91 \pm 0.06$ and $\alpha_K/(\alpha_L + \alpha_M) = 3.75 \pm 0.10$.

A decay scheme consistent with all of our observations was constructed. Arguments for assignments of spins and parities are given. In particular, observation of the 106-keV transition indicates the assignments 5/2- and 7/2+ for the levels at 829 and 934 keV, respectively. Implications of the results for current nuclear models are discussed. (G. Graeffe, C.-W. Tang, G. E. Gordon, and C. D. Coryell)

F. Radioactive Decay to Sb and I Nuclides

We have grouped in this section those reports dealing with studies of radioactive decay in which levels of Sb and I are populated. Our work has been fairly extensive in this region as it is possible to correlate the levels observed in radioactive decay with the levels observed experimentally by G. Bassani, M. Conjeaud, J. Gaslebois, J. M. Laget, J. Picard, and Y. Cassagnow (Phys. Letters 22, 189, 1966) and P. D. Barnes, C. Ellegaard, B. Herskind, and M. C. Joshi (Phys. Letters 23, 266, 1966) in (^3He , d) reactions on Sn isotopes and theoretically with the calculations of L. S. Kisslinger and R. A. Sorensen (Rev. Mod. Phys. 35, 853, 1963). In this

latter venture, we wish to express our appreciation to Prof. L. S. Kisslinger who has supplied us generously with detailed calculations for many of the nuclei under study.

As a whole, the agreement with the KS calculations is good, sufficiently good that we often emphasize the areas of disagreement to a greater extent than the areas of agreement. This occurs because we doubtless hope that in the areas of disagreement will lie the clue to even better calculations (based on a better understanding of the forces that contribute to nuclear structure) that will have fewer areas of disagreement.

As much of this work is still in progress and no real overall review has been initiated, it is not possible to describe in detail the overall comparisons to the theory. Two areas that are worth noting concern $\log ft$ values for what should be allowed β decay and the presence of an extra low-lying $5/2+$ level in I nuclides that is not present in Sb nuclides nor predicted in either. There is a wealth of data that yields $\log ft$ values from 1 to 4 units higher than expected for allowed β transitions from the $d_{3/2}$ ground state of Sn and Te nuclides to the lowest-lying $1/2+$ and $3/2+$ levels in Sb and I nuclides. The nature of such a strong hindrance is difficult to understand in any current theoretical picture. The $1/2+$ and $3/2+$ levels in I and Sb are probably 1-phonon levels, and some hindrance would be expected as the creation of a phonon is required, but the size of the hindrance is unexpected.

The extra $5/2+$ level in I nuclides is also interesting as its position relative to the lower $5/2+$ level (the $d_{5/2}$ single-particle level) is seemingly independent of neutron number at the same time the spacings between other levels increase with increasing neutron number. This second low-lying $5/2+$ level is several hundred keV lower than the KS calculations indicate for I nuclei and has no counterpart in Sb nuclei. We have some evidence for a third $5/2+$ level lying 1084, 997, and 1021 keV above the lowest $5/2+$ level in ^{129}I , ^{131}I , and ^{133}I respectively, again showing little change in position relative to the lowest $5/2+$ level. This third $5/2+$ level is characterized by a lower $\log ft$ value than nearby $1/2+$ and $3/2+$ levels in each nuclide.

1. Decay of 42-min ^{123}Sn and 10-min ^{125}Sn . The radiations from the decay of 42-min ^{123}Sn have been studied in order to gain information about the levels of ^{123}Sb and to try to determine which of the ^{123}Sn isomers is the ground state. A decay scheme consistent with our observations and the results of the $^{122}\text{Sn}(^3\text{He}, d)^{123}\text{Sb}$ studies of Bassani, et al., and Barnes, et al., is shown in Fig. 1.4. The Q_β has been determined by measuring the β spectrum in coincidence with 160-keV γ rays using a 3-mm deep Si(Li) detector in coincidence and a NaI(Tl) detector. From a Fermi-Kurie plot, the β endpoint was determined to be 1215 ± 10 keV. This gives a Q_β of 1375 ± 10 keV for the 42-min isomer and, when compared with the Q_β of 1399 ± 10 measured by R. L. Auble and W. H. Kelly (Nucl. Phys. 81, 442, 1966) for the 125-day isomer indicates that the 42-min isomer is 24 ± 14 keV lower than the 125-day isomer whose spin is $11/2-$.

Figure 1.4
Decay scheme of 42-min ^{123}Sn .

We have also studied the decay of the 10-min ^{125}Sn isomer whose spin and parity are $3/2+$. We are able to observe the same levels as observed earlier by S. H. Devare and H. G. Devare (Phys. Rev. 133, B568, 1964) as well as obtaining evidence for additional levels at 1350 and 1915 keV. As the level at 1350 appears to be weakly fed, if at all, in β decay it may be the same level observed by R. L. Auble and W. H. Kelly (Nucl. Phys. 79, 577, 1966) in the decay of the 9.7-day ^{125}Sn isomer whose spin and parity are $11/2-$.

The low-lying levels that are observed in both nuclei are in accord with the KS predictions both with regard to the number of levels observed of a particular spin and with regard to the approximate positions of those levels.

Most of the features of the decay of the $h_{11/2}$ isomers of ^{123}Sn and ^{125}Sn have been reported in the two articles by Auble and Kelly, however, no γ transitions were observed following the decay of either isomer that populated the first excited state whose spin is $5/2+$. At the time of the earlier studies the energies of those $5/2+$ levels were not well known and it would have been difficult to recognize such transitions.

The energy values for the $5/2+$ levels are now well known, and we are currently attempting to determine if they are populated in the decay of the $h_{11/2}$ isomers. (D. A. Muga and W. B. Walters).

2. Decay Schemes of ^{115}Te and ^{117}Te . Studies of the decay of 6-min ^{115}Te and 62-min ^{117}Te have been carried out by irradiating enriched ^{112}Sn and ^{114}Sn respectively with 30-MeV ^4He ions in the MIT Cyclotron and observing the γ rays and positrons emitted from the samples. The preliminary data on ^{117}Te decay indicates the presence levels in ^{117}Sb at positions similar to analogous levels in ^{119}Sb populated in the decay of the $1/2^+$ isomer of ^{119}Te . The low-lying $1/2^+$ and $3/2^+$ levels are also in accord with the ($^3\text{He}, d$) studies of Bassani, et al. By observing the positrons in coincidence with the 720-keV γ rays, we were able to determine an end-point energy of ~ 1.7 MeV for the positron group that feeds the 720-keV level. This is not in agreement with F. D. S. Butement and S. M. Quain (J. Inorg. Nucl. Chem. 27, 1729, 1965) who postulated that the maximum positron energy in the decay of ^{117}Te was less than 1 MeV. As the 720-keV γ ray decays with a 62-min half-life, this also contradicts their assertion that the 1.7 MeV positron group belongs to a 1.9-h isomer of ^{117}Te . The initial spectra indicate levels at 720 and 924 keV in accord with the results of Bassani, et al., though no 530-keV γ rays could be observed that would indicate feedings to the $7/2^+$ level observed at 530 keV. As the $7/2^+$ level was fed only weakly if at all, in the decay of the $1/2^+$ isomer of ^{119}Te , little feeding to this level is expected unless there is a high-spin isomer present.

The γ -ray spectrum from the decay of ^{115}Te is similar to that obtained by R. Reising and B. D. Pate (Nucl. Phys. 61, 529, 1965) using a NaI(Tl) detector. The improved resolution of the Ge(Li) detector permits a better assignment of energies and in conjunction with the data of Bassani, et al., gives an indication that the decay scheme proposed by Reising and Pate is not wholly correct. (W. B. Walters and G. Graeffe)

3. The Decay of the Isomers of ^{119}Te to Levels of ^{119}Sb . The following paragraph is the abstract of an article that has been submitted for publication. The work was carried out in conjunction with Prof. D. G. Sarantites and E. J. Hoffman of Washington University in St. Louis, Mo. The decay scheme is shown in Fig. 1.5.

Abstract: The decays of the 4.7-day ^{119m}Te and the 16-h ^{119g}Te have been investigated with the use of Ge(Li) and NaI(Tl) γ -ray detectors, and Si(Li) electron detectors. Coincidence relationships among the γ rays were determined in γ - γ coincidence experiments. It was established that the decay of the 4.7-day ^{119m}Te populates levels at 270.6, 1048.3, 1212.7, 1249.6, 1365.8, 1406.7, 2129.3, 2226.0, 2277.8, 2283.6, and 2360.4 keV in ^{119}Sb ; and the decay of the 16-h ^{119g}Te populates levels at 270.6, 644.3, 700.0, 1338.5, 1413.2, 1487.4, 1749.5, and 1821.0 keV in ^{119}Sb . Many spin assignments have been made from present and previously reported internal conversion electron data, from $\log ft$ values, and from γ - γ directional correlation measurements. Trends of the low-lying levels of odd-A antimony isotopes from mass 119 to 125 are discussed and compared to the pairing-plus-quadrupole model for nuclei. (G. Graeffe)

Figure 1.5
Decay scheme of the isomers of ^{119}Te .

4. The Decay of ^{127}Te to Levels of ^{127}I . The decay of 105-d $^{127\text{m}}\text{Te}$ in equilibrium with 9.3-h $^{127\text{g}}\text{Te}$ was reinvestigated in order to set a lower limit on the $\log ft$ of the β decay of the 9.3-h isomer to the $1/2+$ level at 375 keV. As the spin and parity of the 9.3-h ^{127}Te isomer are $3/2+$, allowed β decay to the $1/2+$ level of ^{127}I is expected. The spin and parity of that level have been determined by J. S. Geiger (Phys. Letters 7, 48, 1963) in the decay of ^{127}Xe , but the level was not seen to be populated in the decay of ^{127}Te by Auble and Kelly (Nucl. Phys. 73, 25, 1965). The present study revealed a weak β branch to the level for which a $\log ft$ value of 9.6 could be calculated. In addition, a new γ ray at 649.5 keV was observed that could be assigned as a transition from the level at 649.5 keV to the $5/2+$ ground state. (W. B. Walters)

5. The Decay of ^{129}Te . The decay scheme of ^{129}Te has been obtained and the resulting paper accepted for publication in Nuclear Physics. The paper is a joint paper with Professor W. H. Kelly, L. M. Beyer, and G. Berzins of Michigan State University and presents the experimental findings of both groups and a single decay scheme in agreement with both sets of data. The following paragraph is the abstract of that paper.

Abstract: Gamma-rays emitted in the decay of 70-min ^{129g}Te and 33-day ^{129m}Te have been investigated with Ge(Li) and NaI(Tl) detectors. Results of Ge(Li)-NaI(Tl) coincidence studies, coupled with relative intensity measurements for both isomers, suggest a decay scheme considerably different from those recently proposed by other workers. Excited levels are placed in ^{129}I at 27.7, 278.4, 487.4, 559.8, 696.0, 729.8, 768.9, 829.8, 844.7, 1050, 1111.4, 1260, 1291, and 1402 keV. Beta decay of ^{129g}Te feeds all of these except the ones at 696.0, 729.8, 768.9, 844.7, 1050, and 1402 keV. Beta transitions from ^{129m}Te populate all of the latter set of levels and the ground state. The I. T. branching fraction of ^{129m}Te is about 72 percent. With some exceptions the levels of ^{129}I agree rather well with those predicted by Kisslinger and Sorensen. Considerable evidence for the previously suggested hindrance of β decay caused by phonon mixing of the wave functions has been observed. (W. B. Walters and G. E. Gordon)

6. Decay Scheme of ^{133}Te . Several recent studies of the decays of odd-A Te isomers have provided detailed information on the trends of levels in the 53-proton daughter I isotopes as a function of (even) neutron number (see, for example, Walters, Bemis, and Gordon, Phys. Rev. 140, B268, 1965; Berzins, et al., Sect. I.F.5, this report; Beyer, Berzins, and Kelly, Bull. Am. Phys. Soc. 11, 395, 1966). In order to extend these studies to mass 133, we are investigating the decay schemes of 50-min ^{133m}Te and 12-min ^{133g}Te .

Samples containing 560 mg of $\text{UO}_2(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ were irradiated in the MIT reactor for 25 sec at a flux of $2 \cdot 10^{13} \text{n/cm}^2\text{-sec}$. Samples were transferred to the laboratory within 6 sec after the irradiation via the pneumatic-tube system. Then a fast Sb separation was performed by a stibine-generation method (Menon, Aras, and Irvine, J. Inorg. Nucl. Chem. 27, 767, 1965). After allowing about 4 min for partial decay of 2.7-min ^{133}Sb , the Te daughters (largely ^{133}Te activity) were precipitated as Te metal. The Te was filtered, washed with 3 M HCl, and mounted on a sample card.

Gamma-ray singles spectra were taken with a Ge(Li) detector. Because of the short half life of ^{133g}Te , it was necessary to add the spectra from several consecutive experiments in order to obtain statistically significant numbers of counts for low-intensity peaks. The resulting spectrum is shown in Fig. 1.6. Energies, intensities, and assignments of the gamma rays are listed in Tables 1.II and 1.III. The observed gamma rays were assigned to the isomers by following their decay in a set of consecutive spectra. Gamma-gamma coincidences were observed with a NaI(Tl)-Ge(Li) detector combination. Data from this experiment were stored event-by-event with the buffer-tape unit (see Sect. V.A) and later sorted into appropriate groupings by searching the tape with various digital-gate settings on the 4096-channel analyzer.

Figure 1.6a
Sum of several individual gamma-ray spectra of ^{133}gTe isomers observed with a 5-cm³Ge(Li) detector.

Figure 1.6b

Sum of several individual gamma-ray spectra of ^{133}Te isomers observed with a 5-cm³ Ge(Li) detector.

Table 1.II

Energies and Relative Intensities of γ Rays following Decay of ^{133g}Te

E_{γ} (keV)	Rel. Intensity ^a	E_{γ} (keV)	Rel. Intensity
105.8	0.08	931.1	6.3
126.5	0.06	998.8	10.9
312.0	(100)	1021.0	3.8
384.6	0.4	1062.3	2.0
407.8	42.5	1251.9	1.6
476.0	1.7	1310.7	1.8
587.0	0.7	1333.4	14.0
592.6	0.2	1406.2	0.9
613.6	0.4	1629.0	0.2
697.6	D. E. of 1718.3 ^b	1718.3	4.6
720.1	9.4	1825.1	0.8
787.4	7.9	1849.6	<0.1
845.2	4.6	1882.4	2.0
		2137.6	0.3

^aUncertainties in relative intensities are $\pm 10\%$ or less.

^bSymbol D. E. indicates double annihilation-escape peak.

Table 1.III
Energies and Relative Intensities of γ Rays following the Decay of ^{133m}Te

E_{γ} (keV)	Rel. Intensity ^a	E_{γ} (keV)	Rel. Intensity
72.6	1.1	648.0	33.7
75.2	1.7	654.0	3.2
88.1	2.4	864.6	22.4
95.3	10.0	885.4	6.5
169.0	9.5	913.6	(100)
177.6	1.2	979.0	10.9
193.1	1.4	1395.9	3.6
214.0	3.3	1518.5	D. E. of 2540.6 ^b
261.8	18.0	1588.7	4.0
334.3	16.1	1683.6	6.4
343.7	0.3	2005.6	4.0
357.4	1.7	2028.0	S. E. of 2540.6 ^b
428.6	1.3	2052.1	0.9
445.6	2.6	2275.5	0.5
546.7	6.4	2461.0	1.0
574.0	2.7	2540.6	0.8
630.2	2.7		

^a Uncertainties in relative intensities are $\pm 30\%$ or less.

^b Symbols S. E. and D. E. indicate single and double annihilation-escape peaks.

In Fig. 1.7 is shown a tentative decay scheme for ^{133g}Te . The low-lying levels observed in ^{133}I agree well with the trends projected from the lower-mass I isotopes.

This study is being continued with particular emphasis on the decay of ^{133m}Te .
(B. Parsa, W. B. Walters, and G. E. Gordon)

Figure 1.7
Tentative decay scheme of 12-min ^{133}gTe .

G. Decay Scheme of 3.9-Day ^{127}Sb

The β and γ rays emitted in the decay of 3.9-day ^{127}Sb have been studied with the use of Si(Li), Ge(Li), and NaI(Tl) detectors in conjunction with coincidence equipment and our multi-parameter 4096-channel analyzer in order to construct the level scheme of ^{127}Te . In order to check on interference from other Sb isotopes, mainly 12.5-day ^{126}gSb and 9.6-hr ^{128}Sb which are also produced in fission, sources were prepared by separating Sb directly from fission, by milking Sb from separated Sn fission products, and by the use of the $^{128}\text{Te}(\gamma, p)^{127}\text{Sb}$ and $^{124}\text{Sn}(\alpha, p)^{127}\text{Sb}$ reactions followed by appropriate chemical separations. The methods of separation were previously described in detail (R. C. Ragaini, G. E. Gordon, and W. B. Walters, MIT-LNS Progress Report, Dec. 31, 1965).

Difficulty was encountered in determining the characteristics of the γ rays at 667, 698, and 722 keV in the presence of the interfering major γ rays of ^{126}Sb at 665, 695, and 720 keV. Because of the high ratios of activities $^{127}\text{Sb}/^{126}\text{Sb}$, the ^{126}Sb lines did not cause serious difficulty in obtaining direct γ -ray spectra of ^{127}Sb soon after irradiations with the use of Sb samples separated directly from fission products. However, coincidence experiments performed with those samples were difficult to interpret because of the very strong coincidence relationships that exist among the ^{126}Sb γ rays. Therefore, for most of the work reported here, we have used samples prepared by milking Sb from fission-product Sn. The (γ, p) and (α, p) reaction studies were employed to verify the results of the milking experiments. Recently the decay of ^{127}Sb has been studied using the buffer-magnetic tape system in conjunction with the 4096-channel multiparameter analyzer to record γ - γ coincidences.

The decay scheme of 3.9-day ^{127}Sb is shown in Fig. 1.8. Energies are given in keV. The dots on the beginning and end of indicated γ -transitions show observed γ - γ coincidences. The dots on the end of several of the β transitions represent observed β - γ coincidences. A total of 34 γ rays were observed, of which 33 have been placed in the level scheme of ^{127}Te . The unassigned γ ray, 745.9 keV (0.4) is difficult to assign because of its low intensity and its proximity to the 746-keV γ ray of 9.6-h ^{128}Sb . The properties of the low-lying, even-parity levels of ^{127}Te are in reasonable agreement with the predictions of Kisslinger and Sorenson. (Rev. Mod. Phys. 35, 853, 1963). (R. C. Ragaini, G. E. Gordon, and W. B. Walters)

H. Decay of ^{129}Cs and ^{131}I

The following is the abstract of an article that has been accepted for publication in the Physical Review.

Abstract: The decay schemes of ^{129}Cs and ^{131}I have been investigated using Ge(Li) and Si(Li) semiconductor detectors as well as various coincidence techniques. Gamma-ray energies and relative gamma-ray intensities were determined as well as conversion coefficients for many transitions. In ^{129}Xe , levels at 322.0 and 904.9 keV were proposed, which have not been reported earlier. The spin and parity assignments for 322.0-keV level are likely $5/2^+$. In ^{131}Xe , a level at 404.8 keV has been found, which was not previously known. The spin and parity assignments for this level are $1/2^+$ or $3/2^+$. Beta-gamma coincidence measurements were used to indicate that the 503-keV gamma ray in ^{131}I decay feeds the $11/2^-$ -isomer of ^{131}Xe . (G. Graeffe and W. B. Walters)

I. Decay of ^{130}Cs

The radioactive decay of 30-min ^{130}Cs has been studied using Ge(Li) and NaI(Tl) gamma-ray detectors in conjunction with our 4096-channel MPA. The ^{130}Cs was produced by irradiating ^{127}I with 24-MeV ^4He ions in the MIT Cyclotron. The ^{130}Cs was isolated in the same manner as ^{129}Cs (G. Graeffe and W. B. Walters, Sect. I.H). Gamma rays with the following energies (in keV) have been observed: 511, 536, 586, 683, 895, 1122, 1257, 1263, 1613, 1686, 1703, and 1997. A level whose spin and parity are 2^+ has been established at 1122 keV. As the spin and

parity of ^{130}Cs are $1+$, the β decay will be to levels whose spins and parities are $0+$, $1+$, and $2+$. The $0+$ levels will decay mainly to the lowest $2+$ level at 536 keV, the $1+$ levels should decay to both the $0+$ ground state as well as to excited $1+$ and $2+$ states and the $2+$ levels should decay principally to the $2+$ level at 536 keV as well as to the ground state and perhaps the $4+$ level at 1190 keV. We have not observed any gamma rays in the 1190-keV region that would indicate the $4+$ level was being fed. We expect to perform coincidence studies to determine the positions of the low-spin levels of ^{130}Xe . (G. Graeffe and W. B. Walters)

J. Search for Isomerism in ^{91}Zr

According to the effective-interaction calculations by Auerbach and Talmi (Nucl. Phys. 64, 450, 1965) and by Vervier (*ibid.* 75, 17, 1966), ^{91}Zr is expected to have a long-lived isomer analogous to the well-known $21/2+$, 7-h isomer at 2.4 MeV in ^{93}Mo .

We have attempted to produce the predicted isomer by two different reactions, the first being $^{88}\text{Sr}(\alpha, n)^{91}\text{Zr}$. Enriched ^{88}Sr (99.8 percent), as $\text{Sr}(\text{NO}_3)_2$, was bombarded with 30-MeV ^4He ions from the MIT cyclotron. After the irradiation, Zr was chemically separated and the γ -ray spectrum was observed with a Ge(Li) detector. No evidence for γ -rays emitted in the decay of an isomer was obtained. A negative result from a similar experiment has also been reported by Vervier (*op. cit.*).

As we felt that the $21/2$ level was perhaps not well populated in the (α, n) reaction, we also tried the reaction $^{93}\text{Nb}(d, \alpha)^{91}\text{Zr}$ by bombarding Nb metal with 15-MeV deuterons. This reaction has the advantages of non-zero target and projectile spins, $9/2$ and 1 , respectively. Because of the small amount of interfering activity produced, we simply counted the target directly with a Ge(Li) detector. Again there was no evidence for an isomer of ^{91}Zr . The major activity present was that of $21/2+$ ^{93m}Mo , formed by $^{93}\text{Nb}(d, 2n)$, indicating that the deuteron-induced reactions are capable of producing large amounts of the high-spin isomer. Thus, we conclude that no $21/2+$ isomer of half life more than a few minutes exists. The experiments reported by Vervier set much lower limits on the half life, but it is not clear that high-spin states were highly populated in the reactions used. Apparently, a level of spin intermediate between $21/2$ and $13/2$ falls between levels of those spin values. It has been suggested by Vervier that a $15/2-$ level occurs in between the $21/2+$ and $5/2+$ ground state, and thus greatly reduces the half life for de-excitation of the $21/2+$ level. (B. Parsa and G. E. Gordon)

K. A New Nuclide: 115-sec ^{46}K

A new nuclide, 115-sec ^{46}K , has been discovered and its decay scheme determined by observations of the β and γ rays emitted (B. Parsa and G. E. Gordon, Phys. Letters 23, 269, 1966). The new species was produced via the $^{48}\text{Ca}(d, \alpha)^{46}\text{K}$ reaction by bombarding CaCO_3 (enriched in ^{48}Ca) with 15-MeV deuterons from the MIT cyclotron. By multiscaling counts produced by the most prominent gamma ray, 1.35 MeV, we found the half life to be 115 ± 4 sec. The decay scheme shown in Fig. 1.9 was constructed from the singles (both NaI(Tl) and Ge(Li)) and coincidence gamma-ray spectra and the maximum beta-endpoint from this work plus the knowledge

of ^{46}Ca levels from nuclear-reaction studies by Belote, et al., (Phys. Rev. 138, B1067, 1965) and D. C. Williams (Los Alamos Scientific Laboratory, private communication). Energies and intensities of the gamma rays emitted are listed in Table 1.IV. (B. Parsa and G. E. Gordon)

Figure 1.9
Decay scheme of 115-sec ^{46}K

Table 1.IV
Gamma Rays from 115-sec ^{46}K Observed with Ge(Li) Detector

E_γ (MeV)	Relative Intensity
1.347 ± 0.001	(100 ± 1)
(1.439 ± 0.002)	3 ± 1.5
(1.670 ± 0.002)	5 ± 2
1.780 ± 0.002	9 ± 2
2.274 ± 0.002	9 ± 3.5
3.015 ± 0.005	10 ± 5
3.700 ± 0.005	31 ± 1

L. A New Isomer, ^{154m}Eu

A 47-min isomer has been discovered in ^{154}Eu that has characteristics similar to those of the 96-min isomer of ^{152}Eu characterized by K. Takahashi, M. McKeown, and G. Scharff-Goldhaber (Phys. Rev. 137, B763, 1965). The isomer was discovered in samples of separated ^{153}Eu that were irradiated with thermal neutrons during experiments seeking a 0- isomer similar to the 9.3-h isomer of ^{152}Eu . No γ rays could be found that would indicate the presence of such a 0- isomer. Two γ rays of 67.2 and 100.9 keV were found to remain with the europium fraction in chemical separations and to decay with a 42-min half life. In subsequent experiments, the isomer was produced by the $^{154}\text{Sm}(p, n)^{154m}\text{Eu}$ and $^{153}\text{Eu}(d, p)^{154m}\text{Eu}$ reactions. The europium was separated from the target by reducing it to a +2 state in a Jones Reductor and precipitating europous sulfate.

