

BROOKHAVEN NATIONAL LABORATORY

Quarterly Progress Report

April 1 - June 30, 1950



Associated Universities Inc.
under contract with the
United States Atomic Energy Commission

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FOREWORD

This is the second of a series of Quarterly Progress Reports. While most of the departments have summarized their work or used a form comparable to abstracts, the Chemistry Department has given both abstracts and complete reports on its work. The major part of the progress in the Reactor Science and Engineering Department is being presented simultaneously in a separate classified report.

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PHYSICS DEPARTMENT

The research progress of the Physics Department is described under five subdivisions: 1) dynamic properties of atomic nuclei, 2) stationary properties of nuclei, 3) high energy particle physics, 4) research in other branches of physics carried out with the use of neutrons or other nuclear techniques, and 5) theoretical topics not included under the above headings. Under subdivision (1) are included investigations of radioactivity and nuclear reactions induced by gamma rays, neutrons, and particles accelerated in the cyclotron or Van de Graaff accelerator. Under (2) are the measurements of nuclear mass and moment. Investigations listed under (3) are chiefly concerned at this time with the cosmic radiation, but will eventually deal with effects produced with the Cosmotron. Those listed under (4) include neutron diffraction studies of the solid state and measurements of coherent scattering amplitudes. Needless to say, the grouping is somewhat arbitrary.

Dynamic Properties of Atomic Nuclei

Gamma Rays from Po²¹⁰

An investigation with the lens spectrograph of the gamma rays from Po²¹⁰ was prompted by reports in the literature by Chang (Phys. Rev. 69, 60 (1946)) of several range groups of alpha particles, suggesting a number of excited states of the residual nucleus, Pb²⁰⁶. It was also known from a study of Bi²⁰⁶ (BNL 39 (AS-3), p. 15, (July-December, 1949)) that the Pb²⁰⁶ resulting from K capture emitted an unusually rich gamma spectrum. A study of the excitation of this nucleus by alpha emission was expected to assist in determining the decay scheme. A source of Po²¹⁰ having an alpha activity of 480 mc was mounted in the spectrograph, and the internally converted electrons were studied at 1.9% resolution. In another run, the gamma rays were converted externally in uranium foil, and the spectrum was studied at 4% resolution. In both runs, a single gamma ray was found at 803 kev, agreeing within 0.5% with one of the gamma rays found in the spectrum of Bi²⁰⁶. Since careful search has failed to reveal other gamma rays from Po²¹⁰, it is probable that the observed line is due to a transition from the first excited to the ground state of Pb²⁰⁶. This is probably the same excited level found from the triton groups in the cyclotron-induced reaction, Pb²⁰⁷(d t) Pb²⁰⁶, which has been reported at 860 kev (MIT Laboratory for Nuclear Science and Engineering, Progress Report, April 1, 1950). In the present work, the K:L ratio of the internal conversion in Po²¹⁰ has been determined as 3.7±0.5. However, since the theoretical values of K:L have not been calculated for the high atomic numbers, one cannot yet infer the multipole order of the transition. Comparing with the values of K:L calculated for atomic number 35, which is not a reliable procedure, a spin change of 4 is indicated. If this were the correct spin change, an 803-kev state would have a lifetime of 0.01 sec. However, such a large spin change is not consistent with the finding at MIT that both triton groups are of nearly the same intensity. As another conclusion from this work, it may be noted that only one gamma ray is emitted for about 10⁵ alpha particles;

hence, the excitation of this level could not explain the structure of the alpha spectrum reported by Chang. A report of this work will soon be submitted for publication in Physical Review.

(D.E. Alburger)

Gamma-Ray Transitions

New gamma rays have been found in the following cases:

Cd^{115} (2.5d), previously reported to have a 520-kev gamma ray, is shown to have two gamma rays, of 495 and 529 kev, respectively.

W bombarded in the Oak Ridge reactor is found to have high energy gamma rays which yield photoneutrons from Be but not from D. The activity decays with a half-life of approximately 3 months, and may be due to W^{188} formed by successive neutron capture from $\text{W}^{186}(\text{n } \gamma)\text{W}^{187}(24\text{h})(\text{n } \gamma)\text{W}^{188}$.