We show in Fig. 1.10 a decay scheme for the isomer. The energies of the γ rays are in excellent agreement with those of two γ rays observed in the capture γ -spectra from the $^{153}\text{Eu}(n, \gamma)^{154}\text{Eu}$ reaction by S. Orcher (Z. Naturforsch. 18, 576, 1963) whose energy values we have used in the decay scheme. The energy of the isomeric transition was obtained by measuring the energy of the L conversion electrons in coincidence with the 100.8-keV γ ray using a 0.5 mm Si(Li) electron detector and a NaI(Tl) γ -ray detector. Both the conversion coefficients and lifetimes of the 100.8- and 67.2-keV γ rays were measured in capture γ -ray studies by A. M. Berestovoi, I. A. Kandurov, and Yu. E. Loginov (Izv. Akad. Nauk SSSR Ser. Fiz. 28, 1701, 1964). (W. Zoller and W. B. Walters)

Figure 1.10
Proposed decay scheme of ^{154m}Eu .

M. Compilation of j-j Coupling in Odd-Odd Nuclei

The spins of the low-lying levels of odd-odd nuclei with $20 < A < 140$ and $192 < A < 212$ are being analyzed using the j-j coupling model. The experimental spins are compared to the spins predicted by the coupling rules of Brennan and Bernstein (Phys. Rev. 120, 927 (1960)). The observed magnetic moments of odd-odd nuclei are compared with predictions based on the j-j coupling model, and to empirical magnetic moments, in which g factors obtained from the moments of adjacent odd-even nuclei are used instead of the single-particle Schmidt g factors. Since the original article was published six years ago, many new levels have been studied and characterized. The 1960 study included nuclei with $20 < A < 120$. We are extending the analysis to include the isotopes of Sb and I below $A = 140$, and we are also analyzing the levels in the region of the doubly-closed shells of 82 protons and 126 neutrons, specifically Tl and Bi isotopes. It is of interest to determine whether or not, in the light of the newer data, the predictions will continue to be in generally good agreement with the experimental results. One principal reason for making this compilation is that, in regions where the coupling rules are applicable, they are helpful guidelines for the design and interpretations of experiments involving poorly characterized nuclei. Brennan-Bernstein Rule R2, in particular, has been very useful in the prediction and understanding of isomerism in odd-odd nuclei. Extension of the compilation into the region $120 < A < 140$ is important to the work of this laboratory, as many of our decay-scheme studies have been concentrated here. (R. C. Ragaini and G. E. Gordon)

II. Nuclear Fission Studies

A. Prompt Monte Carlo Calculations on Fission

Monte Carlo calculations on the fission process representing an extension of the calculations reported by Gordon and Aras (in Physics and Chemistry of Fission, IAEA, Vienna, 1965, Vol. 2, p. 73) have been performed. In the previous calculations it was assumed that average total kinetic energy is a function of mass ratio of division, but for a given mass division, is the same for all charge divisions although it is known that total energy release varies with charge division. In the new treatment, we also tested the opposite assumption, namely that for a given mass division, the average sum of the fragment excitation energies remains constant for all charge divisions and average total kinetic energy release varies as the total energy release with changing charge ratio.

In the previous calculations it was assumed that the excitation energy distributions of complementary fragments of given mass and charge division are uncorrelated. In this work we also tried the assumption of complete positive correlation.

In addition to those changes of the assumptions, we also modified the program in order to obtain various kinds of information that were not printed out in the earlier version. Of particular interest, in connection with the study of shielded nuclides (see Nakahara, Harvey, and Gordon, Section II.C), was the total kinetic energy of events leading to production of given secondary

fragments. The kinetic energy deficits of shielded nuclides predicted by the calculations under the various combinations of assumptions are listed in Table 1.V. By comparison of these results with the experimental data in Table 1.VII, Sect. II. B one may note that:

- (a) there is not enough difference between the calculations for "no correlation" and "positive correlation" to allow one to make a distinction between those assumptions on the basis of the deficits for shielded nuclides;
- (b) of the four values for deficits, only that for ^{86}Rb from ^{233}U fission is better fitted by the assumption of constant kinetic energy; therefore, these results favor the assumption of constant excitation energy for various charge divisions of a given mass ratio;
- and (c) the energy deficit for ^{136}Cs from ^{233}U fission was not well fitted by any of the calculations.

Additional details of the calculations and results are given in the thesis of H. Nakahara. (G. E. Gordon, H. Nakahara, and M. Furbush)

Table 1.V
Predicted Secondary-Fragment Kinetic Energy
Deficits of Shielded Nuclides

Fissioning nuclide	Shielded nuclide	Kinetic energy deficit (MeV)			
		No correlation		Positive correlation	
		k. e.	energy	k. e.	energy
^{234}U	^{86}Rb	4.3	7.5	2.2	8.4
	^{136}Cs	3.4	4.2	1.2	4.1
^{236}U	^{86}Rb	2.9	9.2	-0.1	8.8
	^{136}Cs	6.6	8.7	7.1	10.4

B. Ranges of Shielded-nuclides in Thermal-neutron Fission

Since our last progress report (Nakahara, Harvey, and Gordon, 1965 LNS Progress Report, p. 21), the ranges for shielded nuclides ^{86}Rb and ^{136}Cs plus a number of chain-yield species from thermal-neutron fission of ^{233}U and ^{235}U have been measured via the thin-target, thick-catcher method. The ranges of the shielded species and a few chain-yield products were determined radiochemically. In the case of ^{233}U , ranges for species in 15 mass chains were determined by gamma-ray spectrometry on the catcher foils with a Ge(Li) detector as described in Sect. II.C. A summary of the measured ranges is given in Table 1.VI. Ranges were transformed to secondary fragment kinetic energies with essentially the same expressions as those developed by Aras, Menon, and Gordon (Nucl. Phys. 69, 337, 1965). The resulting secondary fragment kinetic energy values are also listed in Table 1.VI.

Table 1.VI

Measured ranges and secondary-fragment kinetic energies of products from thermal-neutron fission of ^{233}U and ^{235}U .

Fission product	^{233}U		^{235}U	
	Range ^a (mg/cm ² Al)	Kin. energy (MeV)	Range (mg/cm ² Al)	Kin. energy (MeV)
$^{85\text{m}}\text{Kr}$	4.18 ± 0.05 (G)	101.1 ± 2.4		
^{86}Rb	3.88 ± 0.04	97.3 ± 1.1	3.76 ± 0.03	92.2 ± 0.7
^{89}Sr	4.10 ± 0.02	100.2 ± 1.0	4.15 ± 0.02	101.7 ± 1.0
^{90}Sr	4.14 ± 0.03	102.3 ± 1.5	4.17 ± 0.07	103.0 ± 3.5
^{91}Sr	4.16 ± 0.04 (G)	104.1 ± 2.0		
$^{95}\text{Zr}-^{95}\text{Nb}$	4.03 ± 0.03 (G)	100.1 ± 1.5		
$^{97}\text{Zr}-^{97}\text{Nb}$	4.08 ± 0.05 (G)	101.1 ± 2.0		
^{99}Mo	$\left\{ \begin{array}{l} 4.01 \pm 0.03 \text{ (G)} \\ 4.01 \pm 0.02 \end{array} \right\}$	100.6 ± 1.0	3.97 ± 0.02	98.8 ± 1.0
^{103}Ru	3.94 ± 0.05 (G)	98.0 ± 2.0		
^{111}Ag	3.54 ± 0.02	83.8 ± 2.0	3.48 ± 0.02	80.7 ± 0.9
^{115}Cd			3.32 ± 0.02	75.7 ± 0.9
^{131}I	3.31 ± 0.02 (G)	77.5 ± 1.4		
$^{132}\text{Te}-^{132}\text{I}$	3.27 ± 0.03 (G)	76.3 ± 1.4		
^{133}I	3.14 ± 0.04 (G)	74.0 ± 2.0		
^{133}Xe	3.24 ± 0.03 (G)	75.4 ± 1.4		
^{135}Xe	3.21 ± 0.03 (G)	74.7 ± 1.4		
^{136}Cs	2.80 ± 0.02	62.8 ± 0.9	2.81 ± 0.02	62.8 ± 0.9
^{137}Cs	3.00 ± 0.02	67.6 ± 0.9	3.03 ± 0.02	68.3 ± 0.9
$^{140}\text{Ba}-^{140}\text{La}$	$\left\{ \begin{array}{l} 3.00 \pm 0.03 \text{ (G)} \\ 2.92 \pm 0.02 \end{array} \right\}$	68.4 ± 1.4 65.6 ± 0.9	3.02 ± 0.02	68.5 ± 0.9
^{141}Ce	2.97 ± 0.02 (G)	67.5 ± 0.9		
^{143}Ce	2.91 ± 0.03 (G)	66.0 ± 1.4		
^{144}Ce	2.87 ± 0.03 (G)	65.0 ± 1.4		
^{147}Nd	2.77 ± 0.02 (G)	62.3 ± 0.9		

^a G indicates measurement by Ge(Li) spectrometry, otherwise value was measured radiochemically.

As is well known, shielded nuclides have ranges and, thus, kinetic energies smaller than those of neighboring chain-yield species. In order to determine the secondary-fragment kinetic energy deficits of the shielded fragments, a curve of secondary-fragment kinetic energies was constructed from the values for chain-yield species in Table 1. VI and from the results of instrumental studies of fragment energies (Schmitt, Neiler, and Walter, *Phys. Rev.* 141, 1146, 1966; Thomas, Gibson, and Safford, in *Physics and Chemistry of Fission*, IAEA, Vienna, 1965, vol. 1, p. 467; Milton and Fraser, *Can. J. Phys.* 40, 1626, 1962). Deficits of the shielded nuclides were taken as the displacements of values of their kinetic energies given in Table 1. VI from the smooth curve constructed from the chain-yield species and the instrumental results. In Table 1. VII we summarize the values of the deficits from this work as well as our re-analysis of previous studies. Some of the implications of these results are discussed by Gordon, *et al.*, in Sect. II. A. (H. Nakahara, J. W. Harvey, and G. E. Gordon)

Table 1. VII
Secondary-fragment kinetic energy deficits of shielded nuclides

Fissioning nuclide	Shielded nuclide	Kinetic energy deficit (MeV)		
		This work	Niday ^a	Brown and Oliver ^b
²³³ U	⁸⁶ Rb	4 ± 1.5		
	¹³⁶ Cs	9 ± 1.5		
²³⁵ U	⁸⁶ Rb	8 ± 1.5	10.4	
	¹³⁶ Cs	10 ± 1.5	8.0	8.5

^a From our re-analysis of the data from J. B. Niday, *Phys. Rev.* 121, 1471 (1961).

^b From our re-analysis of the data from F. Brown and B. H. Oliver, *Can. J. Phys.* 39, 616 (1961).

C. Fission Experiments by Direct γ -Ray Spectrometry with Ge(Li) Detectors

In a paper that recently appeared in *Nucleonics* (Gordon, Harvey, and Nakahara, *Nucl.* 24, No. 12, 62, 1966), we described a method developed for studies of fission by observation of the gross fission-product γ -ray spectrum with a Ge(Li) detector at various times after irradiation. The resolution of the counting system was sufficiently good that we were able to identify and measure areas under the peaks produced by γ rays of about 20 fission products in 15 mass chains. We were able to measure the average ranges of these products by stacking Al foils against a thin ²³³U target. After irradiation, we took the stack of foils apart and measured the γ -ray photopeak areas in the spectrum obtained from the foil next to the target relative to the areas of the peaks obtained by observing the foils farther from the target. Ranges could be calculated from the ratios of photopeak areas with the use of the thin-target - thick-catcher treatment discussed by Aras, Menon, and Gordon (*Nucl. Phys.* 69, 337, 1965). The results (see Sect. II. B, Nakahara, Harvey, and Gordon) for ²³³U fission are in good agreement with the few values obtained by standard radiochemical methods and with range values predicted from instrumentally measured

fragment kinetic energies (Thomas, Gibson, and Safford in Physics and Chemistry of Fission, IAEA, Vienna, 1965, vol. 1, pp. 467-480).

Mass yields from thermal-neutron fission of ^{233}U were determined relative to those from ^{235}U by simultaneously irradiating ^{233}U and ^{235}U samples and observing the gross fission-product γ -ray spectra from the two sets of samples. One of the major problems involved in obtaining the ^{233}U yields in this way is that of the selection of the best values of the yields for ^{235}U fission which is taken as the standard. In the Nucleonics paper we used a combination of the ^{235}U yields listed by Katcoff (Nucleonics 18, No. 11, 201, 1960) and Farrar and Tomlinson (Nucl. Phys. 34, 367, 1962). However, a more detailed analysis of the yield-mass data shows inconsistencies that may be due to errors in one or both of the sets of ^{235}U yields cited above. We are now carefully re-evaluating the yields from both ^{233}U and ^{235}U , including new data on both fissioning species from the Idaho reactor group (Maeck, et al., IDO-14667 and IDO-14676). In addition we have recently recounted the various samples. The latest count of the samples used to obtain the data reported in the Nucleonics paper was 33 days after irradiation. Many of the species having half lives in the range of days or weeks have decayed sufficiently that we are now able to observe several long-lived species (^{95}Zr , ^{95}Nb , ^{103}Ru , ^{137}Cs , ^{141}Ce , and ^{144}Ce) that could not be seen earlier.

Also we have obtained some ^{229}Th from the AEC and will soon attempt to determine mass yields from thermal-neutron fission of it with the use of the new method. This fissioning system is of considerable interest as it is the lowest-mass species known to give an appreciable amount of fission with thermal neutrons. Furthermore, the compound nucleus, ^{230}Th , is very close to those (^{227}Ac and ^{228}Ac) for which the yield-mass curves exhibit three peaks, two from asymmetric fission and a central peak from symmetric fission (Fairhall, Jensen, and Neuzil, Proc. 1958 Geneva Conf., vol. 15, paper P/667). Rather large discrepancies exist between the two sets of yields that have been reported for thermal-neutron fission of ^{229}Th , one set obtained radiochemically (Ravindran, Flynn, and Glendenin, J. Inorg. Nucl. Chem. 28, 921, 1966) and the other with the use of mass spectrometers (Harvey, Clark, Thode, and Tomlinson, Can. J. Phys. 44, 1011, 1966). (G. E. Gordon, J. W. Harvey, H. Nakahara, and M. Kay)

D. Half Lives of the Short-Lived Lanthanum Isotopes Produced in Fission

Since the last progress report (see Petrick, Coryell, and Walters, MIT-LNS Chem. Prog. Rep., Dec. 31, 1965) we have continued the investigation of the half lives of the La isotopes. Continuous extraction of Ce(IV) nitrate from 10 M HNO_3 into hexone is being used. The procedure is as follows: a sample of U-235 is irradiated for 20 sec and then transferred to an extraction flask via a pneumatic transport system. NaBiO_3 is added and extraction with hexone started, the hexone already containing Ce(IV) carrier plus ^{139}Ce tracer. (The exchange between Ce(IV) organic and Ce(IV) aqueous is very rapid.) Samples of the hexone at known times after the end of irradiation are collected. The Ce is then back-extracted into 5 N HNO_3 and precipitated, the yields of the various Ce and Pr isotopes are determined by counting the samples with Ge(Li) detectors and a multi-channel analyzer and timed spectra are taken allowing the

determination of the half-lives of the various gamma-ray peaks seen. The yield of one of the Ce, Pr isotopes can then be determined from these data, and compared to the yield determined for other extraction samples at different times. This information can then be related back to the half-lives of the La precursors.

The information obtained from the first series of fission experiments gives the ratio of 5.96-h ^{145}Pr to 33-h ^{143}Ce . This ratio is the same as what was reported last year. These surprising results should be clarified by future experiments. (J. L. Fasching and C. D. Coryell)

E. Studies of Short-Lived Zn and Rb Fission Products

Chemical procedures have been developed for rapid separation of Zn and Rb from fission-product mixtures in order to make samples for study of the decay of short-lived isotopes of those elements. A procedure slightly modified from that given by Paper 71, Feldman and Glendenin (in The Fission Products, Vol. 2, edited by Coryell and Sugarman, McGraw-Hill, New York, 1951, p. 654) has been developed that allows separation of Zn in under 3 min with a separation factor of about 10^5 from other fission products. In the case of Rb, a fast procedure (< 3 min) employing precipitation steps and an ion-exchange separation on an ammonium molybdo-phosphate column has been studied with the use of ^{86}Rb tracer. (W. H. Zoller and G. E. Gordon)

III. Physico-Chemical Studies

A. Some Thermodynamic Quantities for the Distribution of Anions between Benzene Solutions of Alkylammonium Salts and Aqueous Electrolyte Solutions.

The following is the abstract of a paper which was presented at the International Conference on Solvent Extraction Chemistry, Gothenburg, Sweden, 30 September 1966. The paper will be published in full in the Proceedings of the Conference.

Using tetraheptylammonium salts (THAX) in benzene, the distribution of tracer Br^- and ReO_4^- between the organic phase and aqueous lithium salt solutions has been measured as a function of THAX concentration, aqueous ionic strength, and temperature. From these data ΔH , ΔG and ΔS have been determined for the reaction $\text{RX} + \text{Y}^- = \text{RY} + \text{X}^-$. The values obtained are compared with those calculated from a model based on ion-pair formation in the organic phase and changes in ion hydration in the aqueous phase. (G. Scibona, J. F. Byrum, K. Kimura, J. W. Irvine, Jr.)

B. Solvent Extraction in the System: Molten Lithium-Potassium Nitrate-Tetraheptylammonium Nitrate-Polyphenyl. I. The Distribution of Chloride and Perrhenate Ions.

The following is the abstract of a manuscript which has been submitted to the Journal of Physical Chemistry for publication:

The distribution of chloride and perrhenate ions between a eutectic molten salt mixture of LiNO_3 - KNO_3 and a solution of tetraheptylammonium nitrate in a polyphenyl solvent was studied

at 150°C. The distribution of the anions has been interpreted in terms of a simple anion-exchange equilibrium followed by polymerization of the species in the organic phase. The equilibrium constants for the anion-exchange and the dimerization constants were calculated and the dependence of the perrhenate distribution on the temperature was determined. The activity coefficients of the chloride and nitrate salts in the melt follow, up to a chloride mole fraction of 0.1, an expression derived from a simple model of molten salt mixtures. (I. J. Gal, J. Mendez, and J. W. Irvine, Jr.)

C. Solvent Extraction in the System: Molten Lithium-Potassium Nitrate-Tetraheptylammonium Nitrate-Polyphenyl. II. The Distribution of Silver (I)-Chloride Complexes. The Solubility of AgCl.

The following is the abstract of a manuscript which has been submitted to the Journal of Physical Chemistry for publication:

The distribution of silver (I) between a eutectic molten salt mixture of LiNO_3 - KNO_3 containing LiCl - KCl and a solution of tetraheptylammonium nitrate in a polyphenyl solvent was studied at 150°C. The results have been interpreted on the basis of an anion-exchange equilibrium between AgCl_2^- and NO_3^- and the formation of silver (I)-chloride complexes. The solubility of AgCl(s) in the eutectic melt was measured at 150°C as a function of chloride ion concentration. The stability constants of AgCl and AgCl_2^- were calculated. (J. Mendez, I. J. Gal, and J. W. Irvine, Jr.)

D. Solvent Extraction in the System: Molten Lithium-Potassium Nitrate-Tetraheptylammonium Nitrate-Polyphenyl. III. The Distribution of Some Metal Nitrates.

The following is the abstract of a manuscript which has been prepared for submission to the Journal of Physical Chemistry:

The distribution of Ag(I) , Cu(II) , Hg(II) , Co(II) , Cd(II) , and Fe(III) between a molten $(\text{Li, K})\text{NO}_3$ phase and an organic phase containing tetraheptylammonium nitrate in a polyphenyl solvent was studied at 150°C. The extraction of all metallic species, except Hg(II) , increases with the concentration of the quaternary ammonium salt in the solvent. The experimental data indicate that Ag(I) is extracted as a $\text{Ag(NO}_3)_2\text{T}$ species, while Cd(II) is probably extracted as a mixture of $\text{Cd(NO}_3)_3\text{T}$ and $\text{Cd(NO}_3)_4\text{T}_2$ (T = tetraheptylammonium cation). To prevent the precipitation of some polyvalent metal cations as oxides, the molten nitrate mixture was kept about 10^{-3} molal in ammonium nitrate. (I. J. Gal, J. Mendez, and J. W. Irvine, Jr.)

E. The Solubility of AgCl and AgBr in Molten Lithium-Potassium Nitrate Eutectic Mixture.

The following is the abstract of a note prepared for submission to the Journal of Physical Chemistry.

The solubilities of AgCl and AgBr in molten LiNO_3 - KNO_3 eutectic mixture were measured as a function of temperature and halide ion concentration. The temperature was varied between 150 and 200°C and the concentration of halide ion between 1×10^{-3} and 2×10^{-1} molal. The data

were interpreted assuming the formation of AgX and AgX_2^- complexes. The solubility products of the silver halides and the stability constants of the complexes were calculated. The dependence on temperature of the stability constants follows the generalized quasi-lattice model developed by Blander. (J. Mendez, I. J. Gal, and J. W. Irvine, Jr.)

F. The Chemistry of Astatine

We have begun a tracer study of the chemistry of astatine with regard to oxidation-reduction and ion exchange. The tracer used is $^{211}_{85}\text{At}$ ($t_{1/2} = 7.2$ h), which decays by electron capture and α emission. It is produced by the $^{209}\text{Bi}(\alpha, 2n)^{211}\text{At}$ reaction at the MIT cyclotron with 26-MeV α 's on about 500 mg of Bi_2O_3 powder wrapped in Al foil.

The tracer is separated by dissolving the target in conc. HClO_4 , extraction into CCl_4 containing one mg/ml I_2 , and re-extraction into 0.5 M SO_3^{--} solution. The yield is about 80 percent, and the tracer is generally counted in a 3" x 3" NaI(Tl) well counter connected to a single-channel analyzer.

Initially we attempted to ascertain the potential for the half-reaction $\text{At}^- \rightarrow \text{At}^0 + e^-$ using couples with pH-controlled potentials such as $\text{VO}^{++}/\text{VO}_2^+$ and $\text{V}^{+3}/\text{VO}^{++}$, but this gave ambiguous results; in addition, the nature of the vanadium species in solution could not be reliably determined to use with the Nernst equation

$$E = E^0 - \frac{2.3 RT}{nF} \log \frac{[\text{oxidized}]}{[\text{reduced}]}$$

We are now working on batch-method distribution ratios between Dowex 1-X8 anion-exchange resin in the chloride form and aqueous solutions of NaCl . Initial experiments indicate that, as might be expected, At^- is quite strongly held by the resin (the trend is $\text{I} > \text{Br} > \text{Cl} > \text{F}$), and is held less strongly with increasing Cl^- concentration in the solution. Further experiments to determine any time dependence of the ratios are in progress. (J. F. Wild and C. D. Coryell)

G. Separation of Tellurium Isomers by Chemical Means

It was noted previously (J. E. Esterl and W. B. Walters, LNS Prog. Report, Dec. 1965, p. 16) that the possibility existed to separate the 70-min ^{129g}Te isomer from the 33-day ^{129m}Te parent isomer by taking advantage of the chemical transformation that accompanies the isomeric transition. A procedure was worked out that permitted the continuous extraction of the ^{129g}Te from the ^{129m}Te parent. It was subsequently applied to the isomers of ^{133}Te and yielded small samples of 12-min ^{133g}Te free of 50-min ^{133m}Te . Because of the small amount of isomeric transition (13 percent) and the short half life of ^{133g}Te the samples were not intense enough to use as sources for study of the decay of ^{133g}Te with a Ge(Li) detector. (J. E. Esterl, B. Parsa, and W. B. Walters)

IV. Activation Analysis and Earth Sciences

A. Rare Earths in Manganese Nodules

The rare earths have been determined in manganese nodules from eight Atlantic, Pacific, and Indian oceanic localities, from the Baltic Sea and a fresh water lake, and from a Paleozoic sedimentary rock. Several phosphatic samples and the sediment associated with one oceanic nodule were also analyzed, and in three cases, the variation of rare earths with location within a nodule was studied. Enrichment factors of concentration relative to chondrites invariably show a smooth trend with atomic number with the exception of cerium and europium. Cerium is singularly enriched three to five times in most marine nodules but not in the nodules from the Baltic Sea, Ship Harbor Lake, or Paleozoic era. A cerium depletion is observed in phosphatic material associated with manganese nodules from the Blake Plateau. Europium is low to about the same extent as previously observed in many sedimentary materials. One marine nodule shows the same trend of enrichment factor with atomic number as its associated sediment, implying that rare earths in marine nodules are derived from the underlying sediment. (A. Ehrlich, J. W. Winchester, and C. D. Coryell)

B. Neutron Activation Analysis for Vanadium

A fast, convenient method for determination of V concentrations in natural materials by neutron activation analysis has been developed. Samples containing atmospheric V (rain and washes from aerosol filters) were concentrated to small volume by boiling. The samples were irradiated for 2 min in the MIT reactor to produce 3.8-min ^{52}V and transferred to the laboratory via the pneumatic-tube system. Solvent extraction of the V from the samples was accomplished in under 2 min by the use of a slight modification of a standard method (Proc. 4, Fukai, R., in NAS-NS-3022, p. 59).

Gamma-ray spectra of the samples were obtained with a 5-cm³ Ge(Li) detector or 3-x 3-in NaI crystal and the 4096 channel analyzer. The 1.43-MeV gamma ray from ^{52}V was used for determination of the amount of V present. Chemical yields were determined with the use of 16-day ^{48}V as a tracer by counting its 1.31-MeV gamma rays later. Amounts of V as low as several nanograms can be measured with this technique which requires only about 25 min per sample. The method is particularly applicable to systems in which good chemical separation is not possible as advantage of the high-resolution of Ge(Li) detectors can be taken if a moderate amount (10^{-8} g) of V is present. (R. A. Duce, Depts. of Chemistry and Meteorology, University of Hawaii, and W. H. Zoller, MIT Nuclear Chemistry Group) (This work was in part supported by the Office of Naval Research.)

C. Activation-Analysis Studies of Rare Earths with Ge(Li) Detectors

In recent years it has become apparent that rare-earth distributions in various geological media and in meteorites can give important information about the conditions of formation of some classes of material (see, for example, Haskin, Frey, Schmitt, and Smith in Physics and Chemistry

of the Earth 7, Pergamon Press, New York, in press). One of the important methods for determinations of rare-earth concentrations has been that of neutron activation analysis. The main difficulty with that method, however, is that the rare-earth elements in general have to be chemically separated from the sample and then the individual rare earths must be separated from each other. The latter is a very complicated and time consuming step. Therefore, we have done a preliminary experiment designed to find out how many of the rare earths could be determined by merely separating them as a group and observing their gamma-ray spectra with a high-resolution Ge(Li) detector, thus eliminating the second separation step.

In the preliminary experiment, a mixture of the rare earths (made up by the Geochemistry group for use as a monitor in their rare-earth studies, see Ehrlich and Winchester, Sect. IV.A) was irradiated for 2 hrs in the MIT reactor. At various times up to two days after the irradiation, gamma-ray spectra of the mixture were obtained with a Ge(Li) detector and the 4096-channel analyzer. Although this did not allow sufficient time for gamma rays of some of the longer-lived species to show up in the spectra, we were able to see lines produced by isotopes of La, Sm, Eu, Dy, and Ho. This project is being continued by one of us (G. E. G.) in cooperation with Prof. Gordon Goles at the University of California at San Diego.

In connection with this project we wrote a computer program designed to give a crude prediction of gamma-ray spectra obtained with Ge(Li) detectors. It was successful; however, it is not sufficiently refined to be useful in analyzing experimental spectra, but may be helpful in predicting which elements can possibly be determined by instrumental neutron-activation analysis with Ge(Li) detectors. (M. Weisfield, G. E. Gordon, and J. W. Harvey)

D. Determination of Silver in Minerals and Ores by Neutron Activation Analysis and High-Resolution Gamma Spectrometry

The following is the abstract of an article published in Analytical Chemistry 38, 432 (1966).

Abstract: A procedure is described for quantitative determination of Ag in natural minerals. The analysis is based on the use of a Ge(Li) detector for high-resolution spectroscopy of gamma-ray activity induced by 5-sec irradiations in the thermal-neutron flux ($8 \times 10^{12} \text{n/cm}^2 \text{ sec}$) of the MIT reactor. The intensities of the 660-keV gamma ray from 24-sec ^{110}Ag were measured in the sample and in standards. The limit of detectability of Ag in minerals rich in Mg (~50 percent MgO by weight), an interfering element, is about 15 p.p.m. Confidence limits are calculated directly from the counting data. This procedure obviates the need for any chemical processing or spectrum stripping. Sample sizes ranging from milligrams to greater than 10 grams can be analyzed by this method. (G. L. Schroeder, R. D. Evans (Dept. of Physics), and R. C. Ragaini)

V. Instrumentation and Data Handling

A. The Multiparameter Pulse-Height Analyzer System.

Nearly all of the work described in this report that involved the detection and identification of large number of gamma rays required the use of the 4096-channel multiparameter pulse-height analysis system (MPA) installed in mid-December, 1965. This system includes a 4096-channel memory, dual 1024-channel analog-to-digital converters, an eight-channel digital gate and a high-speed parallel printer. The system was augmented in October 1966 by a buffer memory and control system and a computer-compatible magnetic tape data-handling system. A high speed plotter was also installed in May 1965 to aid in the handling and interpretation of data. The variety of uses that are possible with this system are best seen by reviewing the earlier sections of this report and the publications of the group. As the buffer memory and magnetic tape were only recently installed, a brief description of their utility is included here.

The functions of the buffer memory and control system can be separated into two categories, the first involving the rapid readout of data from the 4096-channel memory onto magnetic tape and the return of that data to the memory. As the magnetic tape is computer compatible, it is now possible to treat the data in the computer in any manner desired. This is especially valuable in the study of short-lived nuclides and of mixtures of different nuclides where addition and subtraction of spectra are desired.

The other function of the buffer system is the collection and storage of related address pairs on magnetic tape and the subsequent analysis of that data. In this mode of operation, the binary addresses of events in coincidence are stored sequentially in the buffer memory until the buffer memory is full (252 events) at which time the contents of the buffer memory are dumped onto magnetic tape. In this mode of operation all the addresses of coincidence pairs are stored on the tape and the data may be analyzed at a later time either by the MPA system or the computer to determine the coincidence relationships among the observed gamma rays.

Prior to the installation of the buffer memory system, the Ge(Li) spectra in coincidence with four or eight preselected areas of the NaI(Tl) spectrum could be accumulated at one time. All other coincidence data was lost and in order to obtain the Ge(Li) spectrum with another area of the NaI(Tl) spectrum, another experiment was required. As the selection of proper areas for gating required some knowledge of the decay scheme, generally many experiments were required in order to obtain the exact coincidence data required. As all coincidences are now stored on tape, only analysis of the tape is required to determine the Ge(Li) spectrum in coincidence with any desired area of the NaI(Tl) spectrum. (W. B. Walters)

B. Ge(Li) Detectors.

In addition to the purchase of the MPA system, the addition of two Ge(Li) detectors and FET preamplifiers has extended our capability to detect and resolve gamma rays in complex spectra. The better of the two detectors has a 1.2 cm³ volume and gives a full-width at half maximum (FWHM) of 2.3 keV for the 662-keV gamma ray following the decay of ¹³⁷Cs while the

other detector has a volume of 5 cm³ and a FWHM of ~ 4.5 keV for the ¹³⁷Cs gamma ray. For supplying these detectors and helping in their care and feeding we wish to thank Prof. N. C. Rasmussen, Dr. V. J. Orphan, and Mrs. Bonnie R. Hites of the Department of Nuclear Engineering at MIT. (G. Graeffe)

C. Lifetime Studies

We have examined several commercial systems that permit the use of a time-to-amplitude converter (TAC) in lifetime studies of systems with lifetimes of $\gtrsim 0.1$ nsec and placed on order for such a system. When utilized with our XP1021 fast photomultiplier tubes and 2" x 2" NaI(Tl) detectors it will be possible to determine lifetimes of levels in complex decay schemes. For less complex systems, plastic detectors will be used in both γ - γ and β - γ coincidence studies. (M. B. Perkal and W. B. Walters)

D. Data Processing

Programs have been written to permit the treatment of data obtained by the MPA system on magnetic tape. As the magnetic tape unit was installed in October, these programs are not yet either extensive or in final form. They do, however, permit computer treatment of both the direct spectra and the coincidence data. As the LNS Computation Center will switch to a new IBM System 360 Computer during 1967, work has begun on programs for that computer to permit us to treat our data. (M. Furbush, J. Siegel, and W. B. Walters)

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INSTRUMENTAL CHEMISTRY GROUP

I. Plasma Emission Spectroscopy

Detailed effects of a number of important secondary variables on the sensitivity, reproducibility and linearity of plasma emission spectroscopy have been studied. A considerable number of minor improvements have combined to make the overall apparatus much more flexible, stable, and dependable. The samples, normally aqueous, are nebulized by means of an ultrasonic generator and the resulting fog and vapor carried to the plasma chamber in a stream of supporting gas. Considerable quantities of water vapor are carried with the sample and are known to affect the plasma. A bypass has been made such that a continuous and unvarying stream of nitrogen can be fed to the plasma chamber, a known fraction of which is passed through the nebulizing chamber thereby giving a more controllable rate of sample feed and also the possibility of studying directly the effect of water vapor at a quantitative level.

The effect of water vapor has been found to be considerable with some systems. Relatively easily excited atoms such as the alkaline earths show the effect least and emission intensity is found to be a linear function of sample addition governed by the fraction of the nitrogen carrier gas which is passed through the nebulizer chamber. It is evident that the energy absorbed by the water vapor is not sufficient to cause interference under normal operating conditions with these elements. In the case of elements which are more difficultly excited than the alkaline earths, nickel and zinc for example, increasing the amount of sample fed into the plasma by increasing the fraction of carrier passed through the nebulizer results under normal operating conditions in almost no increase in emission intensity; in fact, there may be a slight decrease at high flows. With these elements the cooling of the plasma through absorption of energy by the water vapor counterbalances the effect of increased metal concentration. With elements which also form very refractory compounds on high-temperature evaporation a very striking effect is observed. The emission intensity first increases rapidly with increasing sample speed, passes through a maximum and then descends. Up to a certain point the increased sample concentration gives increased emission, thereafter the cooling effect of water vapor predominates. As a result the efficiency of the plasma for some elements such as aluminum and tin may be highly dependent upon the amount of water vapor in the plasma chamber. In spite of this sensitivity to water it was found that good stability and reproducibility were obtainable with the present apparatus, showing that the plasma adjustment, the control of atomization and the sample splitting were under very satisfactory control. It should be noted that for all the elements studied, under a given set of nebulizing conditions, i. e., a given amount of water being fed to the plasma per unit time, good sensitivity and reproducible calibration curves with substantial positive slopes were always obtained. It is evident, however, that the conditions are much more critical for some elements than for others.

The effect of the water content on the emission sensitivity metals such as aluminum and tin, which form very stable and refractory oxides, suggests that the same factor might influence the degree to which anions interfered with alkaline earth emission. Suppression of alkaline earth emission by phosphate and aluminum is the classical example of anion interference in flame photometry and one of the great advantages of the plasma emission source has been that these interferences under the usual operating conditions in this laboratory have been eliminated. On examination it was found that over the entire range of water feed rates available in our apparatus no effect of phosphate on calcium could be detected. On the other hand, aluminum, which evidently requires a considerably higher temperature for elimination of interference, was found to depress calcium emission appreciably at all but the lowest 20 percent of water feed rates. This again emphasizes the necessity for checking the effect of all variables before using any practical analytical application of this technique.

Non-linear calibration curves, both concave and convex, have been observed for a number of elements, even under optimum conditions. Further study has shown that this is due to changes in the emission profiles within the plasma as the concentration of sample is changed. Both horizontal and vertical emission profiles were run for representative elements (alkaline earths, refractory oxide formers, and difficultly excitable metals) and a consistent pattern was found. The atomic lines, particularly of easily excitable elements, are found in the outer mantle and the emission is of fairly uniform intensity over a fairly large part of the plasma. Ion lines and lines of difficultly excitable elements on the other hand appear strongly only very close to the torch tip. With increasing concentration of sample the point of maximum intensity tends to rise in the plasma and due to the changed concentration of ions within the plasma the shape of the plasma may change also. All these effects tend to cause deviations from linearity in the working curves. No serious problem is introduced in analytical applications however if one is aware of the non-linearity and takes account of it in calibration.

A survey is being made of the effect of organic vapors particularly in low concentration on the dry plasma. By scrupulous removal of water from the system and introduction of a supplementary nitrogen flow above the plasma so as to blanket it completely and prevent the introduction of oxygen and water vapor through the vent, the background is reduced and considerably simplified. All organic materials introduced into the plasma are thoroughly decomposed and an emission characteristic of carbon compound decomposition products is observed. The emission is quite sensitive and as little as 10 micrograms per minute of carbon may be detected. Chlorine-containing compounds have several unique peaks, which may be used to identify and monitor the amount of that halogen. Investigation into the detection of organic materials containing sulfur and phosphorous are now being carried out. (A. L. Malenfant and D. N. Hume)

II. Photochemistry of 9,10 Dihydroxyanthracene

Anthraquinone (AQ) derivatives photoreduce to 9,10-dihydroxyanthracene (9,10DHA) derivatives. With 3650 Å light, photolysis of 9,10DHA does not occur. With 2537 Å light, the photolysis continues giving the following hypothetical product sequence:

There are two possible explanations. One would involve photoreaction from the second excited singlet of I. The other would be photoreaction from the keto tautomer of I.

With this background in mind, the purpose of this research is to characterize the reaction sequence, to measure the quantum yields of the individual steps, to study the short-lived radical and triplet intermediates and their kinetics with flash photolysis, and to explain the wavelength-dependent photoreduction of 9,10-dihydroxyanthracene.

9,10-Dimethoxyanthracene (9,10DMA), m.p. 203-204°, was prepared according to the literature, recrystallized three times from benzene, and zone refined. When a degassed solution of 9,10 DMA in ethanol was photolyzed by an unfiltered xenon lamp, all the 9,10 DMA absorbance was gone within 5 hrs. The blue fluorescence (max. at 4340 Å) of 9,10DMA was replaced by a three-band fluorescence centered at 3750 Å. Continued photolysis, considerably reduced the 3750 Å fluorescence with no new fluorescence developing.

Gas chromatographic analysis of the 9,10DMA photolysis product showed the presence of 2 components (in an approx. ratio of 9:1) which had longer retention times than 9,10DMA. Using the appropriate filter solutions and a potassium ferrioxalate actinometer system, the quantum yield of disappearance of 9,10DMA, $\phi(d)$, was measured at different wavelengths. $\phi(d)$ at 2537 Å < 0.025. $\phi(d)$ at 3130 Å < 0.005. $\phi(d)$ at 3650 Å < 0.005. By comparison to a quinine bisulfate standard, the $\phi(\text{fluorescence})$ of 9,10DMA was estimated to be 0.8. (S. A. Carlson and D. M. Hercules)

III. Mechanistic Study of the Photochemical Fries Rearrangement

The photochemical analogy of the Fries rearrangement was discovered recently. This reaction is quite general and proceeds for a variety of esters, anilides, and similar compounds.

The mechanism of the reaction is as yet uncertain. In some cases it appears to be intermolecular and in others intramolecular. A diradical mechanism has been proposed and also an ionic mechanism has been suggested. By using flash photolysis it should be possible to determine whether the intermediate is ionic or radical. Several cases of the rearrangement will be studied, and it is hoped that a comprehensive mechanism can be formulated. (C. E. Kalmus and D. M. Hercules)

IV. Chemiluminescence of Electron-Transfer Reactions

Much of the progress achieved since December 1965 is reported in the preliminary note of D. M. Hercules and F. E. Lytle, *J. Am. Chem. Soc.* **88**, 4745 (1966). Two records of invention have been filed with the Atomic Energy Commission Patent Branch. Currently a patent application is being drafted for one of the inventions.

Research since publication of the above note has pertained to stopped-flow kinetics. The instrument which has been constructed is described in the Progress Report of Edward Cutler. A computer program has been written to analyze the stopped-flow chemiluminescence profiles as a function of reaction kinetics. The object of the program is to identify the mechanism of an experimental reaction by the controlled simulation of a kinetic scheme utilizing digital computing techniques. Other information created by the program are rate constants, concentrations as a function of time and the derivative of the concentrations as a function of time. Necessary experimental data are one or more curves of concentration as a function of time, initial concentrations and initial rate constants.

Currently the program is being used to determine the experimental conditions necessary to build a chemical laser from a chemiluminescent reduction-reaction, in solution. (F. E. Lytle and D. M. Hercules)

V. Chemiluminescence of Lucigenin

Lucigenin (I) has long been known to give an intense chemiluminescence when reacted with H_2O_2 in basic solutions. When water is used as the solvent at room temperature the emission is green and peaks at about $480 \text{ m}\mu$. If, however, the temperature is raised to around 50°C or mixed solvent systems are used, the emission is blue and peaks at about $440 \text{ m}\mu$. The emitting species in the "blue" reaction has been identified as N-methyl acridone.

(1)

An attempt has been made to identify the reaction products of the aqueous (Green) lucigenin chemiluminescence. The separation of these products by gas chromatography has proven extremely difficult. Separation of products has been accomplished by employing column chromatography on silica gel. The presence of at least five fluorescing species has been observed after total consumption of lucigenin by H_2O_2 . The major product of this reaction is N-methyl acridone. Work on identification of these products is continuing.

It has recently been reported (1) that N-methyl acridone ketyl reacts with benzoyl peroxide in non-aqueous solvents to give a luminescence characteristic of N-methyl acridone's fluorescence. Since it was known that N-methyl acridone is the emitting species in the "blue" lucigenin reaction, the possibility of this ketyl being an intermediate in the lucigenin reaction was studied. N-methyl acridone ketyl was found not to give light when reacted with H_2O_2 under the conditions of lucigenin chemiluminescence. However, it was noted that benzophenone ketyl reacts with benzoyl peroxide in anhydrous ether to give a weak luminescence. Further work has not been done on this system.

The electrochemical behavior of lucigenin has been studied in both aqueous and non-aqueous media using cyclic voltammetry at platinum electrodes. It was noted that in aqueous media lucigenin was irreversibly reduced and that the reduction product remained on the electrode surface due to its insolubility in water. The potential of lucigenin reduction was found to be independent of pH. The reduction product on the electrode was washed with distilled water and dissolved in benzene. The absorption and fluorescence spectra of this solution correspond exactly to those reported in the literature of dimethyl biacridene (II). This compound was prepared by zinc reduction in glacial acetic acid according to the method of Decker and Petsch (2). The spectra obtained for the product of the zinc reduction were identical to those obtained for the electrochemically generated product.

1. E. A. Chandross and F. I. Sontag, J. Am. Chem. Soc. 88, 1089 (1966).
2. H. Decker and W. Petsch, J. Prakt. Chem. 143, 211 (1935).

(II)

It has been postulated (1) that the initial step of the lucigenin chemiluminescence is a reduction of lucigenin by H_2O_2 to dimethyl biacridene and subsequent oxidation of dimethyl biacridene to the emitting species. The electrochemical data of Figure 2.1 show this to be impossible. Here oxygen is reduced to HO_2^- (which is then probably reduced further to OH^- at nearly the same potential) at a peak potential of -0.28V . Lucigenin is reduced to dimethyl biacridene at $-.47\text{V}$. Clearly, in basic solutions, H_2O_2 cannot reduce lucigenin to dimethyl biacridene.

It has been reported (2) that a basic solution of lucigenin when electrolyzed gave light at the cathode. This experiment could not be reproduced. It seems unlikely that the previously observed luminescence was due to electrogenerated H_2O_2 as in basic media O_2 is reduced essentially completely to OH^- instead of HO_2^- . Up to two volts cathodic potential was applied to the electrode and no light was observed. Switching back and forth from anodic to cathodic potentials and the addition of mixed solvents in an attempt to dissolve the very insoluble dimethyl biacridene did not result in any visible luminescence. (K. D. Legg and D. M. Hercules)

Figure 2.1

1. J. R. Totter, Photochem. and Photobiol. 5, 177 (1966).
2. B. Tamamushi and H. Akiyama, Trans. Faraday Soc. 35, 491 (1939).

VI. Chemiluminescence of Luminol

This is a continuation of the Progress Report covering the same project for the period 1 May 1965 - 30 April, 1966.

Studies on the absorption and fluorescence of 3-amino phthalate (3APA) have been continued in the pH range 1.0 - 13.0. The solutions were buffered with acetate or bicarbonate buffers and the pH's were adjusted with HCl or NaOH. The absorption spectrum at pH = 1.0 shows a small band at 275 m μ and a larger band at 329 m μ . Upon increasing the pH, the 275 m μ band decreases in intensity and the 329 m μ band increases at about pH = 3.0, the 275 m μ band is completely gone and the 329 m μ band begins to shift to shorter wavelengths. At pH = 6.0 the band has shifted to 304 m μ and remains there as the pH is increased to 13.0.

These are reasonable values to expect for 3-APA, since the literature reports the pKa's of phthalic acid as 2.95 and 5.41. (1)

The fluorescence spectra showed an increase in intensity and a shift in λ_{max} from 458 m μ to 424 m μ as the pH was increased to about pH = 6.0. The λ_{max} remained at 424 m μ and the intensity leveled off at higher pH values. The $\lambda_{\text{max}} = 424 \text{ m}\mu$ is in agreement with the luminol CL which is observed in basic solution.

White and Bursey (2) have observed the fluorescence peak at 424 m μ in water and at 485 m μ in dimethyl sulfoxide (DMSO). In mixed DMSO-H₂O solvents they observed two peaks which increased or decreased in intensity as the mole percent DMSO-H₂O was varied. They made this observation in the CL spectrum of luminol as well as in the fluorescence spectrum of 3-APA and attributed the occurrence of the two emission peaks to the formation of two different kinds of excited state molecules: an amino phthalate ion hydrogen bonded to water (424 m μ) and an excited amino phthalate ion not bonded in this way (485 m μ).

The absorption and fluorescence spectra in pure DMSO have been obtained. The absorption spectrum shows a broad band at 342 m μ and the fluorescence peak occurs at 442 m μ . A solution of 3-APA in DMSO with potassium t-butoxide added shows strong absorption at 314 m μ , and the fluorescence peak is at 480 m μ , as reported by White and Bursey.

1. Huntress, E. H., Stanley, L.W., and Parker, A.S., J. Am. Chem. Soc. 56, 241 (1934).
2. White, E. H., and Bursey, M. M., J. Am. Chem. Soc. 86, 941-42 (1964).

The reason that the CL reaction mechanism for luminol is different in DMSO and water could be due to the fact that there is a tautomeric equilibrium and in each solvent one of the tautomeric forms of luminol predominates. The following is proposed:

A DMSO-H₂O mixed solvent study was done to see if the luminol did exist in these different forms. Solutions of the mono sodium salt of luminol were prepared using mixed solvents of the following compositions: 100%, 70%, 40%, 10%, 2%, 1%, 0.4% and 0.05% (pure DMSO) H₂O. Some of the absorption spectra (uncorrected for solvent shifts) for these mixed solvents are shown in Figure 2.2. The absorption spectrum of the luminol sodium salt in H₂O is quite different than that in DMSO and indicates that one does have different species in each solvent. However, the spectra do not definitely rule out hydrogen bonding as the reason for the different spectra and different mechanisms.

In order to support the above ultra-violet absorption data, infrared absorption spectra of the luminol mono sodium salt were taken in a number of solvents and the hydroxyl and carbonyl regions were examined. Unfortunately, the luminol salt is not very soluble in useful infrared solvents, and the absorption was not strong enough to confirm or reject the presence of the postulated tautomeric species.

A stop-flow kinetic apparatus has been constructed which will permit investigation of the kinetics of the CL reaction of luminol in DMSO. The decay curves of the CL will be recorded as a function of luminol, O₂ and potassium-*t*-butoxide concentrations in order to provide some new information concerning the reaction mechanism. Decay curves will also be examined for the CL reaction in DMSO-H₂O mixed solvents.

In the future a study will be made of the absorption and fluorescence spectra of 3-APA in mixed DMSO-H₂O solvents. In addition to a study of the kinetics of luminol, the kinetics of a few derivatives of luminol will probably be investigated in DMSO along with a look at the kinetics of the persulfate-luminol CL reaction (1).