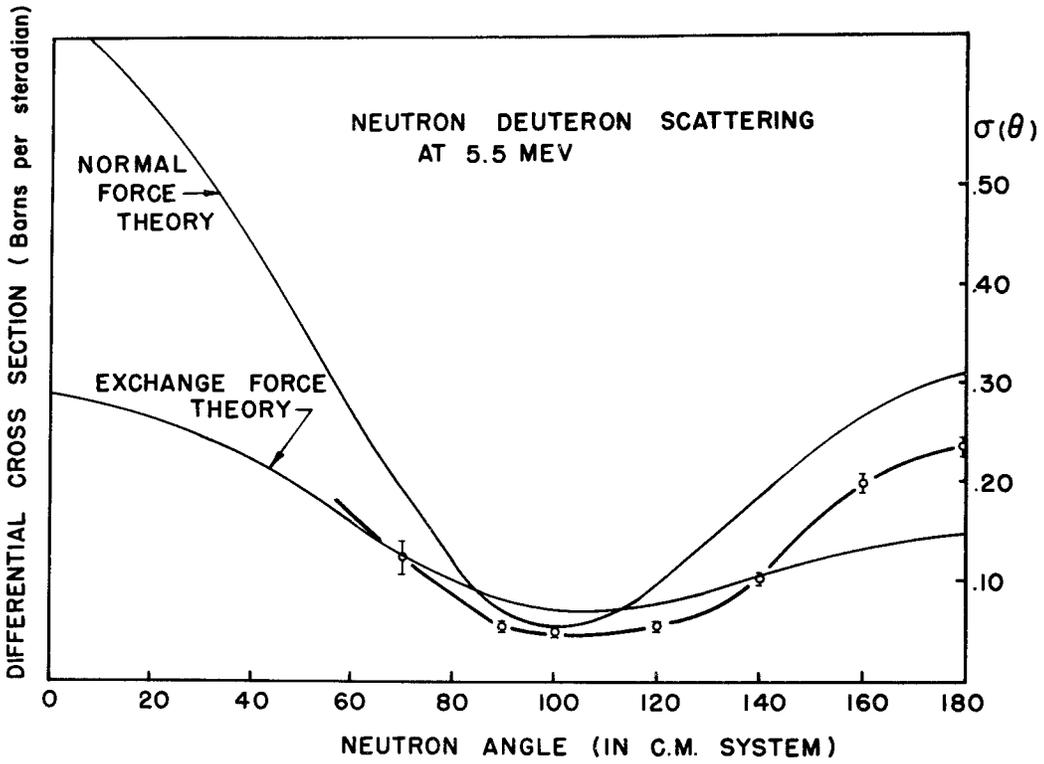
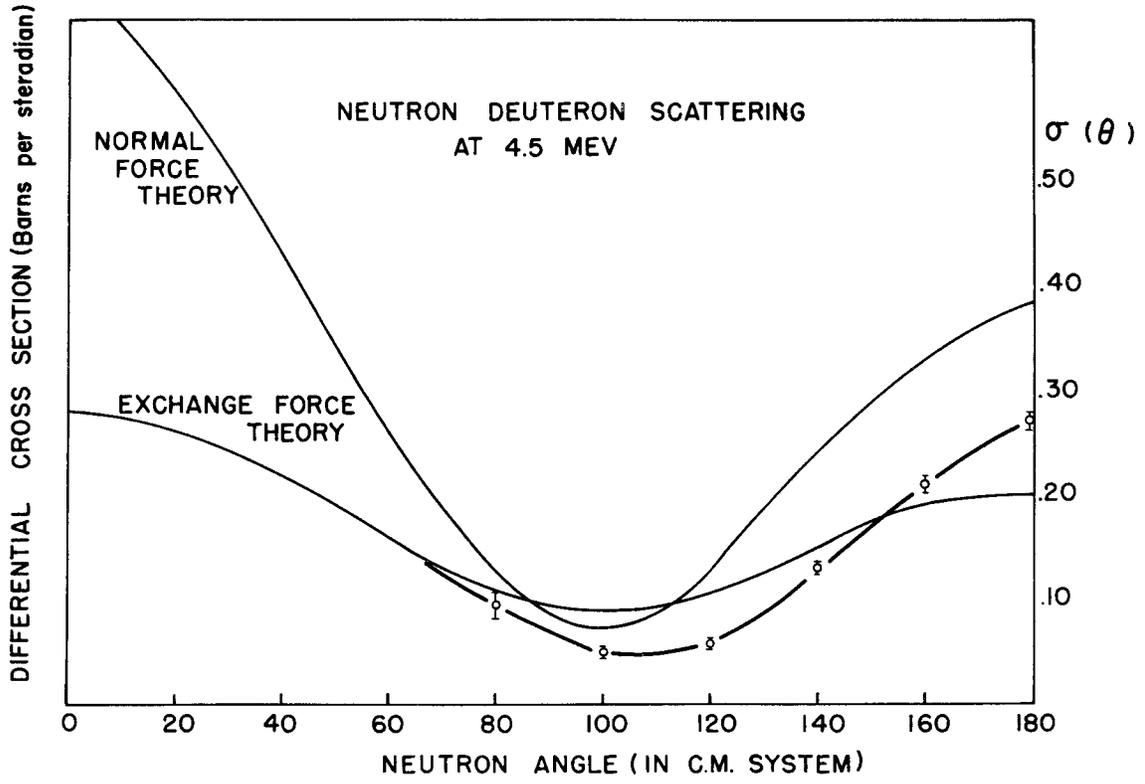
(D.E. Alburger, E. der Mateosian, M. Goldhaber)