It will also be important to measure the quantum efficiency of 3-APA and the photon efficiency of the luminol CL reaction. Energy transfer in the luminol CL reaction mechanism has been suggested, so a study will be made to determine if true energy transfer from 3-APA is occurring. This will involve consideration of transfer from the singlet and triplet states of 3-APA.

1. Rauhut, M. M. Semsel, A. M., Roberts, B.G., J. Org. Chem. 31, 2431 (1966).

Figure 2.2

Figure 2.3

Fluorescence lifetimes will be measured, and the quenching of 3-APA fluorescence by a variety of species will be studied. (J. D. Gorsuch and D. M. Hercules)

VII. Chemiluminescence and Energy Transfer

Chemiluminescence has been observed in the autoxidation reactions of hydrocarbons^(1,2), thermal decomposition of peroxides and hydroperoxides in solution^(3,4), and thermal decomposition of peroxides with possible energy acceptors (fluorescent molecules) present.

Kurtz⁽⁵⁾ has reported chemiluminescence from a system consisting of dibenzaldiperoxide and a fluorescent aromatic compound (i. e., anthracene, violanthrone) in paraffin solvent. Upon addition of the peroxide to a solution of violanthrone at a temperature exceeding the decomposition point of the peroxide (200°C), bright red chemiluminescence is observed. Kurtz proposes a mechanism involving a transannular bridged peroxide

Kasha⁽⁶⁾ has proposed a general theory for chemiluminescence in systems capable of evolving oxygen (thus, peroxidic systems). Energy transfer is thought to occur from excited oxygen molecular pairs ($[^1\Delta_g^+ + ^1\Sigma_g^+]$) at 60kcal/mole and $2[^1\Sigma_g^+]$ at 75kcal/mole to available fluorescent acceptors. Due to the low probability of formation of such excited oxygen molecular pairs the mechanism is characterized by extremely low quantum yields.

The purpose of this work is to study chemiluminescence from thermal decomposition of peroxides with possible energy acceptors present. The dibenzaldiperoxide-violanthrone system was chosen to be studied first.

Work up to the present has been concerned with the preparation and purification of starting compounds (the peroxide and aromatic fluorescers), design and construction of necessary instrumentation, and kinetic analysis of the decomposition of dibenzaldiperoxide.

An apparatus for measurement of chemiluminescent intensity versus temperature was recently completed, as shown in Figure 2.3. A DTA cell is used as the reaction compartment.

1. Vasil'ev, Doklady Akademii Nauk SSSR, 144, No. 1, 143-6 (May 1962).
2. Vasil'ev and Rusina, Doklady Akademii Nauk, SSSR, 156, 6, 1402-5 (June 1964).
3. Lloyd, Trans. Far. Soc., 61, 2173-93 (1965).
4. Bowen and Lloyd, Proc. Roy. Soc. A, 1963, 275, 465.
5. Kurtz, Ann. N.Y. Acad. Sci. 16, 399 (1954).
6. Kasha, J. Am. Chem. Soc. 88:7, 1574 (1966).

The reaction occurs in a glass capillary inserted in the heating block. A thermocouple in the heating block is led into an F and M temperature programmer which controls the block temperature. A second thermocouple in the heating block is led through a cold junction thermocouple, into an amplifier and then to the x-axis of a recorder (thus temperature is the x-axis of our plot). Light from the reaction is monitored by a photomultiplier tube. The signal is led into a cathode follower and then to the y-axis of the recorder. Thus a plot of I versus T is obtained.

To specify the energetics of the aromatic compounds used in energy transfer systems (i.e., violanthrone), full spectral analysis is required. The quantities necessary to characterize a luminescent compound are lifetime of the excited state, the absorption, fluorescence and phosphorescence spectra, and quantum yields of both fluorescence and phosphorescence. Instrumentation for absorption, fluorescence and phosphorescence spectra are available in the analytical laboratory. Other members of Prof. Hercules's group are currently at work on lifetime instrumentation. It was my task to work on Fluorescence quantum yield determinations (quantum yield is the ratio of photons emitted to photons absorbed). The Turner 210 "Absolute" Spectrofluorometer was used. This allows determination of the quantum yield through comparison of the fluorescence spectra of an unknown compound versus that of a compound of known quantum yield.⁽¹⁾ Since the Turner has just been marketed, it had to be tested. Quantum yields for fluorescein, anthracene, diphenylanthracene and perylene gave results reproducible to better than 5% and agreed with 10% (considered good) with values reported in the literature.

Work was begun on the chemiluminescent system of dibenzaldiperoxide and violanthrone. Qualitative experiments were done to test our proposed theory of energy transfer from an excited state formed by the decomposition of the peroxide to an aromatic acceptor. For example:

In diethylene glycol solutions of various aromatic fluorescent acceptors (5 mg in 10 ml) heated to 200°C, dibenzaldiperoxide (5 mg) was added and chemiluminescence was observed visually. The experiments were done in a completely darkened room, the observer dark-adapting his eyes for half an hour (a crucial point since upon 10 minute dark-adaptation, no CL was observed for systems that clearly chemiluminesced upon half-hour adaption). A summary of the results follows:

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7. Turner, Science 146, 183 (1964).

Acceptor	CL	E_S	E_T
violanthrone	bright red, 50 sec.	47	--
benzanthrone	bright green, 20 sec.	73	41.4 ϕCHO $E_S = 76$ Kcal/mole
rubrene	bright, 40 sec.	55	--
coronene	bright, 75 sec.	70	55 $E_T = 72$
9,10-DPA	bright 20 sec.	72.7	--
anthracene	bright, 80 sec.	74.5	42.5 ϕCOOH $E_S = 74$
fluorescein	bright, 20 sec.	57	51
fluorescer #1	bright 65 sec.	84.5	-- $E_T = 69$
fluorescer #2	weak, 20 sec.	62	--
fluorescer #3	weak, 10 sec.	76.4	-- O_2 levels (Kasha)
phenanthrene	bright, 90 sec.	83	62 $2 [^1\Sigma_g^+] 75$
naphthacene	bright, 55 sec.	59.5	29 $[^1\Delta_g^+ + ^1\Sigma_g^+] 60$

Where the color of chemiluminescence is not reported, this is because the eye could not distinguish a color. In all cases, the fluorescence of the solution before and after peroxide addition was the same (therefore, the acceptor didn't undergo rearrangement, dimerization, etc.) Where E_T is left blank, this is because no phosphorescence has been observed for the molecule.

The results contradict a bridged peroxide mechanism. Molecules such as

coronene

and fluorescein are not

expected for form bridged peroxides. The results do favor energy transfer from the excited state benzaldehyde to the acceptor.

To establish which state of the acceptor (singlet or triplet) is emitting, a spectrograph must be used. The donor in energy transfer is probably benzaldehyde and the state involved, a triplet. Benzaldehyde is a highly efficient phosphorescer and the triplet state with its long lifetime relative to the singlet (usually 10^{-3} to 10 sec vs 10^{-6} to 10^{-9} sec) favors transfer from the triplet.

Present work will also be concerned with the study of the effect of oxygen on the chemiluminescence (oxygen quenches triplets) and kinetic analysis of the system.

Kinetic studies of the decomposition of dibenzaldiperoxide were performed. Dibenzaldiperoxide was dissolved in refluxing isopropylbenzene ($T=153^\circ\text{C}$, added 0.8 g peroxide to 100 ml solvent). Aliquots were taken in 15 minute intervals, and peroxide decomposition was followed iodometrically and by gas chromatography.

Log C vs time plots for benzaldehyde appearance and peroxide disappearance were linear, indicating first-order kinetics, as expected. The respective rate constants (slope of the graphs) were

$$k_1 \text{ (for peroxide disappearance)} = 4.0 \times 10^{-5} \text{ sec}^{-1}$$

$$k_2 \text{ (for benzaldehyde appearance)} = 6.8 \times 10^{-5} \text{ sec}^{-1}$$

Ideally k_2 should be twice k_1 . However, it would be expected to be low due to decomposition of some benzaldehyde at 153°C. Future studies on this decomposition will be done.

Comparison of the peroxide decomposition rate with light emission rate is also planned.
(S. R. Abbott and D. M. Hercules)

VIII. Chemiluminescence of Grignard Reagents

The reaction of various organo-magnesium halides with oxygen is accompanied by a faint chemiluminescence. At concentrations of 1/8 Molar to 1.5 molar in ether solution the light emitted is reported to be green or blue in color -- depending on the organic moiety -- and is brighter for aryl compounds than for alkyl compounds (1,2,3). Of these, phenyl magnesium bromide and para-chloro phenyl magnesium bromide are two of the brightest and this report describes a study of their chemiluminescence.

Determination of the identity of the molecule emitting light during the reaction is a key step in investigating the reaction mechanism. For such a molecule, radiational deactivation of an excited state is preferred and a search must first be made for highly fluorescent compounds among the reaction products. The matching of a molecule's fluorescence spectrum with the chemiluminescence spectrum of the reaction would confirm it as the emitter.

Approximately 1 molar solutions of phenyl magnesium bromide and para-chloro phenyl magnesium bromide in (a) diethyl ether; (b) di n-butyl ether and (c) triethylamine were prepared under nitrogen atmospheres by conventional methods. The resulting orange solutions gave a bluish chemiluminescence with oxygen, visible only in a darkened room. The solutions resulting from oxidation of phenyl magnesium bromide in dibutyl ether and in triethylamine were analyzed in the following manner. Samples of each were hydrolyzed with dilute hydrochloric acid and the residual magnesium salts were removed by extraction with water. The non-aqueous layers were separated and dried over anhydrous magnesium sulphate. Fluorescence spectra taken of all the diluted reaction product solutions before and after hydrolysis on the Turner 210 spectrofluorometer were identical. Gas chromatographic analysis of the product solutions gave complex chromatograms indicating reaction with the solvent but the peaks corresponding to very high-boiling fractions were independent of the solvent used and unaffected by the hydrolysis.

These fractions were isolated by preparative gas chromatography and of the fluorescence spectra taken of the fractions in n-butyl ether, one matched the fluorescence spectrum of the original product solution. About 5 milligrams of this fraction was separated and it was identified as para terphenyl

by infra-red, ultra-violet and mass spectroscopy

1. R. T. Dufford, D. Nightingale and S. Calvert, J. Am. Chem. Soc. 45, 2058 (1923).
2. W. V. Evans and R. T. Dufford, J. Am. Chem. Soc. 45, 278 (1923).
3. W. V. Evans and E. M. Diepenhorst, J. Am. Chem. Soc. 48, 715 (1926).

and melting-point (213°C) and by comparison with a known, pure sample.

The only chemiluminescence spectra published for oxidation of Grignard reagents were taken using 1 molar solutions of reactants (1, 2). At this concentration reabsorption of the emitted radiation could cause a pronounced red shift of the luminescence spectrum. To obtain accurate spectra, the dilute solutions required were prepared by direct dilution of the 1 molar grignards using very pure solvents.

An instrument was constructed to determine the spectrum of low intensity or fluctuating luminescent emissions (Fig. 2.4). The light path between a chemiluminescence cell and a Bausch and Lomb grating monochromator was interrupted by a thin transparent quartz plate, held at 45° to the incident light so as to deflect a fixed proportion of it at a right angle. An RCA 1P21 photomultiplier placed in the path of the deflected light monitored the intensity of light emitted from the chemiluminescence cell. Light emerging from the monochromator exit slit was measured by a similar photomultiplier.

Figure 2.4

Photons striking the photomultiplier cathode produce individual anode pulses lasting 10 nanoseconds. The pulses were amplified by a cathode-follower pre-amplifier circuit with a 10 nanosecond time constant and counted by feeding the output to EKCO N530F and Baird-Atomic 132 automatic scalars. The rate of counting observed should be proportional to the rate of photon impingement on the photomultiplier.

With the monochromator set at a wavelength λ , the luminescent reaction was run for 100 seconds with both photomultipliers counter readings and a point on the spectrum recorded as the fraction of emitted light detected at wavelength λ : $\left[\frac{\text{Monochromator PM counts}}{\text{Deflector PM counts}} \right]$.

This procedure repeated for different wavelengths without altering the position of the luminescence cell enabled a spectrum to be built up. Individual points recorded were, however, subject to statistical errors resulting from the random spacing of the photomultiplier output pulses. To obtain a smooth spectrum a large number of points were determined and the best line drawn through

1. W. V. Evans and E. M. Diepenhorst, J. Am. Chem. Soc. 48, 715 (1926).

2. R. T. Dufford, D. Nightingale and S. Calvert, J. Optical Soc. America 9, 405 (1924).

them. Fluorescence spectra were also taken by illuminating a square cell at 90 degrees to the path of the emission detection system. The resultant spectra are not corrected for monochromator transmission efficiency and photomultiplier spectral response.

A comparison of the para terphenyl fluorescence spectrum and phenyl magnesium bromide chemiluminescence spectrum taken with this spectrometer is shown in Figure 2.5. The observed red shift of the chemiluminescence spectrum might be expected if the Grignard solution had a strong absorption band just below 360 m μ . Work is in progress to check this absorption and to identify the emitting molecule in the para-chloro magnesium bromide reaction. (R. L. Bardsley and D. M. Hercules)

Figure 2.5

IX. Chemiluminescence of Tetrakis(Dimethylamino)-Ethylene

Urry and Sheeto (1), J. P. Paris (2), and Fletcher and Heller (3), have proposed three different reaction mechanisms to predict the behavior of oxidizing tetrakis-dimethylamino ethylene (TDAE). (4) Work in this laboratory is intended to test these proposals by analysis of data obtained from stopped-flow reaction kinetics studies. Such an approach makes possible more precise observation of the TDAE oxidation than that of the previous investigations. Time-dependent chemiluminescence and fluorescence will be observed with the stopped-flow apparatus. Thus, the existence of possible transient states may be detected.

1. W. H. Urry and J. Sheeto, *Photochem. Photobiol.* **4**, 1067 (1965).
2. J. P. Paris, *Photochem. Photobiol.* **4**, 1059 (1965).
3. A. Fletcher and C. Heller, NAVWEPS Report 9055, April, 1966.
4. TDAE was first synthesized by R. Pruett, J. Barr, K. Rapp, C. Bahner, J. Gibson, and R. Lafferty, Jr., *Amer. Chem. Soc. J.* **72**, 3646 (1950). An entirely different method is offered by A. Weingarten and W. White, *J. Org. Chem.* **31**, 3427 (1966).

Laboratory work to date has accomplished:

- (1) Assembly of a stopped-flow reaction kinetics apparatus.
- (2) Construction of a vacuum distillation apparatus (part of a scheme to purify TDAE after filtering through anhydrous aluminum oxide).
- (3) Setting up a glove bag and dry box for work with TDAE in a dry, oxygen-free atmosphere.
- (4) Planning an all-glass TDAE purification system which can be used outside a glove bag or dry box.
- (5) Performance of experiments to learn about TDAE's properties and oxidation mechanism, qualitatively.

The stopped-flow apparatus consists of a syringe pump which pushes two syringes of 50 ml or 100 ml capacity at any one of 12 selected rates. The syringe pushing block is stopped at a preset point by means of two brass bars on either side of the apparatus. The reactants flow at a known rate from both syringes into a T-shaped mixing chamber made of about 2 mm i.d. pyrex capillary. Three pieces of 80 mesh platinum gauze have been sealed into the mixer where the solutions meet to improve mixing efficiency (one piece at each inlet and one at the outlet). The mixed fluids flow down the exit tube to a receiving syringe, from which they are later expelled as waste. The capillary mixer is thoroughly covered with black electrical tape, except for a tiny slit of about 1 mm² area about a centimeter beyond the place where mixing begins. A 1P21 photomultiplier tube is placed about a centimeter away from the slit to detect chemiluminescence. The appropriately amplified signal from the photomultiplier is displayed on an oscilloscope whose trace is triggered by the stopping of the syringe pushing block. A Polaroid picture is taken of the oscilloscope trace; thus giving a permanent record of relative chemiluminescent light intensity versus time.

Qualitative experiments have yielded the following results:

- (a) The following solvents do not allow the greenish-blue chemiluminescence of TDAE during air oxidation: dimethyl sulfoxide, chloroform, carbon tetrachloride (forms a bright red solution) monobromo benzene, diphenyl ether, and acetone. The following solvents do allow chemiluminescence during TDAE air oxidation: fluorocarbon polymer liquids, aqueous ammonia (12M), triethylamine, cyclohexane, and n-hexane. Other solvents have been (1,2,3) and will be tested.
- (b) TDAE glows when air oxidized over 12 M aqueous ammonia, but the glow dies out more quickly (and is of a different color) than TDAE oxidized over water. TDAE exposed to air over citric acid solution oxidizes much more rapidly than over neutral water. (The glow continues for 10 minutes or so after a bottle of TDAE over water has been opened to the air and then closed. The glow dies away in about a minute over citric acid.) TDAE reacts instantly with pure formic acid with transient production of a dark brown solution

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1. See ref. 2, previous page.
  2. See ref. 3, previous page.
  3. See ref. 4, previous page.

which quickly clears (if excess acid is present), but no chemiluminescence is observed. With excess of TDAE, the dark brown solution remains colored for days in the open air. (c) TDAE has been made to glow by air oxidation (liquid phase) and ultraviolet illumination and radio frequency discharge (liquid and vapor phase). All three methods of excitation appear to be equally effective in producing the same color and intensity of light. (E. T. Cutler and D. M. Hercules)

X. Efficiency of Electroluminescence from Organic Redox Reactions

Luminescence resulting from the overall electron transfer reaction $R^+ + R^- \rightarrow 2R + h\nu$ where R is an aromatic hydrocarbon, R^+ is the radical cation and R^- is the radical anion, has been investigated in this group during the past two years. The intermediate steps which might occur have been discussed but methods for differentiating between them have not been worked out as yet. One possibility is the measurement of the currents for the electrochemical generation of first one radical, then the other and simultaneously measure the luminescence-time curve. In principle, these data contain information about the amount of reactants formed and therefore the total possible light energy if the reactants diffused together, to form neutral species and luminescence. The measured light intensity then can be used to assign an efficiency figure, ϕ_e , to the reaction and comparison can be made with efficiency of fluorescence ϕ_f . Indications of intermediate steps would be obtained if, for example, it was found that ϕ_e was $1/2 \phi_f$. This value would be consistent with triplet intermediates, R_T^* , viz.:

If ϕ_e is greater than $1/2 \phi_f$, then direct formation of singlet states, R_S^* , is indicated.

The problem to be solved first was the rate of diffusional mixing of R^+ and R^- when they are sequentially produced at the same electrode. Direct solution of Fick's laws in closed form is not possible. The problem was discussed with Dr. Steven Feldberg of Brookhaven National Laboratories, since he had developed a method to obtain empirical solutions to similar problems through machine calculations. He was able to solve the problem (1) and subsequent experiments have been performed here.

The model system for this type of measurement was found to be rubrene, dissolved in either dimethylformamide (DMF) or acetonitrile (AN) with tetrabutylammonium perchlorate as supporting electrolyte. In most respects, the experimental conditions were similar to those reported earlier, except that the photomultiplier tube was calibrated.

Some results, in terms of efficiencies, ϕ_e , are listed below along with values of ϕ_f as measured with the same solvents on the Turner spectrophotofluorometer.

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1. S. W. Feldberg, J. Am. Chem. Soc. 88, 390 (1966).

Solution	ϕ_f	ϕ_e
10^{-3} M Rubrene in DMF	0.41	0.28
10^{-4} Rubrene in AN	0.31	0.12

As might be expected, traces of oxygen quenched the fluorescence markedly. In addition, evidence was found for the involvement of impurities in the luminescence-producing reactions. Some light could be produced by generating R^+ and then switching the potential to a point where R^- was not formed, but where a small impurity reduction wave was recorded. (D. K. Roe and D. M. Hercules)

XI. Excimers in Electroluminescence

The main objective of this work is to correlate the electrochemiluminescence and photochemical behavior of anthracene and its 9- and 9,10- substituted derivatives. Specifically, the discrepancy in the ratio of excimer/monomer emission in the two processes and the relationship of excimer formation to photodimer formation will be investigated.

The acetonitrile was originally purified by a literature procedure (1). To this was added a spinning band column distillation from calcium hydride or magnesium sulphate. The final distillate had an absorbance of 0.1 at 200 m μ and greater than a four volt span electrochemically. On standing for a few days, even in a glove bag, the short wavelength absorbance increases noticeably. Because of the time involved in the purification and the short life time of the high purity final distillate, spectral grade acetonitrile was compared with the final distillate both spectrally and electrochemically. Matheson, Coleman and Bell spectral grade acetonitrile was found to favorably compare with the purified acetonitrile and was used without further purification for the work below.

TLC studies of 9-methylanthracene from James Hinton showed the presence of a minor component. Zone refining the 9-methylanthracene did not remove the impurity, probably because the low melting point (80°C) of 9-methylanthracene prevents efficient purification by this method.

One minor component was detected by TLC for 9-methylanthracene. This compound was synthesized last summer and purified by repeated crystallization from ethanol. Further purification by column chromatography using silica gel column and benzene as an eluent was unsuccessful. TLC showed that the minor component was still present when various fractions were collected and concentrated by solvent stripping.

The anthracene used in the work below was scintillation grade and was not subjected to further purification. The 9,10-dimethyl-anthracene, 9,10-diphenylanthracene and 9-phenyl-anthracene were taken straight from the Aldrich bottle while the 9,10-dimethoxyanthracene was

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1. Anal. Chem. 37, 1161 (1965).

zone refined. The 9-cyanoanthracene was synthesized (1) and recrystallized once from ligroin.

The photochemical reactor containing 350 mu lamps was used to photodimerize a 10^{-2} M solution of 9-methylanthracene in acetonitrile. The reaction vessel was a pyrex test tube which was deoxygenated by the freeze-thaw technique.

After photolyzing for 5.25 hours the solution was yellow and contained a white precipitate. A UV spectrum of the solution showed increased absorption in the 400-500 mu and 230-320 mu regions over that of pure 9-methylanthracene. The white precipitate was submitted for C-H analysis and the results were consistent with the expected values for the photodimer.

TLC studies on the yellow solution after the white precipitate had been removed were compared with TLC studies on the original 10^{-2} M 9-methylanthracene. This solution gave two spots, the photolyzed one gave four. The darkest spot on each plate had the same R_F value and can be concluded to be 9-methylanthracene. A UV spectrum showed the concentration of 9-methylanthracene remaining in the photolyzed solution to be about 10^{-4} M. Because of its slight solubility the concentration of the photodimer was considerably smaller than this.

The electrochemistry of anthracene and seven substituted anthracenes was investigated. Current-voltage curves were taken and light from plus-minus annihilation was observed for all eight compounds. All measurements were made in deoxygenated acetonitrile and are vs a Ag/AgBr reference electrode. A Wave-Tek generator supplied the square wave input needed for light observation. The table below summarizes the results.

Compound	Concentration	$E_p(\text{Red.})$	$E_p(\text{Oxid.})$	Condition of Light Obs.
Anthracene	1.44×10^{-3} M	-1.70	+1.50	R^+ to R^- , R^- to R^+
9-methylanthracene	1.2×10^{-3} M	-1.70	+1.43, +1.76	R^+ to R^- , R^- to R^+
9-methylanthroate	1.2×10^{-3} M	-1.35	+1.74	R^- to R^+ , see (i)
9,10-dimethylanthracene	1.1×10^{-3} M	-1.74	+1.36, +1.69	R^- to R^+ , R^+ to R^- (see ii)
9-phenylanthracene	1.3×10^{-3} M	-1.68	+1.53, +1.76	see (iii)
9-cyanoanthracene	1×10^{-3} M	-1.14	+1.89	see (iv)
9,10-diphenylanthracene	sat'd. $<10^{-3}$ M	-1.60	+1.56, +1.94	R^+ to R^- , R^- to R^+
9,10-dimethoxyanthracene	1×10^{-3} M	-1.66	+1.25	R^- to R^+

- (i) When R^- was generated and the potential switched to a point just before R^+ generation, no light was observed. This would rule out a solvent-radical reaction which would give the light.
- (ii) The light was brighter here than the previous cases and could be seen for sweep rates of 0.01, 0.1 and 1 c/sec. Normally, the 0.01 c/sec sweep rate was used in the light investigation.
- (iii) When switching from the reduction peak to the first oxidation peak and vice versa a bright blue flash could be seen at sweep rates up to 10 c/sec. When the potential sweep was increased to include the second oxidation peak, the light was observed only when the negative radical was generated first and the potential switched to that of the second oxidation peak.
- (iv) Light was observed only when the negative radical was generated and the potential switched to that of positive radical generation. Even in this case a ten minute dark-adapted eye was needed to observe the light.

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1. Helv. Chim. Acta. 2, 482 (1919).

An attempt was made to establish a relationship between dimer formation and electrochemiluminescence for 9-methylanthracene. This compound is known to form both excimers and stable photodimers under UV excitation. A 1.6×10^{-3} M solution of 9-methylanthracene in acetonitrile was subjected to a square wave input of sufficient amplitude to generate R^+ and R^- on alternate cycles. After four hours no solid dimer appeared in the solution, however, TLC plates showed four spots with R_F values similar to those obtained from TLC studies of a photolyzed solution of 9-methylanthracene. Thus, there appears to be some evidence of at least slight dimer formation during electrochemical annihilation.

A Zeiss three prism f6.3 spectrograph is being used in an attempt to obtain electrochemiluminescence spectra. The advantage of the spectrograph is that any intensity change in the light pulse will be integrated over the whole spectrum. Satisfactory fluorescence spectra were obtained on this instrument for exposures of 20 minutes to one hour. However, a preliminary 16 hour exposure of the unusually bright electrochemiluminescence of rubrene resulted in only a faint plate darkening. A larger electrode area and improved cell design and degassing technique will be necessary before a decision can be made on the feasibility of obtaining electrochemiluminescence spectra of anthracene derivatives. (T. C. Werner and D. M. Hercules)

XII. Electrochemiluminescence of Aromatic Hydrocarbons

Via

Homogeneous Electron Transfer Reactions

Chemiluminescence has been reported to occur upon mixing solutions of aromatic hydrocarbon cation radicals (R^+) and anion radicals (R^-) (J. Am. Chem. Soc. 88, 1089 (1966)). Similar luminescence has been observed from electrochemically generated hydrocarbon cation and anion species in aprotic solvents. In most cases, the emission has been attributed to a radical cation - radical anion annihilation reaction in the diffusion layer which leaves one of the product molecules in an excited state. (Reviewed in "Advances in Electroanalytical Chem." 1, 197 (1966)). The interaction of aromatic radical cations with electron donors other than the corresponding anion radical has been reported recently (J. Am. Chem. Soc. 88, 4578 (1966)). However, the electron donors used in those cases were considered to be relatively slow in electron transfer (e.g., H_2O , triethylamine, etc.). It is the purpose of this work to study the mechanism of the luminescence reaction from both the energetics of the reaction path and the possible side reactions which might involve light emission.

Acetonitrile (AN), Benzonitrile (BN), and Dimethyl formamide (DMF) have been further purified and thereby made to be more suitable for continued studies of electrochemiluminescence of both the rubrene cation and anion radical. The following table summarizes the potential range for which each solvent can be used.

Useful Potential Range of Solvents

	Anodic*	Cathodic*
CH ₃ CN	+2.0	-2.0
DMF	+1.4	-2.2
Benzonitrile (purified)	+1.6	-1.7
Benzonitrile (Spect.)	+1.7	-1.8

Potential Measured versus Ag/AgCl (0.1 N NaCl) aqueous reference electrode.

Matheson Coleman and Bell Spectrograde benzonitrile was found to compare favorably with the purified benzonitrile and was used without further purification. Benzonitrile also has the advantage of minimum water and maximum aromatic hydrocarbon solubility.

The spectrophotometric and electrochemical apparatus used have been previously reported by this laboratory. The electrochemiluminescence cell was constructed from a 1 cm square fluorescence cell with indicating electrode directly behind one face and inserted into the cell from the top. The counter electrode compartment was sealed on to the main stem as a side arm. The reference electrode compartment was sealed on to the main stem as a side arm. The reference electrode was brought directly behind the indicating electrode and extended above the fluorescence cell in order to minimize solution resistance. One tenth molar tetrabutyl ammonium perchlorate has been selected as supporting electrolyte (both tetrabutylammonium methane sulfonate and sodium perchlorate were tested for this purpose). Prepurified nitrogen was used to purge oxygen from the solvent. Chemiluminescence spectra were recorded by integrating electronically the output light pulses at different wavelength.

Current-voltage curves for the oxidation and reduction of rubrene have been recorded at various conditions. Both the oxidation and reduction process behave reversibly under cyclic voltammetric scan rate up to 0.4 v/sec. Light emission is observed when the rubrene system is scanned from +1.0 to -1.5 volts. Figure 2.6 shows the relative intensity versus various anodic potentials obtained when a square wave form is applied from -1.70v to various positive potentials in the reverse cycle. Very intense emission is observed on both anodic and cathodic cycles, if the positive step potential is more positive than $E_{1/2}$ for rubrene oxidation. However, as the potential is less anodic than the cation formation, a decrease in emission intensity was observed. The intensity of the light pulse decreases exponentially until -0.20 volt where no detectable emission was recorded under the optimum experimental condition. Similar emission is observed when the anodic potential of the potential step is fixed while the cathodic limit is varied. The exact mechanism of light emission over these wide potential ranges is as yet uncertain.

Figure 2.6

When an electron donor is added to a solution of rubrene in benzonitrile, light intensity is increased in the potential region where the electron donor is reduced to a radical. Several different donor-hydrocarbon and acceptor-hydrocarbon pairs have been studied and results are summarized in the table below. In all cases studied, the chemiluminescence observed is similar to that of hydrocarbon fluorescence. This indicates that the lowest excited singlet state of the aromatic hydrocarbon is the emitting species.

Energy of Electron Transfer Reactions

	$E_{1/2}R \rightarrow R^+$	$E_{1/2}R \rightarrow R^-$	$\Delta E_{1/2}(R^+ + R^-)$	$\Delta E_{1/2}(R^+ + D)$	$\Delta E_{1/2}(R^- + A)$	$E_{\text{singlet}}^{\text{ev}}$
Rubrene	+0.88	-1.47	2.35	1.60	1.63	2.39
9,10diphenyl Anthracene	+1.32	-1.72	3.04	2.04	--	2.85
9,10dimethyl Anthracene	+1.16	-1.82	3.02	1.88	--	3.05
Tetracene	+0.83	-1.55	2.48	1.64	1.71 ³	2.58
Naphtho-quinone D ¹	--	-0.72	--	--	--	--
<chem>CN(C)c1ccc(N(C)C)cc1</chem> +0.16	--	--	--	--	--	--

1. p-benzoquinone (-0.60v), anthraquinone (-0.80) are also used as donors.

2. p-phenylene diamine is also used as acceptor.

3. data abstracted from flow experiment performed in Prof. A. Weller's laboratory.

Columns 1 and 2 give the $E_1/2$ of $R \rightarrow R^+$ and $R \rightarrow R^-$ couples. Column 3 gives the free energy of reaction between R^+ and R^- in electron volts. If the entropy change for the reaction is neglected ($T\Delta S$ has been estimated to be about 0.2 ev), then column 3 represents the total energy available to form an excited state molecule. Column 6 lists the singlet excited state energy level for each hydrocarbon used. It is clear that the energy released from the cation-anion annihilation reaction is not sufficient but very close to the promotion energy required to excite the hydrocarbon molecule to the lowest singlet state. Columns 4 and 5 give the energy available if the reaction between R^+ and donor or R^- and acceptor is considered. In all these cases, the energy of reaction is much less than the excitation energy, however chemiluminescence from the first excited singlet state is observed. It is necessary to account for the emission from the singlet state by a bimolecular process which is sufficiently energetic to leave a molecule in the lowest excited singlet state. It is possible that the lowest excited triplet state is responsible for this bimolecular process as previously commented by Professor Hoijsink (Symposium on Chemiluminescence, Durham, N.C., 1965); however, direct evidence for the triplet-triplet annihilation is still not available at present. (J. C. M. Chang, D. K. Roe, and D. M. Hercules)

XIII. Photochemical and Electrochemical Studies of Phenazine

The photochemistry of phenazine (P) has been studied by several workers who reported that during the course of reduction to 9,10 dihydrophenazine (PH_2) violet and blue species were found (1,2,3). Other workers studied this system further by flash photolysis (4) and by ESR (5). The present study is an extension of earlier studies on photo-induced luminescence and photo-voltaic effects (6).

Most of the work to date has involved gathering electrochemical data. At a spherical platinum electrode in 0.1 M NaCl, 0.1 M Acetic acid, and 0.1 M Sodium Acetate in methanol, phenazine exhibits a two-electron reduction wave ($E_p - 0.45$ V vs Ag/AgCl). The anodic wave in the course sweep appears at -0.13V, a separation of ca. 320 mV. Polarograms at the dropping mercury electrode show $E_1/2 - 0.25$ V and a diffusion coefficient of 3.4×10^{-6} cm²sec⁻¹ as calculated from the simple Ilkovic equation using measured values for m , n , and t .

In 0.1 M HCl, 0.1 M NaCl in methanol, two reduction waves were found. The first appears at +0.25V and has been shown by coulometry to be a one-electron reduction. Preparative electrolysis at +0.1V produces a relatively air-stable green species believed to be PH_2^+ . PH_2^+ undergoes a further one-electron reduction to an almost colorless substance ($E_p - 0.1$ V) (all

1. Ch. Dufraisse, A. Etienne and E. Toromanoff, *Compt. rend.* **235**, 759 (1952).
2. E. Toromanoff, *Ann. de Chim.* (13^e) **1**, 115 (1956).
3. A. Claus, *Lieb. Ann.* **1**, 168 (1873)
4. A. V. Buettner, Ph.D. Thesis, U. of Minnesota, 1962.
5. K. H. Hauser, A. Habich and V. Franzen, *Zeit. fur Naturforsch* **16a**, 836 (1961); D. W. Schiesser and P. Zvirblis, *J. Chem. Phys.* **36**, 2237 (1962); L. D. Tuck and D. W. Schiesser, *J. Phys. Chem.* **66**, 937 (1962).
6. J. J. Surash, Ph.D. Thesis, Lehigh U., 1960.

potentials vs Ag/AgCl/ 0.12 M NaCl in MeOH). A UV-VIS spectrum of PH_2^+ has been obtained and ESR data will shortly be obtained to confirm its existence.

When an attempt was made to determine the pH dependence of the reduction wave at +0.25V, a third wave appeared at +0.1V. Since the only practical way of raising the pH in this region was to lower the concentration of HCl, this third wave (+0.1V), which appeared at the expense of the wave at +0.25V was at first thought to be due to insufficient buffering of the solution. However, when the concentration of phenazine was reduced 10-fold to raise the buffer:phenazine ratio, this same effect was noted.

It is also known that both reduction waves (i. e., +0.25V and +0.1V) produce the same eventual product because the return anodic is the same for both cases and is almost pH invariant. Since this pH region in question is very near the pKa of phenazine as determined by titration in the same medium, and since proton exchange ($\text{P} + \text{HA} \rightarrow \text{PH}^+ + \text{A}^-$) is probably slow then this behavior may be explained on the basis of two different electrode reactions:

Some work has also been done in non-protonic solvents such as acetonitrile (AN) and dimethyl-formamide (DMF). In AN, containing only tetra-n-butyl ammonium perchlorate as electrolyte, phenazine shows a reduction wave at ca. -1.0V. This wave is extremely irreversible, its corresponding oxidation wave occurs at +0.1V. This behavior was explained as lack of available protons since a similar situation occurs in unbuffered methanol. Reduction in DMF at -1.2V proceeds to a violet species which is stable only in the vicinity of the electrode. Although attempts have been made to generate this species in the bulk of the solution, they have not yet been successful, possibly due to traces of oxygen and/or water in the solvent.

Progress in the photochemical reduction has consisted mainly of gathering together and setting up apparatus for the observation of the photochemical reaction. In methanol 0.1 M HCl, 0.1 M NaCl and 10^{-4} M P, the solution turns dark green (PH_2^+ ?) almost immediately upon exposure to 3650 Å radiation in a photochemical reaction. Upon long exposure (48 hr) the solution turns from dark green to a much darker yellow-orange. The yellow-orange color is also produced when a methanol solution of P containing 0.1 M acetic acid and 0.1 M NaCl is exposed for a long time to this same radiation. In both cases the solutions were contained in Pyrex vessels and no attempt deaeration was made. (D. N. Bailey, D. K. Roe, and D. M. Hercules)

XIV. Analysis of Surface Adsorbed Oxygen on Solid Electrodes

In review, this research has been undertaken in order to determine the amount of oxygen bound to a pretreated platinum surface and the effect of this oxygen on electrochemical processes at the electrode. Consequently a platinum indicator electrode is to be prepolarized in various ways, removed from solution, placed in a vacuum system, and heated electrically. This heat treatment will liberate surface oxygen, thereby allowing the quantity of liberated gas to be

measured mass spectrometrically. In this case an omegatron is to be employed as an oxygen partial pressure transducer.

During the previous year, attention has been devoted to the design of the apparatus necessary to make these measurements -- primarily the vacuum system which contains the omegatron and cell. Although some vacuum problems have not yet been solved, a compact system has been constructed which is capable of being evacuated to 10^{-7} torr and which can be sealed from the pumps by a bellows valve for prolonged periods of time (at least twenty-four hours) without allowing the pressure to rise above 5×10^{-5} torr. However, when a platinum electrode is heated in this system, the pressure inevitably rises to at least 10^{-4} torr. At these pressures the filament of the omegatron can easily burn out; therefore, a method of working at higher vacuums needs to be employed.

For this purpose a method of dilution has been initiated. This method involves liberating all volatile materials from the electrode surface into the closed vacuum system, then sealing a portion of this gas in the cell compartment by closing the cell valve, pumping away the excess gas remaining in the main manifold, and finally opening the cell valve to allow this small representative sample to escape into the sealed manifold. Preliminary experiments have shown that even with this dilution the final operating pressure is in the 5×10^{-5} to 5×10^{-4} torr range. At these pressures the lifetime of the tube is seriously reduced. Technological problems prohibit either increasing the volume of the main system or decreasing the size of the electrode in order to obtain further dilution. Alternatively, continuous leakage of the evolved gas into the omegatron chamber itself as suggested by Zdanuk (1), would allow quantitative measurements to be made at about 5×10^{-6} torr. A design of this type is now being considered, since only minor alterations of the present system will be necessary.

Cell construction has been solved by placing a small coating of epoxy around the platinum-to-glass seal. This was found necessary because the high currents needed to heat the electrode dictate using platinum wire which cannot be sealed properly to pyrex. Although soft glass seals are adequate, the ease of construction and low expense of the pyrex cell seems to warrant its use. The epoxy never contacts the electrochemical solution; therefore, organic contamination from this source does not occur.

In spite of the fact that no quantitative data on the amount of liberated oxygen has been collected, indicative readings with a cold cathode gauge have shown that pressure differences after heating a platinum electrode are dependent on the history of the electrode. An electrode was heated in vacuum for one minute and then anodized in 0.74 N HClO_4 in order to deposit oxygen, dried in a low vacuum system, and then heated in the high vacuum system. A pressure rise with the pumps operating from 1×10^{-6} to 1×10^{-4} torr was observed. Then the same cell was again treated similarly; however, it was kept at open current in the solution for 1 min. Under these conditions the pressure only rose to 1×10^{-5} torr.

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1. Zdanuk, E.J., Bierig, R., Rubin, L.G., and Wolsky, S.P., Vacuum 10, 382 (1960).

Meanwhile, the electrochemical pretreatment conditions have been investigated in order to determine the most reproducible method of surface preparation. It has been discovered that pretreatment of the electrode in hot nitric and fuming perchloric acid is not as acceptable for obtaining a clean surface as either heating the electrode in vacuum after several cyclic sweeps or prepolarizing it at -0.1 volts (vs Ag/AgCl in 1 M NaCl) for at least two hours. Of the latter two the vacuum heat treatment seems most acceptable because prepolarization sometimes results in impurity waves, but a reproducibly clean surface has always been obtained by the vacuum heating procedure. (D. Shive and D. Roe)

XV. Electrochemical Studies of Single Crystal Electrodes

Spherical single crystals of silver have been prepared and used for electrochemical studies as described in previous reports. From examinations of current-potential-time data, a model was developed for deposition of silver ions on regions of "controlled" growth sites, that is the stepped area surrounding a (III) facet on the crystal. The model relied on direct transfer of ion to the immediate vicinity of the growth site: no surface migration of adatoms was proposed in order to account for the experimental behavior. In contrast, the deposition mechanism on the (III) facets displayed a very different current-potential behavior, as noted before. Capacitive measurements of the facet-solution interface were finally completed and these results have added valuable detail to the model of the mechanism of the silver electrode.

A simple voltage-step technique was used to determine the capacities and resistive components of the cell which consisted of a (III) silver plane on the crystal sphere contacted by a drop of electrolyte from a Vycor capillary tip. The counter electrode was a large silver/silver perchlorate electrode. A fixed potential could be applied to the cell with a superimposed square wave of 3 mv amplitude. Current-time curves during the period of the square wave were recorded from an oscilloscope display. The slope of the plot of log current vs time was $-1/2.303$ RC and the intercept at zero time was V/R where R is the cell and circuit resistance, C, is the electrode capacity and V is the square wave amplitude. Capacities were determined as a function of the fixed potential applied to the cell and therefore could be compared directly with recorded current-potential curves.

Proper operation of the circuit was checked with standard capacitor and resistor. An overall check of the system was provided by measurements of the double layer capacity of silver facet in contact with 0.1 M HClO_4 solutions at applied potentials where silver is essentially an ideal polarized electrode. Measurements of electrode capacity using an electropolished silver have been reported recently (1) and include, e.g., that $C = 59 \text{ uf/cm}^2$ at 0.4 v vs standard hydrogen electrode (S.H.E.). A value of 48 uf/cm^2 was obtained from a single crystal electrode at the same potential and the difference is in accord with the expected difference in surface

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1. L. Ramaley and C. G. Enke, J. Electrochem. Soc. 112, 947 (1965).

roughness of the electrodes.

Measurements of electrode-solution capacity in the presence of silver ion (0.05M) were unexpectedly low. Over a potential range of 25 mv, ending within a few millivolts of the point where large cathodic currents would commence, the capacities were in the range of 28 to 36 $\mu\text{f}/\text{cm}^2$. If the mechanism of nucleation involved clusters of adatoms on the surface, then a pronounced increase (greater than ten-fold) in capacity would be observed at the cathodic limit of the "zero current" plateau. It has been shown (1) that there should be a direct proportionality between the surface concentration of adatoms and their contribution to the electrode capacity. Therefore, the evidence indicates that adatoms are not present in significant numbers on these electrode surfaces.

Observations of the deposits that formed on these facets showed that nucleation occurred at only one or two small regions and resulted in small crystallites. It would seem that the deposits were a result of growth of defects in the facet rather than nucleation due to adatom supersaturation. These results and conclusions are being prepared for publication. (W. M. Krebs and D. K. Roe)

XVI. Mechanism of Oxidation of Formic Acid at a Platinum Electrode

A sequence of reactions was previously proposed for the oxidation of formic acid in H_2SO_4 solution (2). The steps involved decomposition to CO_2 and adsorbed hydrogen which was then oxidized. A second decomposition also occurred which produced H_2O and adsorbed CO, the latter having been assumed to deactivate the electrode as a catalytic surface for the first decomposition reaction. Subsequent oxidation of CO at increased anodic potentials effectively reactivated the catalytic surface.

At the present time the intent is to examine in detail the rates of the two decomposition reactions as a function of potential. This quantitative information will be useful in explaining the unusual current-potential-time behavior of formic acid, including the potential oscillations which were investigated earlier in this project.

In addition, an attempt will be made to use the omegatron system, also discussed in this report, to identify the species which is suspected to deactivate the electrode surface. (L. Marincic and D. K. Roe)

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1. H. Gerischer, Z. Electrochemi. 62, 256 (1958).
  2. D. K. Roe and W. R. Matson, presented at the San Francisco Meeting of the Electrochemical Society, May 13, 1965.

XVII. Current-Time Relationships at the Dropping Mercury Electrode

The relationship between current and time at a dropping mercury electrode under diffusion controlled conditions was first derived by Ilkovič in 1934. The original derivation involved a number of simplifying assumptions, particularly sphericity of the drop, planar diffusion and a sufficiently thin diffusion layer to justify dropping all but the first term in a series. Ilkovič's equation has given an adequate first approximation to average and maximum currents and many workers have subsequently attempted to refine the derivation to give a better experimental fit. Von Stackleberg in 1952, Koutecký, Lingane, and Matsuda independently in 1953 derived more exact expressions involving additional terms in the expanded series and taking into account the shielding of the electrode by the capillary, spherical diffusion, and diffusion layers of finite thickness. Experimental studies have been relatively few and most workers have been concerned only with the prediction of the maximum current at the full growth of the drop or the average current during the life of the drop. Studies on current as a function of time for individual drops revealed many discrepancies, particularly in the early part of drop life, and showed a striking difference between the first drop and subsequent drops. This difference is attributable to depletion of electroactive material in the solution around the drop. The most extensive current time studies have been made by Smoler in Czechoslovakia but under circumstances which were not ideally adapted to accurate measurement, particularly in the early stages of drop life, and left many unanswered questions about the interaction of significant variables. In the present study, an effort has been made to examine all significant variables taking advantage of modern high speed measuring and recording equipment.

The important variables which have been identified and examined are as follows:

1. Variability of mercury flow. A number of workers have observed fluctuations in the flow of mercury through the capillary as a function of drop development. In extreme cases there can be a temporary halt in the flow just after the falling of the drop and an observable suck-back of mercury into the capillary before the next drop begins. This very undesirable effect can be eliminated by maintaining a sufficiently great head of mercury on the capillary. Without a constant flow, deviations from the Ilkovič equation, either in its simple or extended forms, is inevitable.
2. Convection. At ordinary dropping rates, insufficient time exists for convectational flow to become significant. Careful examination is being made of results obtained by previous workers who used very long drop times to determine if effects due to convection are detectable there.
3. Migration. The presence of a considerable concentration of inert supporting electrolyte is normally assumed to eliminate any significant contribution to the total limiting current by migration. Certain of Smoler's results involve calculated correction for the contribution due to migration, which is rather large and without which his results would deviate greatly from the theoretical. Attempts are being made to verify the correctness of his estimation of the migration current and to assess its importance, if any, in our own work.

4. Residual current. The effect of residual current requires what is usually a small correction when one is measuring average or maximum currents. For individual drop time curves the residual current correction may become very large at the beginning of drop life. Proper correction for this factor requires high speed measuring equipment which has not been available to previous workers.
5. The effect of surface active agents. Streaming of the liquid in the vicinity of the drop resulting from inhomogeneous fields can destroy the diffusion layer and produce the very large deviations from theoretical behavior. Traces of surface active substances frequently inhibit this streaming but may also have other effects on the electrode performance. Extensive study of the effect of surface active components on streaming for various configurations of electrodes and conditions was found to be necessary in this work.
6. Vibration. Gross vibration results in large deviation from expected behavior. It is not generally appreciated that relatively slight vibration, although not causing a serious deviation from the Ilkovič equation, can produce a very considerable change in the apparent diffusion coefficients of the species being reduced.
7. Depletion. Removal of electroactive material by the electrode reaction changes the concentration particularly in the vicinity of the drop in the early stages of its life. While this effect can be avoided by working with single "first" drops, its effect in conventional polarography is quite important.
8. Wetting of the capillary. Much evidence exists that some liquid rises within the capillary even when it is filled with mercury, and the electrolysis of this film has a significant effect upon electrode behavior. Silicone treatment tends to avoid this problem but introduces other complications.
9. The physical characteristics of the end of the capillary, e.g., roughness, planarity, micro fissures, etc., are observed to affect both dropping characteristics and currents.
10. The angle of the capillary with the horizontal. All theoretical equations have been derived assuming the capillary to be in a vertical position. Smoler in particular has introduced the use of horizontal capillaries and capillaries held at a 45° angle. Each of these configurations has its advantages and disadvantages.
11. Concentration of supporting electrolyte. The supporting electrolyte not only affects the contribution due to migration but has an influence on diffusion coefficients, the thickness and characteristics of the double layer, and the position of the electrocapillary maximum.
12. The shielding effect. Conventional thick-walled capillaries exert a significant shielding effect upon the electrode which essentially is hanging not in free space but tangent to a plane. This can affect diffusion and convection patterns. The use of sharply pointed capillaries has been recommended and some workers have suggested that the depletion effect is minimized by such an approach.

Extensive studies were made on a large number of capillaries horizontal and vertical and 45° both thick walled and thin walled or pointed and under a variety of experimental situations designed to test the contribution of the variables outlined above. Most of the work done using a recording oscillograph capable of following with accuracy the current-time variations even in the

first few hundredths of a second of drop life. An operational amplifier circuit was used to prevent potential fluctuations during the growth of the drop. A special apparatus was built to eliminate vibration and provision was made for simultaneous electrical and optical-microscopic observation of the drops during growth. A large mass of data was accumulated which is currently in the process of analysis. Linearity of $It^{-1/3}$ vs $t^{-1/6}$ curves is used as a criterion of adherence to the Matsuda equation and the values for the diffusion coefficient calculated from the equation serve as a criterion of absolute numerical fit. To date it has become apparent that under very carefully controlled experimental conditions the Matsuda equation does give an excellent representation of the data over essentially the entire drop life. The values of the diffusion coefficient of cadmium in potassium chloride determined from these plots are in satisfactory agreement with those determined by other methods. Vibration, residual current, depletion and the presence of maximum suppressors are significant variables and must be controlled with great care. In conventional polarography the depletion effect is very significant particularly in the early part of the drops. The use of finely pointed capillaries does not eliminate the depletion effect although it changes its magnitude appreciably. The use of vertical capillaries is preferable to the use of 45° capillaries from the standpoint of stability and reproducibility. The elimination of the depletion effects by a 45° capillary is not sufficient advantage to make it as attractive as a conventional capillary. Paradoxically, the theoretical equations fit the 45° capillary very closely even though microscopic observation shows the existence of streaming. Studies on the reduction of oxygen with phenolphthalein present indicate that the fit of 45° capillaries to the theoretical equations must be as a result of cancellation of errors. During the growth of a drop at a 45° electrode a considerable body of depleted solution gathers at one side of the drop while fresh material is brought in by streaming at the other. The drop time of 45° capillaries varies differently as a function of potential than does a conventional dropping electrode and the effect is considerably changed by the use of silicone. An attempt is being made to determine experimentally the optimum values of the constants A and B to be used in the various forms of the extended Ilkovič equation under the experimental conditions which best approximate the assumptions used in its derivation. (W. Boardman, D. N. Hume)

XVIII. Electrode-Solution Double Layer Capacity Measurements with Phase Selective AC Polarograph

Phase selective sampling of the AC current signal from a polarographic cell was developed and used during the course of this project. The basis of the technique was to measure the amplitude of the AC current at the point in time when the capacitive current, due to the electrode double layer, is zero; this condition occurs at the peak of the sine wave voltage applied to the cell. By means of an instrumental modification of the AC polarograph described in past reports, it became possible to measure also the capacitive current and therefore the electrode double layer capacity. The method which was developed permits direct recording of capacity-potential curves

even in the presence of diffusion controlled faradaic processes. Several methods have been developed for direct recording of capacity-potential curves but none was able, even in principle, to record capacity functions selectively in the presence of diffusion controlled electrode reactions.

The basis of this new method can be explained in terms of the equivalent circuit of the cell: a capacitor, C , in parallel with a complex (faradaic) impedance, Z_c . Cell resistance can be neglected from the equivalent circuit by proper design of cell and potentiostat. A sine wave potential of small (2-10 mv) amplitude is applied to the cell from a potentiostat, as in AC polarography. Noting the applied potential by $e = E \sin \omega t$, then the current through the capacitor is given by $i_c = I_c \sin (\omega t + \pi/2)$ and the current through the faradaic impedance is $i_f = I_f \sin (\omega t + \pi/4)$, since the phase angle for the latter is 45° for diffusion-limiting rate. The signal from the current amplifier is the vector sum of i_c and i_f . By sampling the height of the wave form of the composite current signal at values of $(\omega t + \pi/4) = 0$ or π radians (135°), the contribution of i_c to the measured signal is zero, that is the amplitude is directly proportional to I_c . Alternatively, the current signal can be sampled at 90° and at 180° along the applied potential sine wave, since these two phase angles were easily obtained. The sum of the two amplitudes is $i = [I_c \sin \pi + I_f \sin 3\pi/4] + [I_c \sin 3\pi/2 + I_f \sin 5\pi/4]$ which is equal to $-I_c$. The recorder was calibrated in microfarads through the relation $C = I_c / \omega E$ or by using standard capacitors.

Initial measurements with capacitors in place of a cell showed that a precision of 1% or better was obtained; accuracy depended primarily upon calibration against standard capacitors. Measurements were made of the double layer capacity of mercury in NaF solutions and the correlation with literature values (1) was within 1% in most cases.

Of major importance was the ability to measure double layer capacity in the presence of diffusion-controlled electrode reactions. For such tests, the selected electrode reactions were the reduction of Tl^+ , Cd^{2+} and Zn^{2+} at a mercury electrode. These three have rate constants (2) for charge transfer of 0.15, 2.9 and 0.006 cm/sec, respectively when the supporting electrolyte is 1MKCl. The reason for choosing these three is to include systems which have different degrees of charge transfer control and diffusion control of rates. Only processes which are strictly diffusion control allow double capacity measurements without error. The results clearly illustrated the considerations to be correct. In addition, it was found that the double layer capacity rose significantly over the potential region of the rising portion of the reduction wave of Tl^+ . Information of this type is of considerable value in the investigation of electrode reactions. In the present case, for example, one is led to the conclusion that the amount of Tl^+ adsorbed on the electrode increases markedly in the vicinity of $E_{1/2}$.

On the basis of these results, the principle of the method was verified by experiment. Applications to detailed studies of electrode reactions are planned for the near future. (T. F. Retajczyk and D. K. Roe)

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1. D.C. Grahame, J. Am. Chem. Soc. 76, 4819 (1954).
  2. From the tabulation by N. Tanaka and R. Tamomushi, Electrochim. Acta. 9, 963 (1964).

XIX. Nickel Bromide Complexes

In studying some of the characteristics of alternating current polarography it was noticed that the alternating current wave of nickel, which is very small and highly irreversible in most supporting electrolytes, became increasingly larger and ultimately reversible in concentrated (7 to 11 M) bromide solutions. Similarly a considerable change in the DC polarographic wave over a similar range of bromide concentrations also indicated increasingly reversible behavior. No such behavior was observed even in very concentrated nitrate or perchlorate solutions.

The most plausible hypothesis for explaining this behavior was the formation of a nickel bromide complex or complexes. Data in the literature indicated the existence of a NiBr^+ species in the 2-6 M region, which would not account for the change in behavior in 7 to 11 M bromide. No valid quantitative data existed for higher nickel bromide complexes although the existence of others, e.g., NiBr_4^{--} , in the solid state and in nonaqueous solutions is known qualitatively.

Spectrophotometric studies were made in lithium and calcium bromide solutions having bromide concentrations in a range of 7 to 11 M. At about 480 $m\mu$ absorption was essentially constant up to around 7 M bromide and then was observed to increase rapidly. The results were analyzed both by conventional graphical methods (McConnell-Davidson and Newton-Arcand) and by a computer technique developed in this laboratory. Because of the very high electrolyte concentrations involved it was necessary to take into account changes in the activity of water (which fell to less than 0.1 in the most concentrated lithium bromide solution) and to make various approximations for the activity of bromide ion. Approximating the activity coefficient of the bromide ion as being equal to the mean molal ionic activity coefficient is admittedly hazardous when the activity coefficient is as high as 235 as it is 11.7 M lithium bromide but without such approximations no quantitative treatment would be possible. The spectrophotometric data indicated the presence of NiBr^+ in the lower concentration ranges where very little electrochemical activity was apparent and a value for the stability constant of that ion was obtained which was in satisfactory agreement with previous published estimates. In the range of bromide concentrations above 7 M it was clear that the species NiBr_2 was forming and becoming predominant. The series of runs in lithium bromide led to a value for K_2 of $5.5 \pm 0.6 \times 10^{-5}$ and from the series in calcium bromide $26 \pm 2 \times 10^{-5}$. The differences are presumed to be due mainly to the uncertainties involved in estimating activity coefficients. No evidence was found of the existence of higher complexes in aqueous solution.

Job (1) in 1937 made a spectrophotometric study of nickel in concentrated hydrobromic acid solutions and concluded that two species were formed each by the addition of 2 bromide ions: NiBr_2 and NiBr_4^{--} . Although Job had made corrections for the activity coefficient of bromide ion, he had overlooked contribution of the activity of water. Recalculation of his data applying corrections for the water activity led to curves which indicated that each step involved only one bromide ion. The resulting estimate of K_2 was 26×10^{-5} which in view of the many assumptions

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1. P. Job, Ann. de Chim. 6, 97 (1937).

made and the necessity of estimating some of his data from published graphs is in remarkable agreement with our own data.

Comparison of the spectrophotometric and electrochemical results reveals that the latter show currents larger than should correspond to the actual concentrations of NiBr_2 , which is presumed to be the electroactive species. From the spectrophotometric data, about 50% of the nickel present is NiBr^+ at 2 M bromide concentration, 95% at 6 M and then the NiBr_2 species becomes more prominent making it up to somewhere between 50% and 80% of the total nickel content at 12 M bromide. A limiting current indicating the presence of a larger amount of species than is known to be there is not unprecedented and may be interpreted as indicating the presence of a kinetic current due to formation of NiBr_2 at the drop. For bromide concentrations less than 6 M, the rate of NiBr_2 formation is too slow to contribute significantly to the total current. Between 6 and 10 M the current is under mixed control by diffusion and the prior chemical reaction forming NiBr_2 . It was noted that the peak height in the kinetically controlled regions decreased with increasing frequency, as would be expected. The appearance of the DC polarograms: the gradual appearance of a new wave at more positive potentials with increasing bromide concentration and the dependence of the wave height on the polarographic conditions also is characteristic of a process under partial kinetic control. (T. F. Retajczyk and D. N. Hume)

XX. Chloranilate Complexes

The reactions of chloranilic acid with metal ions are of interest in connection with the widespread use of the important thorium chloranilate method for the determination of traces of fluoride. We have had occasion to examine the reaction between chloranilate ions and aluminum under conditions similar to those of the fluoride determination and also to re-examine the evidence for the validity of published values for the first and second dissociation constants of chloranilic acid.

Recently Nazarenko and Flyantikova (1) alleged that the dissociation constants of chloranilic acid published by Schwarzenbach (2) and Thamer and Voigt (3) were in error due to a misinterpretation of the steps actually involved. The Russian workers claimed that what previous investigators assumed to be the first and second dissociation steps were actually the dissociation of a protonated species and the first dissociation step of the neutral acid molecule. The spectrophotometric curves which they obtained and the numerical values of the dissociation steps were very similar to those of previous workers, but their interpretation was different. It was claimed that the identification of the yellowish species as a cation, the deep purple form as the un-ionized acid, and the pale violet as the singly charged anion was supported by electromigration measurements.

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1. V. A. Nazarenko, G. V. Flyantikova, Zhur. Obsch. Khim. 35, 211 (1965).
  2. G. Schwarzenbach, H. Suter, Helv. Chim. Act. 24, 617 (1941).
  3. B. Thamer, A. Voigt, J. Phys. Chem. 56, 225 (1952).

Direct determination of the dissociation constant for chloranilic acid by potentiometric titration in water is complicated by the fact that the steps measured are both fairly strong (pK values of approximately 1 and 3) and the solubility of chloranilic acid in water is sufficiently low (ca. millimolar) that very extensive dissociation takes place directly on dissolution in water. In order to make comparisons we have performed potentiometric titrations of 0.02 M solutions of chloranilic acid, benzoic acid, and picric acid in 95% ethanol using 0.2 M diphenylguanidine in 95% ethanol as the titrant. Well-formed potentiometric titration curves were obtained with two clearly defined breaks for chloranilic acid. Using the benzoic and picric acids as comparison substances for calibrating the approximate pKa shift in going from water to 95% ethanol, good agreement was obtained with the spectrophotometrically determined values of pK_1 and pK_2 reported in the literature. The results were not consistent in any way with the interpretation made by the Russian workers.

As a further check electromigration experiments were done in a 1 M perchloric acid medium, under which conditions it was claimed by the Russians that chloranilic acid existed as a singly charged cation. A two hour run in commercial electrophoretic apparatus using fluorescein as a standard showed no movement either of fluorescein or of chloranilic acid. A 16 hour run using pyridinium ion as a standard showed a 3 centimeter movement of the reference compound toward the cathode and a 3 mm movement of the chloranilic acid in the opposite direction. At pH 4.6, at which the presence of the chloranilic and dianion is agreed by all authors, movement of the purple color toward the anode was visible; the mobility being about 6 to 10 times that of sodium fluoresceinate. At no time was there electrophoretic evidence of the existence of a chloranilic cation. As a final check, the spectrum of chloranilic acid in benzene was determined and found to be essentially identical with the spectrum reported by the Russian workers in 5 molar aqueous hydrochloric acid, under which conditions they claimed that all the chloranilic acid was present as the protonated cation. Consequently we have concluded that no evidence exists for chloranilic acid cations in any of the solutions we have seen.

In chloranilic ion solutions of pH between 4 and 5, there is a noticeable intensification of color in the presence of aluminum. Spectrophotometric examination of the reaction by several approaches: continuous variations, slope ratio, mole ratio, and log plots, indicate the formation of a fairly stable complex involving two chloranilic ions per aluminum. An overall stability constant of the order of 10^5 is indicated. In more acidic solutions, e.g., pH 2, where the singly charged chloranilic ion predominates, there is also evidence of the same complex forming, but to a lesser extent because of the competition with hydrogen ion. At pH values higher than 5, hydrolytic precipitation of the aluminum prevents the establishment of equilibrium. (O. Nudelman and D. N. Hume)

XXI. Computer Methods for Calculating Stability Constants

A computer method has been developed for the calculation of stability constants of complexes from spectrophotometric data. The absorbance is expressed directly as a function of the ligand concentration and the stability constants, thereby using the experimental data as input to the program and not requiring weights. Full use is made of all the data, subjectivity of interpretation is reduced to a minimum, and the maximum amount of information is obtained from the data including reliable estimates of the error of the constants and extinction coefficients. In contrast with the usual subjective graphical techniques the calculated constants and error estimates are consistent with the precision of the experimental data.

For a metal ion in a solution of a ligand, the absorbance may be expressed by an equation of the form

$$A = \frac{M_T \sum_{n=0}^N \epsilon_n \beta_n [x]^n}{\sum_{n=0}^N \beta_n [x]^n}$$

which may be solved by the Gauss method. The equation takes various forms for different numbers of species present and absorbing in solution. For example, for three absorbing species the equation becomes

$$A = \frac{\epsilon_0 M_T + \epsilon_1 M_T \beta_1 [x] + \epsilon_2 M_T \beta_2 [x]^2}{1 + \beta_1 [x] + \beta_2 [x]^2}$$

which is of the form

$$A = \frac{C_3 + C_1 [x] + C_2 [x]^2}{1 + C_4 [x] + C_5 [x]^2}$$

where C_1 through C_5 are constants, and from the input data absorbance and ligand concentration the best values of C_1 through C_5 are determined. Initial estimates, which need not be near the true values, are introduced at the outset and refined in repeated iterations. It should be noted that solution for constants C_1 through C_5 supplies the data necessary for the determination of the extinction coefficient and the stability constant of each of the species involved.

The program has been tested on synthetic systems and on data obtained in the laboratory. Comparison of the results obtained by the computer method and by conventional graphical techniques where they are applicable shows the computer gives very similar values as a rule, but invariably with larger standard deviations both of extinction coefficients and stability constants. This is clearly because the computer program is designed to give a realistic estimate of error based on a strict solution of the propagation of variance equations, whereas graphical methods

characteristically involve a series of assumptions which make the results appear to be more precise than they actually are. The program is applied independently to each wave length at which data are taken and can be ordered to calculate the results based on any desired number of the available points. Characteristically a range of results is obtained depending upon the assumptions programmed in and the number of points taken, and the experimenter is ultimately left with the subjective decision of which results should be accepted. If an attempt is made to use all the points, i. e., a wide range of concentrations, the standard deviations of both extinction coefficients and stability constants tend to be higher than if an intermediate number is used. With a very small number of points the uncertainty again rises. Using the criterion of minimum standard deviation and applying, where appropriate, chemical knowledge of a non-statistical nature, the most likely results may be selected. Conventional graphical methods tend to average out the possibilities and it has been noticed that the average of the most probable computer generated values tends to agree fairly closely with the results of graphical methods where the data are clear cut enough to permit unambiguous results by graphical treatment.

The method has been applied to data on the formation of the thallos chloride un-ionized molecule and to the formation of NiBr^+ and NiBr_2 species mentioned separately in this report. The graphical and computer methods were found to be in basic agreement but with the computer method indicating, as usual, the need for a greater amount of caution in accepting the results. Some data obtained in this laboratory on the formation of BiI_4^- , BiI_6^{-3} , BiI_7^{-4} showed remarkably good agreement when computed by both methods. The stepwise stability constants by the computer and graphical methods respectively were 299 and 274 for the tetraiodide, 245 and 258 for the pentaiodide, and 0.2 and 0.14 for the heptaoidide.

To test the program on a different type of equilibrium, the data of Srivastava and Newman (1) at Brookhaven National Laboratory on the complexes of palladium were calculated from their data which were kindly made available to us prior to publication. In this system the complexes were all of the form $\text{PdCl}_m\text{Br}_n^-$ where $m + n = 4$. The comparison of the results with those of the authors who used a normalized curve fitting technique is very gratifying and is shown in the table below. (A. S. Gordon and D. N. Hume)

Comparison of Graphical and Computer Results

A. Replacement Constants $\text{PdCl}_m\text{Br}_n^- + \text{Br}^- = \text{PdCl}_{m-1}\text{Br}_{n+1}^- + \text{Cl}^-$		
	Graphical	Computer Averages
n = 0	35.1 ± 1.1	30.7
n=1	12.6 ± 1.7	11.6
n=2	8.9 ± 1.7	8.4 ± 2.0
n=3	3.54 ± 1.1	3.57 ± 1.4
B. Bismuth Iodides		
K ₄	274 ± 10	299 ± 157
K ₅	258 ± 5	245 ± 60
K ₇	0.14 ± .01	0.3 ± 0.3
C. Nickel bromide in LiBr		
K ₂	5.5 ± 0.6 × 10 ⁻⁵	4.9 ± 0.7 × 10 ⁻⁵

1. S. C. Srivastava and L. Newman, Inorganic Chem. 5, 1506 (1966).

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

In the past year the wax impregnated graphite mercury electrode (1) has been developed as an analytical tool for determinations of traces of Cu, Pb, Zn, Cd, Bi, etc., at 10^{-10} M levels.

We have studied the effect on electrode stability of quantity of mercury, mercury deposition rate, background electrolyte, and stirring rate with N_2 gas, or magnetic stirring bar. The deposition of 10^{-7} m of mercury over 30 min in 0.5 M NaCl gives an electrode which is operable and gives sharp peaks for 100-150 hours of use without refurbishing the mercury surface. After 20-30 days of use the electrodes show increased residual and charging current due to the exposure of graphite, and the wax must be renewed. Polyethylene impregnated electrodes last longer, but otherwise show no differences.

Techniques are being developed using Sephadex molecular sieves and anodic stripping for the investigation of metal organic complexes in natural media most of which seem to have molecular weights above 20,000. Such complexes seem to account for almost all of the trace metals in highly organic lakes and rivers, and varying smaller amounts in ocean water.

The rate of dissolution and the exchange rate of these complexes is slow, and the formation constants large, and it is felt that such complexes play a large role in the geochemistry of trace elements. (W. R. Matson and D. K. Roe)

XXIII. Thermometric Titrations in Isopropyl Alcohol

The characteristics of thermometric acid base titrations in isopropyl alcohol as a solvent have been explored using techniques developed previously in this laboratory (2). The solvent was selected because of its desirable characteristics: ready availability, high purity, stability, low cost, history of successful use in photometric and potentiometric titrations, and its ability to dissolve a wide variety of compounds. The titration characteristics of 31 bases and 18 acids were examined.

For the titration of bases, a tenth molar solution of perchloric acid in isopropyl alcohol was normally used. The ideal acid for use in a titration should be monoprotic, strong, anhydrous, give stable solutions, be nonvolatile, inexpensive, and have little tendency to form insoluble reaction products. Of all the readily available acids, perchloric was found to meet the greatest number of these requirements. The principal drawback to the use of perchloric acid is the difficulty, to say nothing of the undesirability, of preparing absolutely anhydrous solutions. It was found however that the titrant obtained by dilution 72% perchloric acid with commercial isopropyl alcohol contained only 0.5% water, an amount which did not have a deleterious effect on most titrations. In selecting a basic titrant, more difficulty was encountered in that strong inorganic

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1. W. R. Matson, D. K. Roe and D. E. Carritt, *Anal. Chem.* **37**, 1594 (1965).
  2. M. J. Keily, D. N. Hume, *Anal. Chem.* **36**, 543 (1964).

bases tended to produce insoluble reaction products and some of the stronger aliphatic bases gave solutions which were relatively unstable due to volatility. The best compromise appeared to be diphenyl guanidine although its use placed a strict limit on the pK_A of acids which could be titrated to sharp end points.

Organic acids and bases characteristically give good titration curves in isopropyl alcohol. The end point sharpness was, as would be expected, somewhat dependent on acidic or basic strength. Sixteen nonaromatic amines were found to give satisfactory results with a precision (pooled standard deviation) of 0.58%. The general behavior and characteristics were similar to those observed with acetonitrile as the solvent (1). Sixteen aromatic amines showed a similar precision, (pooled standard deviation 0.7%) and the limit of titratability was found to be at about $pK_b = 10.5$ in water. Of the acids examined, all those of pK_a in water less than 4 showed a very good sharp end point break and the pooled standard deviation for acids was 0.49%. In general, differentiating titrations were not found to be practical in this solvent, as in acetonitrile, because the heats of neutralization of a wide variety of compounds were found to be quite similar.

Increasing amounts of water were observed to decrease both the heats of reaction and the sharpness of end points. In the titration of bases either with hydrochloric or perchloric acid, a decrease of approximately 3 kilocalories per mole was observed on going from 0.25% to 0.50% water regardless of the base. No change in heat of dilution was observed however even on going as high as 1% water.

Isothermal heats of neutralization were measured for all the acids and bases in this study. The absolute values of the heat of neutralization of amines in isopropyl alcohol are fairly similar to those observed in acetonitrile (2) except for pyridine and the picolines, which were spectacularly lower. The general pattern of results is consistent with the known solvating characteristics of isopropyl alcohol. For substituted anilines and for pyridines, ΔH was found to be essentially linear with the pK_b of the bases in water while for aliphatic amines no such correlation was observable. For meta and para substituted benzoic acids the ΔH values correlated roughly with pK_a values in water. Plots of ΔH versus the Hammett constituent constant were linear, for the neutralization of meta and para substituted anilines, the relationship being

$$-\Delta H_{iso} = -5.39 \sigma + 9.99 \text{ kcal/mole}$$

(O. Nudelman, and D. N. Hume)

XXIV. Electron Spectroscopy

Work during the past year has centered about setting up facilities for the spectrometer system and investigating the use of a Helmholtz system for nulling the earth's magnetic field. The net field at the spectrometer must be homogeneous and reduced to one part in ten thousand

1. E. J. Forman, D. N. Hume, *Talanta* **11**, 129 (1964).
2. E. J. Forman, D. N. Hume, *J. Phys. Chem.* **63**, 1949 (1959).

of the field used in the spectrometer focusing system. This requires that the residual earth's magnetic field be less than one milligauss.

It is felt that a Helmholtz system consisting of square coils eight feet on a side would be adequate. A model Helmholtz coil system was constructed to test the feasibility of such a system to obtain a constant near zero field in our laboratory. The model is a four foot cubic frame (one-half scale of proposed system) made of aluminum angle stock, and mounted on a one-half inch thick aluminum sheet. The coil system is formed by winding #18 copper wire around the aluminum frame. The system consists of three orthogonal sets of coils, each set having three coils. The three vertical coils have twenty turns of wire; the six horizontal coils each have fifteen turns.

A solid state current regulated power supply was purchased to energize the coil system. The supply has nine independent channels, three of which have a six ampere rating (for the vertical coils), and the remaining six have a three ampere rating (horizontal coils). Preliminary tests indicate the unit has the high stability required.

The model system was used to cancel the earth's magnetic field at the center of the coil system. The results indicate that a zero field can be attained over a satisfactory volume of space, but that very rapid fluctuations of 1-2 milligauss exist. These fluctuations about zero field cannot be tolerated. A system for automatic compensation of ambient field fluctuations is being designed. (J. J. Jack, W. Swartz, D. M. Hercules)

ADDRESSES

- D. M. Hercules, "Chemiluminescence"
 Purdue University Faculty Seminar, Lafayette, Indiana, Feb. 10, 1966.
 North Carolina State University Research Seminar, Raleigh, North Carolina, Feb. 17, 1966.
 Columbia University Faculty Seminar, New York, N. Y., March 2, 1966.
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 Brown University Faculty Seminar, Providence, Rhode Island, March 25, 1966.
 Max-Planck Institute for Spectroscopy, Goettingen, West Germany, June 3, 1966.
 Organic Chemistry Institute, Clausthal, West Germany, June 6, 1966.
 City College of New York, Faculty Seminar, New York, Sept. 27, 1966.
 State University of New York, Plattsburgh, N. Y., December 12, 1966.
- D. M. Hercules, "Chemiluminescence and Electroluminescence", Indiana University Faculty Seminar, Bloomington, Indiana, Feb. 11, 1966.
- D. M. Hercules, "Studies on the Chemiluminescence of Luminol", 151st American Chemical Society Meeting, Pittsburgh, Penna., March 29, 1966.
- D. M. Hercules, "A Spectrophotometric Study of 8-Mercaptoquinoline", 151st American Chemical Society Meeting, Pittsburgh, Penna., March 31, 1966.
- D. M. Hercules, "Electrochemically-Generated Chemiluminescence", Polarographic Institute, Prague, Czechoslovakia, June 1, 1966.
- D. N. Hume, "Plasma Emission Spectroscopy",
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 St. Louis Society of Analysts, St. Louis, Mo., April 16, 1966.
 Departmental Colloquium, Lehigh University, Bethlehem, Penna. October 18, 1966.
- D. N. Hume, "Analytical Research at MIT", Seminar, Howard University, Washington, D. C., February 9, 1966.
- D. N. Hume, "A New Curriculum for the Chemistry Major"
 Philadelphia Section American Chemical Society, Philadelphia, Penna., Feb. 24, 1966.
 Akron Section American Chemical Society, Kent, Ohio, May 19, 1966.

- D. N. Hume, "Determination of Trace Constituents in Natural Water Systems" American Chemical Society, National Meeting, Pittsburg, Penna., March 23, 1966.
- D. N. Hume, "Impact of New Secondary School Programs on the College Curriculum", National Science Teachers Association Convention, New York, April 4, 1966.
- D. N. Hume, "Distribution of Strontium and Barium in the Ocean", Departmental Seminar, University of New Hampshire, Durham, April 12, 1966.
- D. N. Hume, "New Approaches to the Teaching of Chemistry", Baltimore Section American Chemical Society, Baltimore, Md., September 21, 1966.
- D. N. Hume, "A Modern Curriculum for the Modern Chemist", 2nd Conference on the Undergraduate Chemistry Curriculum, North Dakota State University, October 15, 1966.
- W. M. Krebs, "Interpretation of Single Crystal Potentials of Silver", Cleveland Electrochemical Society Meeting, May 6, 1966.
- W. R. Matson, "Trace Metal Analysis of Natural Media by Anodic Stripping Voltammetry", Instrument Society of America, Analysis Instrumentation Symposium, May 11, 1966, Houston, Texas.
- D. K. Roe, "Experimental Verification of Diffusion Theory of Controlled Potential Electrogeneration of Chemiluminescence", Phoenix American Chemical Society Meeting, January 19, 1966.
- D. K. Roe, "Mass Transport in Electroanalytical Methods: a Comparative Treatment", Gordon Research Conference on Analytical Chemistry, New Hampton, N.H., August 21, 1966.

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- A. Gordon, "A Computer Method for the Direct Calculation of Stability Constants from Spectrophotometric Data", Ph.D., August 1966.
- W. M. Krebs, "Electrical Studies on Single Crystal Electrodes", Ph.D., August 1966.
- J. R. Layton, "Spectrophotometric Studies of the Complexes of Thallous Chloride and Thallous Perchlorate", Ph.D., January 1966.
- J. N. Little, "A Study of the Vapor-Liquid Equilibrium of Aqueous Amine Solutions", Ph.D., March 1966.
- T. Retajczyk, "A.C. Polarography in Concentrated Salt Media", Ph.D., September 1966.

ORGANIC ISOTOPE APPLICATIONS GROUP

Summary

Evidence has been obtained that the hydrolysis of benzoyl chloride in less polar aqueous solutions (67-95% dioxane) occurs by a concerted mechanism rather than by the ionization mechanism which operates in water. There is no O^{18} exchange with the water in the less polar solutions, excluding a two-step, water addition - chloride elimination mechanism with the second step rate determining. There is a substantial chlorine Cl^{35}/Cl^{37} isotope effect on the rate, showing that the C-Cl bond is broken in the rate-determining step, excluding simple addition to the carbonyl group as the rate-determining step.

Primary kinetic hydrogen H/T isotope effects have been determined for the enolization of a ketone (α -(4-sulfophenyl)-isocaprophenone sodium salt) in water at 25° catalyzed by hydroxide ion, 2, 2, 2-trifluoroethoxide ion, phenoxide ion, trimethylacetate and water. The values are 16.3 ± 1.0 , 19.1 ± 0.5 , 24.3 ± 1.4 , 21.3 and 18, showing a broad maximum for phenoxide (as predicted, because the Bronsted law slopes were < 0.3 , 0.3, 0.5, 0.8 and > 0.8). However, the values for trimethylacetate and water were extrapolated from data at higher temperatures, and further work is in progress to check them by direct measurement at 25°. These isotope effects are too large to be consistent with a linear three atom model ignoring bending and tunnel effects. Experiments are in progress to test for tunnelling in the enolization catalyzed by phenoxide.

Rate constants for solvolysis of *t*-butyltrimethylammonium bisulfate to trimethylammonium bisulfate at 176° are $k = 2.98, 3.04$ and $3.10 \times 10^{-5} \text{ sec}^{-1}$ in 84.9, 87.8, and 95.2 weight % sulfuric acid. Rate constants for solvolysis of *t*-butylhydrazine dication at 25° are $k = 0.54, 1.09, 1.66, 6.13$, and $16.9 \times 10^{-4} \text{ sec}^{-1}$ in 84.8, 86.6, 88.1, 92.1, and 97.3% sulfuric acid. The product was shown to be hydrazinium dibisulfate by conversion in 93% yield to benzaldehyde azine. These rate variations are inconsistent with transition states containing the elements of water, sulfate ion or bisulfate ion.

The solubilities of three 1, 1, 2, 3, 3-pentacyanopropenide (PCP), five perchlorate and eighteen 1-benzenesulfonyl-1, 2, 3, 3-tetracyanopropenide (BSTCP) salts were measured in a number of concentrations of sulfuric acid between 0 and 70% by weight. The activity coefficients relative to triphenylsulfonium ion, f_+^* , were calculated, using the saturated solution in water as the standard state and the infinitely dilute solution in water as the reference state.

The activity coefficients of triphenyloxonium BSTCP can be accurately predicted up to 2 M ionic strength, using a modified Debye-Hückel equation with a mean ion size of 7.5 Å°. The $\log f_+^*$ values of other cations vary over a range of 0.7 in dilute sulfuric acid; smaller ions have smaller relative activity coefficients, as predicted by the Debye-Hückel theory. Typical values of $\log f_+^*$ in 10% sulfuric acid are -0.452 for diphenylchloronium, -0.130 for diphenylbromonium, -0.123 for diphenyliodonium, -0.024 for triphenyloxonium, 0.000 for triphenylsulfonium, 0.013 for diphenylcarbazolium, and 0.088 for tetraphenylphosphonium ions.

Above 30% sulfuric acid, the activity coefficients of the well-shielded and delocalized cations, diphenylcarbazolium, tetraphenylphosphonium, tetrabutylammonium, triphenyloxonium, triphenylsulfonium, triphenylcyclopropenium, and a number of triarylcarbonium ions, are rather similar. This similarity is interpreted in terms of lack of specific interactions with solvent, in accord with the conclusion of Deno, Taft and other workers for triarylcarbonium ions. The similarity of the activity coefficients of triarylcarbonium ions tends to confirm the validity of the H_R acidity function up to 50% sulfuric acid. The activity coefficients of tropenium ion could be measured at only a few acidities because of instability of the cation, but its behavior is fairly similar to that of triphenylsulfonium ion. Other cations exhibit activity coefficient behaviors differing to varying degrees from that of triphenylsulfonium ion. The alkali metals and silver show very large, positive activity coefficients ($\log f_+^*$ of potassium ion in 70% sulfuric acid is 3.46) as would be expected from their small size and tendency to hydrate. Differences in activity coefficient behavior of the smaller tetraalkylammonium ions are interpreted in terms of interactions with solvent, which is confirmed by nmr evidence for the tetramethyl- and tetraethyl-ammonium ions. Ammonium ions having protons on the nitrogen have large and differing activity coefficients, probably because

of hydrogen bonding. The deviations in activity coefficient behavior of diphenylhalogenonium ions are appreciable and are interpreted in terms of diminished shielding of the positive charge. In 70% sulfuric acid $\log f_+^*$ is 0.182 for diphenylchloronium ion, 0.641 for diphenylbromonium ion and 1.195 for diphenyliodonium ion. Ferricinium ion exhibits moderate activity coefficient variations relative to triphenylsulfonium ion, the change in $\log f_+^*$ between 40 and 60% sulfuric acid being 0.384.
(C. G. Swain)

The relation of structure to reactivity in reactions of radical generation, atom transfer, and termination are under investigation. By use of deuterium and oxygen-18 it has been shown that the cyclization of erythro-5-deuterio-2-hexanol to cis and trans-2,5-dimethyltetrahydrofuran by lead tetraacetate is a two step process. The stereochemistry of atom transfer has been examined with the 4-*t*-butyl-1-methylcyclohexyl radical and with the 2-norbornyl radical. In both systems, chlorine atom transfer from R-O-Cl shows lower selectivity than hydrogen atom transfer from R₃SnH. In the cyclohexyl system transfer affords preferentially the most stable products ("axial" atom transfer); in the norbornyl system, "exo" atom transfer occurs preferentially, affording the thermodynamically less stable products.

In continuation of studies of radicals possessing angular constraint, the 8-hydrindyl radical has been examined by means of the chain decomposition of cis and trans-8-hydrindylcarbonyl hypochlorite. Both reactants afford a common product composition of a 60:40 ratio of cis to trans 8-hydrindyl chloride. Under conditions which give rise to large variations in the ratio of trans to cis-9-chlorodecalin, the ratio of trans to cis-8-chlorohydrindane remains constant, indicating that factors other than angle strain are the definitive ones in these systems.

Evidence for radical cage recombination prior to complete statistical orientation of radical pairs has been obtained. Decomposition of optically active D,D-azo-bis- α -phenylethane in benzene in the presence of scavengers affords 30% 2,3-diphenylbutane of composition meso-41%, DD-38%, LL-21%.

A one-electron transfer to a small ring heterocyclic compound appears to take place between N, N, N', N'-tetramethyl-p-phenylenediamine and 2,3-di-t-butyldiaziridinone, with ultimate reduction of the heterocycle to urea. The implications of this finding to other strained ring compounds and electron transfer agents are under examination. (F. D. Greene)

I. Oxygen and Chlorine Isotope Effects and Oxygen Exchange in the Hydrolysis of Benzoyl Chloride

Water-oxygen isotope effects on the hydrolysis of benzoyl chloride at 25° in dioxane-water mixtures are $k_{16}/k_{18} = 1.0088 \pm 0.0009$, 0.9963 ± 0.0024 , and 0.9991 ± 0.0032 in 50%, 80%, and 95% dioxane (v:v), respectively. The oxygen isotope effect on the hydrolysis of mesitoyl chloride in 80% dioxane-20% water at 25° is 1.0083 ± 0.0018 .

Oxygen exchange between water and benzoyl chloride does not occur (or is at least 500 times slower than hydrolysis) during the hydrolysis of benzoyl chloride in 67% dioxane-33% water at 25°, contrary to previous reports. This result was obtained by studying both the incorporation of isotope from labelled solvent into unlabelled substrate and the loss of isotope from labelled substrate.

The chlorine isotope effect on the hydrolysis of benzoyl chloride in 95% dioxane-5% water at 25° is $k_{35}/k_{37} = 1.0078 \pm 0.0006$.

These results are consistent with the results of previous studies which indicate that the hydrolysis of mesitoyl chloride occurs by an ionization mechanism and that the hydrolysis of benzoyl chloride in polar solvents also occurs by an ionization mechanism. In less polar solvents the lack of oxygen exchange and the observed chlorine isotope effect suggest that the hydrolysis occurs by a concerted mechanism not involving a tetrahedral intermediate. (M. H. O'Leary)

II. Mechanism of Base-Catalyzed Enolization of Simple Ketones in Water Solution at 25°

In continuing work on this problem the values reported in the summary were obtained in water solutions 0.2 M in ionic strength (sodium chloride) by measuring

k_H by rate of racemization and k_T by rate of exchange of tritium-labelled ketone with the water. The approximate values for trimethylacetate and water were extrapolated from data at 97° and 107°. (V. P. Vitullo)

III. Test for Water in the Transition State for Solvolysis of t-Butyl Onium Compounds in 80-100% Sulfuric Acid

Observed first-order kinetics can result from solvent molecules acting as nucleophiles in a bimolecular reaction. The strength of a transient bond between solvent and the central carbon atom of the reactant at the transition state might be anything between that of an ordinary covalent bond (> 50 kcal/mole) and that of thermal molecular motion ($RT = 0.6$ kcal/mole, at 25°). If the energy of this bond were RT at the transition state, the dependence of rate on type of solvent or composition of a mixed solvent should be the same as that predicted for a transition state interacting with solvent by dielectric charge dispersal only.

To decide if there is bimolecular nucleophilic attack or specific solvation stronger than RT at the transition state, we have examined rates of solvolysis of three t-butyl compounds in 80-100% sulfuric acid as a function of concentrations or activities of the principal nucleophiles present: water, sulfate ion and bisulfate ion.

The dielectric constant of 100% sulfuric acid at 25° is 101 ± 8 . The concentrations of water, sulfate ion and bisulfate ion in aqueous sulfuric acid are shown in Tables 3.1 and 3.2. Molecular sulfuric acid is assumed to have negligible nucleophilicity on the basis of its very low basicity. A unimolecular mechanism can be distinguished from bimolecular mechanisms by the dependence of observed rate of solvolysis on nucleophile concentration. For a unimolecular mechanism, the rate should be

$$\text{Rate} = k_o \gamma_s / \gamma_t [S] \quad (1)$$

where k_o is a medium-independent rate constant and γ_s and γ_t are activity coefficients of substrates and transition state. For bimolecular mechanisms, the observed rate should be

$$\text{Rate} = \sum_N k_o [S][N] \gamma_s \gamma_n / \gamma_t \quad (2)$$

where γ_n is the activity coefficient and $[N]$ is the molar concentration of nucleophile N (H_2O , $SO_4^{=}$ or HSO_4^-).

Choice of sulfuric acid as solvent imposes stringent limitations on the substrates employed. The substrate must not vary appreciably in degree of protonation, since the reactivity of the protonated species would be unpredictably greater than that of the unprotonated. The substrate must not be subject to oxidation or sulfonation and must be soluble. t-Butyltrimethylammonium ion (1) and t-butylhydrazine dication (2) are suitable substrates.

1

2

Table 3.1

Vapor pressure and activity of water in concentrated aqueous sulfuric acid

Temperature	H ₂ SO ₄ , % ^a	p _{H₂O} , mm ^b	Activity H ₂ O ^c
25	85	0.0390	0.00164
25	90	0.00765	0.000322
25	95	0.00060	0.0000253
25	99	0.000004	0.00000016
175	85	143.	0.0214
175	90	48.4	0.00723
175	95	12.9	0.00163

a. % sulfuric acid is 100 x g sulfuric acid/g solution.

b. C. H. Greenewalt, Ind. Eng. Chem., 17, 522 (1925); F. C. Blake and C. H. Greenewalt in "International Critical Tables," Vol. III, E. W. Washburn, Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1928, pp. 302-304; E. Abel, J. Phys. Chem., 30, 260 (1946).

c. C. Dieterici, Ann. Phys., 38, 1 (1889); F. G. Keyes in "International Critical Tables," Vol. III, E. W. Washburn, Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1928, pp. 233-234.

Table 3.2
Concentration of species in sulfuric acid at 25° by
Raman spectra^a

% H ₂ SO ₄	SO ₄ ⁼ , M	HSO ₄ ⁻ , M	H ₂ SO ₄ , M
9.1	0.27	0.71	---
24.7	0.97	1.98	---
53.7	1.8	6.0	---
84.3	0.3	12.0	2.8
86.9	0.0	10.3	4.9
92.7	---	6.6	9.8
98.0	---	1.9	14.8

- a. T. F. Young, L. F. Maranville, and H. M. Smith, in "The Structure of Electrolyte Solutions," W. J. Hamer, Ed., John Wiley and Sons, Inc., New York, N.Y., 1959, pp. 35-45.

Ionic Activity Coefficients and Solvation in Sulfuric Acid. Measurements on the variation of activity coefficient of salts in aqueous sulfuric acids (see section IV below) can be used to calculate relative activity coefficients for a variety of cations if the anion is the same in each comparison. Activity coefficients may be related to a reference state of dilute aqueous solution by means of a standard ion assumed to have no activity coefficient variation. Triphenylsulfonium will be used as standard ion because it is stable over the range of acid solutions studied, it has no functional groups that might interact specifically with solvent, and the aromatic groups attached to the positive sulfur atom should have little or no specific interaction with solvent.

Two conclusions can be inferred from solubility studies conducted in 0-70% sulfuric acid which apply to our studies. First, as steric shielding of the nitrogen atom increases in a homologous series of ammonium ions, interaction with water in the solvent decreases. Second, protons bound to the charged nitrogen atom increase interaction with the water in the solvent. The evidence supporting these conclusions is presented in Table 3.3.

Table 3.3

Relative activity coefficients of pentacyanopropenide salts at 25° with triphenylsulfonium ion as standard ion

Cation	$\Delta_{(70-40)}^a$	Reference
$(C_2H_5)_4N^+$	0.950	b
$n-(C_4H_9)_4N^+$	0.130	b
$C_6H_5N(C_2H_5)H_2^+$	2.596	c
$C_6H_5N(CH_3)_2H^+$	2.571	c
$C_6H_5N(CH_3)_3^+$	1.496	b

- a. $\Delta_{(70-40)} = \log(\gamma_{R_4N^+}/\gamma_{Ph_3S^+})_{70\% H_2SO_4} - \log(\gamma_{R_4N^+}/\gamma_{Ph_3S^+})_{40\% H_2SO_4}$
 b. K. G. Harbison, Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, Mass., 1966, p. 62.
 c. R. H. Boyd, J. Am. Chem. Soc., 85, 1555 (1963); adapted to triphenylsulfonium ion as the reference.

Solubility studies were not pursued in acid concentrations greater than 70% because pentacyanopropenide anion protonates above 70%.

For the solvolysis of 1 in aqueous sulfuric acid at 176°, rate constants were determined from the decrease in ratio of area due to C-methyl protons of t-butyltrimethylammonium ion (1) to area due to N-methyl protons of an internal standard by nmr, Table 3.4, B = bisulfate salt. Trimethylammonium ion was identified as a product by nmr spectrum. No attempt was made to isolate products which arise from the t-butyl moiety. Studies on t-butyl alcohol rearrangements in 65, 75, and 96% have shown that the products from this reaction are exceedingly complex.

Table 3.4

Rate constants for solvolysis of t-butyltrimethylammonium bisulfate (1B) in sulfuric acid at $175.84 \pm 0.08^\circ a$, with tetramethylammonium bisulfate (3B), the internal standard

H ₂ SO ₄ , %	Conc. of 1, M	Conc. of 3, M	$k \times 10^5, \text{sec}^{-1}$
84.9	0.0130	0.0061	2.98 ± 0.17^a
87.8	0.0106	0.0079	3.04 ± 0.24
95.2	0.0106	0.0051	3.10 ± 0.07

- a. Error limits are standard deviations from the mean.

For the solvolysis of 2 in aqueous sulfuric acid at 25°, rate constants were determined from the decrease in ratio of area due to the t-butyl group of t-butylhydrazine dication (2) to area due to the N-methyl protons of the internal standard, Table 3.5. The nitrogenous product from this reaction was isolated from a neutralized reaction solution in 93% yield as a derivative, benzaldehyde azine, PhCH=NH=CHPh .

Table 3.5

Rate constants for solvolysis of t-butylhydrazine hydrochloride in sulfuric acid at $25.00 \pm 0.002^\circ$, with tetramethylammonium bisulfate (3B) as internal standard

H_2SO_4 , %	Conc. of 2, M	Conc. of 3B, M	$k \times 10^4, \text{sec}^{-1}$	k , rel.
84.8	0.0881	0.0617	0.54 ± 0.05	1.0
86.6	0.0825	0.0609	0.93 ± 0.06	1.6
86.6	0.0460	0.0363	1.26 ± 0.17	2.4
88.1	0.0769	0.0627	1.67 ± 0.13	3.1
88.1	0.0493	0.0422	1.65 ± 0.11	3.1
92.0	0.0850	0.0599	5.60 ± 0.47	10.4
92.0	0.0765	0.0595	6.70 ± 0.41	12.5
92.0	0.0447	0.0372	6.08 ± 0.39	11.3
97.3	0.0557	0.0406	16.9 ± 1.7	31.5

The variation of rate of solvolysis with % acid is in accord with eq. 1. The activity coefficient of 2, γ_s , should increase with % acid because of the activity coefficient increase of N-ethylanilinium ion, which also has protons bound to the atom bearing the positive charge, Table 3.3. Protons bound to the unalkylated nitrogen atom are not considered because their effects will cancel between ground-state and transition-state. The transition state (4), would have a structure in which the carbon-nitrogen atom bond is substantially broken, the central carbon atom has become nearly planar and the charge is predominately on the t-butyl group, either

sterically shielded or well delocalized by the methyl groups. This charge situation is similar to that of tetraethylammonium ion whose activity coefficient decreases relative to N-ethylanilinium ion as percent acid increases. Thus, the ratio γ_s/γ_t and the observed rate should increase as % acid increases. The variation is inconsistent with the bimolecular mechanisms, eq. 2, because the activity of water at 25° decreases by a factor of 6200 between 84.8 and 97.3% sulfuric acid, the concentration of sulfate ion is not detectable and the concentration of bisulfate ion decreases ten fold in the same region, Table 3.2. Thus, all $[N]\gamma_N$ should decrease sharply. With a partial positive charge on both entering oxygen atom and exiting nitrogen atom of 5, four protons are bound to atoms bearing a partial positive charge. It is assumed that the increase in number of charged bonds would counteract the charge dispersal so that the ratio γ_s/γ_t should be approximately constant. One would thus predict a decrease in rate as % acid increases. The experimental result is that the rate increases by a factor of 32.

t-Butyltrimethylammonium Ion (1) gives the same conclusion. Rate equations 1 and 2 can be applied in this system as in the previous one. The activity coefficient behavior will be different because of the change of substrate and of temperature. The effect of temperature on the activity coefficient behavior of charged species in aqueous sulfuric acid solutions has not been studied. It is assumed that the relative order of activity coefficient dependence is temperature independent. The activity coefficient of 1, γ_s , should vary with % sulfuric acid like that of tetraethylammonium ion, Table 3.3. For the unimolecular mechanism γ_t would again be expected to vary like tetraethylammonium ion. Therefore, the rate should be independent of % acid.

For the bimolecular mechanism, the activity of water at 175° decreases by a factor of 13 between 85 and 95% sulfuric acid. The activity coefficient of transition state (6) should increase rapidly relative to that of the ground state, since two protons bound to an oxygen atom with a partial positive charge are present in 6. For mechanisms with water, sulfate or bisulfate in the transition state, the rate of solvolysis should decrease as % acid increases. Table 3.4 shows that the rate is independent of % acid, in agreement with the unimolecular mechanism.

This study is consistent with a mechanism of solvolysis for tertiary alkyl compounds which is a simple dissociation of substrate. It proves that these transition states are not stabilized by water, sulfate ion or bisulfate ion. Although it provides information about the transition state, it cannot answer the questions whether or not *t*-butyl cation intermediates exist in these solvolyses, and if they exist, whether or not they are solvated specifically by water, sulfate ion or bisulfate ion.

These results are in striking contrast to the enolization of simple ketones in 80-100% sulfuric acid (C. G. Swain and A. S. Rosenberg, J. Am. Chem. Soc., 83, 2154 (1961)), where water was specifically involved in the transition state for cation (hydrogen ion) formation, and sulfuric acid, bisulfate ion and sulfate ion showed little or no ability to replace water in this role. (T. J. Lynch).

IV. Activity Coefficients of Cations in Sulfuric Acid

Complete data supporting those reported in the summary are contained in the Ph.D. thesis of Kenneth G. Harbison, M.I.T., June 1966. (K. G. Harbison)

V. Selectivity in Free Radical Reactions

A. Selectivity in Cage Recombination Reactions

Studies on free radical cage recombination are in progress to ascertain the orientational factors of radical pairs prior to recombination. Both meso and optically active DD-azo- α -phenylethane have been decomposed in benzene at 105° in the presence and absence of scavengers (nitroso-*t*-butane and benzenethiol). The 2,3-diphenylbutane fraction has been isolated and analyzed for the meso and "racemate" forms by vapor phase chromatography. The results are summarized in Table 3.6.

The "racemate" form has been isolated and analyzed for DD-LL components by polarimetry. The optical result is 28% (± 5) optical purity and of retained configuration.

These results indicate that radical cage recombination occurs before complete statistical orientation of the α -phenylethyl radicals in the "cage" is achieved. The

Table 3.6

2, 3-Diphenylbutane (DPB) from decomposition of
azo-bis- α -phenylethane (ABPE) in benzene at 105°

ABPE Reactant	Scavenger	% 2, 3-DPB ^a	2, 3-DPB meso/"dl"
meso	none	88	1.01
meso	(CH ₃) ₃ CNO	20 $\pm$ 1	1.10 $\pm$ .02
meso	C ₆ H ₅ SH	21 $\pm$ 1	1.12
DD	none	89	.95
DD	(CH ₃) ₃ CNO	32	.70
DD	C ₆ H ₅ SH	*	.80

a. Results of several runs at varying initial scavenger concentrations.

distribution of cage products formed from DD-ABPE is: DD-2, 3-DPB 38%, DL(meso)-2, 3-DPB 41%, LL-2, 3-DPB 21%. Analysis of these results in terms of the extent of departure from a statistical distribution indicates that the degree of optical activity is not in quantitative accord with the amount of meso product, possibly due to two distinct routes to products from azo compound. Decomposition in the presence of benzenethiol, deuterated on sulfur, affords 2, 3-diphenylbutane containing no label, indicating that reversible H (or D) transfer from scavenger to α -phenylethyl radical or to reactant azo compound does not occur. Further control experiments with deuterated 2, 3-diphenylbutane (2, 3-methyl-d₃) are in progress to ascertain the extent of dl-DPB meso-DPB equilibration (expected to be low).

Racemization in "tight" ion pairs has been established in a number of cases by H. Goering and others. The above study represents the first case, to our knowledge of the occurrence of this type of phenomenon in radical pairs in solution. (M. Berwick)

B. The 8-Hydrindyl System

Previous results from the decomposition of cis and trans-9-decalylcarbinyl hypochlorite have established the presence of two 9-decalyl radicals. In an effort to

ascertain whether the two forms differ in geometry at the 9-position or in the conformations of the rings, the more strained 8-hydrindyl system has been examined. The cis and trans 8-hydrindylcarbonyl hypochlorites have been prepared, and the structures of the products of decomposition, cis and trans 8-hydrindyl chlorides, have been established. The results of decomposition of the hypochlorites are summarized in Table 3.7. The chlorides are stable to the reaction conditions; the ratio

Table 3.7
Decomposition of cis and trans-8-hydrindyl carbonyl
hypochlorite in CFCl_3

	RCH_2OCl , M.	Temp.	% RCl	RCl <u>cis/trans</u>
cis	1.0	25	39	1.53
cis	1.0	0	30	1.45
cis	1.0	-40	23	1.45
cis	1.0	-78	31	1.52
cis	2.5	25	31	1.7
cis	2.5	0	22	1.8
cis	2.5	-40	16	1.54
cis	2.5	-78	12	1.54
trans	1.0	25	35	1.65
trans	1.0	0	29	1.54
trans	1.0	-40	34	1.45
trans	1.0	-78	29	1.40
trans	2.7	25	32	1.75
trans	2.7	0	35	1.7
trans	2.7	-40	28	1.7
trans	2.7	-78	28	1.75

of cis/trans RCl does not change within experimental error (and is considerably removed from the equilibrium value) over the range of concentrations and temperatures investigated. Under approximately the same conditions which give rise to large variations in the ratio of trans/cis-9-chlorodecalin, the ratio of trans/cis-8-chlorohydrindane remains constant. These data require a common intermediate for the radical from cis and trans precursors in the hydrindyl series. If angle constraint

at C-9 were the reason for detection of two kinds of 9-decalyl radicals, this effect would have been expected to be magnified in the 8-hydrindyl system. The failure to observe an enhancement in stereospecificity in atom transfer in the latter system indicates that factors other than angle strain are the definitive ones (e. g. such as "eclipsing" effects). Although the cis/trans selectivity in atom transfer to the 8-hydrindyl system is the lowest observed to date, this lack of selectivity is uninformative regarding planarity or non-planarity of the 8-hydrindyl radical. If this radical is pyramidal, the energy for cis-trans interconversion must be considerably smaller than the activation energy (estimated at ~ 5 kcal./mole) for the chlorine atom transfer step. (J. P. Engstrom)

C. Stereochemistry of Cyclic Ether Formation by Lead Tetraacetate

The reaction of erythro-5-deuterio-2-hexanol with lead tetraacetate in chlorobenzene at 83° gave a 7% yield of cis-2,5-dimethyltetrahydrofuran and a 14% yield of the trans derivative. Each ether was 84% monodeuterated. Decomposition of the hypochlorite of this alcohol at -78° followed by cyclization under basic conditions afforded 12% of cis-2,5-dimethyltetrahydrofuran and 12% of the trans isomer. Each isomer was 92% monodeuterated. The mixture of isomers obtained from the decomposition of the hypochlorite at 80° was 80-82% monodeuterated. The identity of the extent of deuteration in the cis and trans ethers from the lead tetraacetate cyclization and the hypochlorite decomposition at -78° demonstrates the nonstereospecificity of ether formation. Abstraction of protium from the δ -carbon must occur in a step prior to and distinct from the further reaction of this resulting species to form cyclic ether (lead tetraacetate) or chlorohydrin (hypochlorite). The observed deuterium isotope effect k_H/k_D for the lead tetraacetate closure is 5.8 ± 0.2 at 83° vs. 4.7 ± 0.2 or 4.2 ± 0.1 at 80° for the decomposition of the hypochlorite. This observed isotope effect is a composite of a normal deuterium isotope effect and any steric effect associated with difference in ease of abstraction of protium in the transition states in which the 2- and 5-methyl groups are cis or trans. Although the abstracting species in the hypochlorite decomposition is a free alkoxy radical, in the lead tetraacetate reaction the abstracting oxygen may still be under the influence of the lead moiety.

The synthesis of erythro-5-deuterio-2-hexanol was effected by S_N2 displacement by lithium aluminum deuteride of one of the tosylate groups of meso-2,5-hexyl ditosylate to afford threo-5-deuterio-2-hexyl tosylate; S_N2 displacement by acetate of the second tosylate group to afford erythro-5-deuterio-2-hexyl acetate; and alkaline hydrolysis to afford erythro-5-deuterio-2-hexanol. The stereochemistry of cis and trans-2,5-dimethyltetrahydrofuran was established by stereospecific cyclization from meso-2,5-hexanediol. Cyclizations of 2-hexanol with lead tetraacetate, lead tetraacetate and iodine, mercuric oxide and iodine and decomposition of the hypochlorite are compared. All cyclizations retained the original oxygen-18 when 2-hexanol- O^{18} was utilized. Other low-boiling products of the lead tetraacetate cyclization were 2-hexanone, 2-hexyl acetate, and 2-hexanol.

The mercuric oxide and iodine closure of S-(+)-4-methylhexanol-1 at 80°, photolytically, yielded essentially optically inactive 2-ethyl-2-methyltetrahydrofuran indicating a stepwise, nonstereospecific hydrogen abstraction and ring closure sequence in this reaction also. The absolute configuration of S-(+)-2-ethyl-2-methyltetrahydrofuran was established. A comparison of cyclization of the optically inactive alcohol by lead tetraacetate, lead tetraacetate and iodine, and mercuric oxide and iodine is given. (M. J. L. Rafuse)

D. Stereochemistry of Atom Transfer to the 4-t-Butyl-1-Methylcyclohexyl and the 2-norbornyl radicals

The stereochemistry of chlorine transfer from alkyl hypochlorite to the 4-t-butyl-1-methylcyclohexyl radical has been examined by the free radical chain decomposition of cis and trans-4-t-butyl-1-methylcyclohexylcarbinyl hypochlorites in carbon tetrachloride. The major products of the decomposition are cis and trans-4-t-butyl-1-methylcyclohexyl chlorides. The ratio of trans and cis chloride, found to be independent of the stereochemistry of the starting hypochlorite, was 3.4 (0.19 M at 62°) to 2.9 (0.19 M at -20°), thus indicating a common intermediate for both reactions and preferential formation of axial carbon-chlorine bond in the transfer of chlorine from hypochlorite to the alkyl radical. Reduction of both cis and trans-4-t-butyl-1-methylcyclohexyl chloride with tri-n-butyltin hydride afforded the same cis and trans-4-t-butyl-1-methylcyclohexane in a ratio of ~ 1 to 12. The structures

of the hypochlorites, prepared from the corresponding alcohol, were assigned on the basis of the stereochemistry of the cis and trans-4-t-butyl-1-methylcyclohexanecarboxylic acids, precursors to the alcohols. The structures of the acids were assigned on the basis of the methods of synthesis and conversion with retention of configuration of the trans acid to the known trans-4-t-butyl-1-methylcyclohexanol. The structures for the cis and trans-4-t-butyl-1-methylcyclohexyl chlorides were assigned on the basis of the infrared spectra, ease of dehydrohalogenation, and equilibration reactions.

The chlorine transfer to the 2-methyl-2-norbornyl radical was studied by the free radical chain decomposition of exo and endo-2-methylbicyclo[2.2.1]heptane-2-carbinyl hypochlorite. The 2-exo and endo-chloro-2-methylnorbornanes were found to be the major products from the decomposition of the exo hypochlorite and the minor products from the endo hypochlorite (the major product was the cyclic ether 4-methyl-2-oxa-tetracyclo[4.2.1.0⁴⁻⁸]nonane). The ratio of exo to endo chlorides was found to be the same from both precursors, 4.9 (0.27 M at 0°) to 4.6 (0.27 M at -40°).

Hydrogen transfer to the 2-methyl-2-norbornyl radical was examined by free radical chain reaction of tri-n-butyltin hydride with 2-exo and endo-chloro-2-methylnorbornanes. A ratio of ~ 16 to 1 of 2-endo-methylnorbornane to 2-exo-methylnorbornane was obtained. Thus, both chlorine atom transfer from hypochlorite and hydrogen atom transfer from tri-n-butyltin hydride occur preferentially from the exo-direction, with the latter atom transfer step showing the greater selectivity. (A. Fang)

VI. Mechanisms of Decomposition of Peroxygen Compounds

A. Peroxygen Compounds

α -Methylstyrene oxide, a possible intermediate in the decomposition of β -methyl- β -peroxypropiolactone was synthesized and subjected to the conditions employed to decompose the per lactone. The results obtained from a series of experiments indicate that α -methylstyrene oxide undergoes little rearrangement under

these conditions and is therefore not an intermediate in the decomposition of the perlactone.

1-Phenylcyclopropanol was studied as a possible intermediate in the decomposition of β -methyl- β -phenyl- β -peroxypropiolactone. The cyclopropanol was decomposed under conditions employed to decompose the perlactone. An essentially quantitative rearrangement to propiophenone, the major product of the decomposition of perlactone was observed to occur. A subsequent deuteration experiment, however, involving methyl- d_3 perlactone excluded 1-phenylcyclopropanol as a possible reaction intermediate in the thermal decomposition of the perlactone.

B. Peresters.

A new method has been developed for the preparation of simple methyl (or ethyl) peresters involving the direct alkylation of the salt of the peracid by an oxonium salt. Preliminary results of the thermal decomposition of methyl p-bromoperbenzoate indicate an efficiency in radical generation of 30%, determined by radical-counting experiments with the "Koelsch" radical. Of the remaining 70%, the majority is observed as p-bromobenzoic acid. A distinction between cyclic decomposition vs. cage recombination for this 70% cannot be made at this time.

The rate of decomposition of methyl p-bromoperbenzoate in benzene at 105° is $k = 8 \times 10^{-4} \text{ sec.}^{-1}$, roughly comparable to the rate of decomposition of t-butyl perbenzoate. The methyl perester shows moderate sensitivity towards radical induced decomposition, and high sensitivity towards acid catalysis. 4-Bromobiphenyl, a product of the thermal decomposition, is not a product of the acid-catalyzed decomposition. (G. A. Knudsen, Jr.)

VII. Electron Transfer Phenomena

Attention has been directed towards examination of radical ions formed by charge transfer between organic molecules, principally with use of a new strained ring system recently observed in these laboratories. Reaction of 2,3-di-t-butyldiaziridinone (DZ) with N,N,N',N'-tetramethyl-p-phenylenediamine (W) affords the characteristic blue color of the Wurster's radical cation (W^+). The overall reaction

is dependent on solvent "polarity" and solvent purity. In protic solvents, DZ is converted to the urea. The types of radical anions that may be formed by electron transfer to "strained" rings are of special interest in that these species may remain cyclic or may open to acyclic radical ions. Efforts to observe $[DZ]^{\cdot-}$ by electron magnetic resonance have been unsuccessful. Use of electron transfer agents such as sodium naphthalene leads to the ring-opened dianion of the urea,
 $R-\overset{\ominus}{N}-CO-\overset{\ominus}{N}-R$. (T. H. Lowry)

ADDRESSES

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PHYSICAL CHEMISTRY GROUP

I. Determination of Vapor-Liquid Equilibrium by Static Measurements

A. Apparatus

The apparatus has been working well all the year. The measurements on aqueous sodium chloride are computed and correlated, those on lithium chloride are nearly completed and a few have been made on a model sea salt.

The quantities to be measured are the equilibrium temperature and pressure, the total quantity of each component, and the volume of the vapor phase. The core of the apparatus is shown in Figure 4.1. The two-compartment oil thermostat contains the cell on the left with the thermopile well, W, a side tube, G, with a mercury-sealed ground glass stopper and an annular stirrer, S, which is a soft iron ring enclosed in glass. Another side tube leads to the vapor arm of the small manometer, A₁, and to a mercury U seal. The helium side of this manometer is connected to the large manometer through the Stopcock S₁, and to the vacuum system and helium reservoir through S₂. When the seal U is open, the cell may be connected to the degassing system or to the manifold for the transfer of water or other volatile material. Non-volatile materials are added, and the final solution is removed, through the tube G.

Figure 4.1

W thermopile well; G ground glass stopper; S stirrer, U seal; A₁, A₂ arms of null manometer N; S₁, S₂, stopcocks, S₃, S₄ mercury seals.

The right hand thermostat is kept 0.5° warmer than the left hand side and controlled to 0.01° . The left hand side is controlled to 0.001° with a platinum resistance thermometer, reflecting galvanometer, cadmium photocell and thyatron circuit.¹ The temperature of the cell is determined with a 20-junction copper-constantan thermopile. The stirrer is raised and lowered every six seconds. Twice in each cycle the stirrer breaks the surface, and most of the solution is forced through narrow gaps between the stirrer and the thermopile well and between the stirrer and the cell wall. For pressures less than 25 mm, that is at 25° for water, pressure is read on the small manometer with the helium side evacuated. For larger pressures, the small manometer is used only as a null manometer and the pressure is measured on the large manometer.

After a solution sample has been added and thoroughly degassed, the pressure is measured at 25° , then at 12.5° intervals to 100° . Then the cell is cooled to 25° and all the solution removed with a hypodermic syringe. It is weighed and analyzed gravimetrically as AgCl to give the low-temperature composition. Because of evaporation into the vapor space, the concentration is about 0.1% greater at 75° , and 0.3% greater at 100° , than at 25° . The concentration is determined precisely for each temperature from the total volume minus that of the liquid.

The activity of the water, a_w , in a solution is determined by correcting the ratio of the vapor pressure to that of pure water for the deviation of water vapor from perfect gas behavior. Then the osmotic coefficient ϕ is determined through its definition, $\phi = -\ln a_w / 0.01802 \sum_i m_i$, in which $\sum_i m_i$ is the total stoichiometric concentration of solutes, molecules or ions.

B. Sodium Chloride

Ten solutions of sodium chloride in water, ranging in concentration from 1.0 to 6.1 m (almost saturated) were studied from 25° to 100° . The results for ϕ as a function of T are shown in Fig. 4.2. The ordinate scale is different for each solution, but its location and the 25° concentration are shown for each.

The curves in Fig. 4.2 are determined from the equation

$$\phi = 1 - \frac{\sum_i m_i z_i^2}{\sum_i m_i} S \left[1+x - \frac{1}{1+x} - 2 \ln(1+x) \right] I^{1/2} / x^3 + \sum_{j=1}^p B_j I^j \quad (1)$$

in which z_i is the valence of the i 'th ion, I is the ionic strength, $\sum_i m_i z_i^2 / 2$, $x = A I^{1/2}$, S and B_j are functions of the temperature of the form

$$B_j = B_j^\circ + B_j^{(1)} / T + B_j^{(2)} \ln T + B_j^{(3)} T + B_j^{(4)} T^2 + \dots, \quad (2)$$

S is the Debye-Hückel limiting slope in terms of weight-molal concentrations and is characteristic of the solvent. Its parameters are determined by least squares from the density² and dielectric

1. G. Scatchard, W. J. Hamer and S. E. Wood, J. Am. Chem. Soc., 60, 3061 (1938).

2. International Critical Tables, Vol. III, pp.25-26, McGraw-Hill Book Company, New York, N.Y. (1928)

constant^{1,2} of the solvent as functions of the temperature. A and the parameters of B are characteristic of the solvent and the solute. A is independent of the temperature, 1.5 for sodium chloride in water. The parameters of B may be determined from the measurements of ϕ . We have chosen, however, to accept as exact the values of $\partial\phi/\partial(1/T)$ and $\partial[\partial\phi/\partial(1/T)]/\partial T$ calculated from the tables of Parker³. We have limited the sum in equation 1 to B_3I^3 , and that in equation 2 to $B_j^{(4)}T^2$. This leaves nine parameters to be determined from our osmotic coefficients.

Figure 4.2

Osmotic Coefficient, ϕ . ○● measured, — calculated

The equations are:

For all electrolytes in water, 0° to 250°,

$$S = -289.0653 + 6202.357/T + 54.42507 \ln T - 0.1619930T + 0.00008596094 T^2$$

For NaCl in water, 0° to 100°,

$$B_1 = 458.2852 - 9939.9942/T - 85.71682 \ln T + 0.249167 T - 0.0001218967 T^2$$

$$B_2 = -131.2712 + 2889.6818/T + 24.447833 \ln T - 0.06909258 T + 0.00003256212 T^2$$

$$B_3 = 14.169074 - 311.5423/T - 2.638115 \ln T + 0.007427125 T - 0.000003475629 T^2$$

The average deviation of ϕ from the equation is less than 0.002.

1. B.B. Owen, R.C. Miller, C.E. Milner, and H.L. Cogan, J. Phys. Chem. 65, 2065 (1961).

2. G. C. Akerlöf and H. I. Oshry, J. Am. Chem. Soc. 72, 2844 (1950).

3. Vivian B. Parker, "Thermal Properties of Aqueous Uni-univalent Electrolytes", N.S.R.D.S. NBS-2, 1965.

Fig. 4.3 shows the deviations of our measurements of ϕ at 25°, those of Frazer and Negus¹, those of Olynyk and Gordon² and the tables of Robinson³ and of Scatchard, Hamer and Wood⁴. The tables of Robinson are based largely on the results of Frazer and Negus, of Olynyk and Gordon and those of Shankman and Gordon on aqueous sulfuric acid.⁵ The two latter were not available for the earlier tables of Scatchard, Hamer and Wood⁴, who used also other measurements on both these systems.

Figure 4.3
Deviations of ϕ at 25° from Equation

From the equation for ϕ may be calculated all the other thermodynamic properties which do not depend upon the pressure derivative of the free energy.

The equation may be extended to lower concentrations. It may be extrapolated over a small temperature range. It fits the freezing point curve of Rodebush⁶ within the experimental error of his temperature measurements except at the eutectic point (5.20 m, -21.12°). This measurement is also brought into line if the eutectic concentration, which he did not measure, is raised 0.4 percent to 5.22 m.

The equation agrees well with the activities of water in sodium chloride solutions of Gardner, Jones and de Nordwall⁷ at 125°, but not at higher temperatures. However, inclusion of their results to 275° and those of Frazer and Negus and of Olynyk and Gordon at 25° with ours increases the average deviation of our results only from 0.0018 to 0.0022, even though it almost doubles the number of points and almost triples the temperature range.

1. S. S. Negus, thesis, Johns Hopkins University (1922); J. C. W. Frazer, "The Direct Measurement of Osmotic Pressure. Contemporary Developments in Chemistry", Columbia University Press, New York, N. Y., 1927.
2. P. Olynyk and A. R. Gordon, J. Am. Chem. Soc. 65, 224 (1943).
3. R. A. Robinson, Trans. Roy. Soc. N. Z., 75, 203 (1945).
4. G. Scatchard, W. J. Hamer and S. E. Wood, J. Am. Chem. Soc. 60, 3061 (1938).
5. S. Shankman and A. R. Gordon, J. Am. Chem. Soc. 61, 2370 (1939).
6. W. H. Rodebush, *ibid.* 40, 1204 (1918).
7. E. R. Gardner, P. J. Jones, and H. J. de Nordwall, Trans. Faraday Soc. 59, 1994 (1963); also unpublished results.

C. Lithium Chloride.

We have determined in the same way the osmotic coefficients of seven solutions of lithium chloride between 4m and 18.5m, but we will not attempt an equation until we have made more measurements. We may note, however, that the osmotic coefficients are much larger than those of sodium chloride at the same concentrations and that they decrease almost linearly with increasing temperature. For the most concentrated solution ϕ is 3.054 at 25° and 2.324 at 100°. The activity of the water varies from 0.13 to 0.21.

D. Model Sea Salt

The behavior of sea water and its concentrates is of considerable practical interest at present because of its relation to desalination. It is of more interest to us theoretically because an oversimplified theory proposed by one of us indicates that the osmotic coefficients at 25° may be calculated from those of sodium chloride. Johnson and Rush¹ tested this isopiastically for a model sea salt at 25° and found that it holds remarkably well. We have studied a solution with ionic strength 5.79 at 25° and plan to study one or two more dilute solutions.

The model sea salt has the following equivalent fractions: 0.779 Na⁺, 0.016 K⁺, 0.205 Mg⁺⁺, 0.906 Cl⁻, 0.094 SO₄⁼. It differs from normal sea water mostly in the replacement of 0.033 Ca⁺⁺ by Mg⁺⁺ to prevent the precipitation of CaSO₄. The theory indicates the equation for ϕ of sea salt solutions should be the same as that for NaCl except that $\sum m_i z_i^2 / \sum m_i$ is changed from 1.0 to 1.241.

At 25° the measured value is 0.004 less than the calculated, which is also the average deviation of the two 6.1m solutions of NaCl. At 50° the two are equal. At 62.5° the deviation is -0.013 and it increases to -0.016 at 100°. (H. F. Gibbard, Jr. and George Scatchard)

II. The Osmotic Coefficients and Other Related Properties of Aqueous
12-Tungstosilicic Acid (H₄W₁₂SiO₄₀) at 25°

A paper with this title by S. Y. Tyree, R. L. Angstadt, F. C. Hentz, Jr., R. L. Yoest and George Scatchard was published in the Journal of Physical Chemistry, 1966, 70, 3917. The abstract is:

"We have measured the osmotic coefficient, ϕ , of aqueous 12-tungstosilicic acid at 25° from 0.04 m to 0.87 m by isopiestic (isotonic) comparison with KCl and with NaCl, and determined an analytic expression for it by which $\ln \gamma_{\pm}$ and $\partial \ln \gamma_{\pm} / \partial \ln m$ may be computed. We have compared our results with earlier measurements of light scattering and ultracentrifuge equilibrium.

"We confirm the earlier findings that this acid is a typical highly ionized strong electrolyte."

---

1. R. M. Rush and J. S. Johnson, J. Chem. Eng. Data 11, 590 (1966).

The first three authors were at the University of North Carolina in 1961 when some isopiestic measurements of ϕ over this range were reported in the Ph.D. Thesis of Angstadt, and others were made by Hentz, because those of Angstadt did not fit well with the light scattering and ultracentrifuge measurements below 0.04 m reported by Johnson, Kraus and Scatchard.¹ For the same reason we repeated the measurements from 0.048 to 0.36 m as reported in LNS Progress Report, May 1, 1962, p. 8 and in the Ph.D. Thesis of Yoest, 1964.

The results are expressed by the equation $\phi = 4 \times 1.1170 [1 + x - 1/(1 + x) - 2 \ln(1 + x)] I^{1/2}/x^3 + 0.0061 I + 0.0133 I^2 - 0.000544 I^3$ with $x = 2.690 I^{1/2}$. For a tetrabasic acid $I = 10$ m and $\sum m_i z_i^2 / \sum m_i = 4$.

The results of a few new ultracentrifuge measurements by J. S. Johnson were included.

The discussion of the work of others and much of the writing was done at MIT. (R. L. Yoest (terminated) and G. Scatchard)

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