Angular Distribution of Neutrons Scattered by Deuterons

Because of its bearing upon the nature of nuclear forces, the angular distribution and differential cross section has been investigated for neutrons of 4.5 and 5.5 Mev scattered by deuterons. Neutrons of these energies were obtained from a deuterium gas target bombarded by deuterons in the Van de Graaff accelerator of the Department of Terrestrial Magnetism, Carnegie Institution of Washington. Neutrons emitted within 3° of the forward direction, having a calculated energy spread of ± 100 kev, were incident upon the scatterer, which consisted of either 7.5 cc of deuterium gas at atmospheric pressure, or a 0.001" film of heavy paraffin. Recoil deuterons ejected at various angles from the scatterer were detected by a twofold coincidence telescope consisting of proportional counters filled to a pressure of a few cm Hg with a 25:1 mixture of argon and CO_2 . This arrangement gave a low background when the scatterer was removed.

The count of recoil deuterons at each position of the coincidence telescope was normalized to the same number of counts from a monitor counter which recorded protons from the D-D reaction; it therefore indicated a fixed total yield of neutrons. The absolute yield of the neutrons was obtained by making use of the cross section as measured by Hunter and Richards (Phys. Rev. 76, 1445 (1949)). This, together with the amount of scattering material and the geometry of the apparatus, was used to calculate the absolute values of the n-d differential scattering cross section. When hydrogen was substituted for deuterium in the scatterer, the distribution of recoil protons corresponded to isotropy in the center-of-mass system, and the total n-p cross section agreed with published values of Bailey, Bennett, Bergstrahl, Nuckolls, Richards, and Williams (Phys. Rev. 70, 583 (1946)).

The n-d scattering is compared in the accompanying figures with values derived from the theory of Buckingham and Massey (Proc. Roy. Soc. A179, 123



(1941). The ratio of the differential cross section at 180° to that at the minimum is approximately 5:1 at both energies; this is much larger than the ratio predicted by the theory based upon exchange forces. If one assumes a reasonable extrapolation of the experimental curves over the region where apparatus geometry made it impossible to get data, a value of the total cross section is obtained which is in reasonable agreement with that of Nuckolls, Bailey, et al. This work has been submitted for publication in Physical Review.

(E. Wantuch)

Asymmetries in Angular Distributions of Photoneutrons

In the one-particle model of the nucleus, the angular distribution of neutrons ejected by gamma rays is directly related to the wave function which describes the motion of that neutron in the potential well of the nucleus. Therefore, a systematic study of the angular distribution of photoneutrons from various nuclei with different gamma-ray energies may be expected to throw light on the structure of nuclei and guide further progress in the theory. Using the betatron at the Picatinny Arsenal as a source of 20-Mev gamma rays, the angular distributions of photoneutrons from Bi, Pb, and W have been investigated. In order to limit the investigation to the neutrons coming off with the highest energy, i.e., those most loosely bound to the nucleus, the detector consisted of a stack of aluminum plates enclosed in a cadmium shield; the beta activity induced therein by the n-p reaction, which has a threshold at 4.6 Mev, was measured with a thin-walled G-M counter. After a 10-minute irradiation in the betatron beam, the aluminum plates were counted. A decay curve was plotted to determine the activity of the 9.6m half-life of Mg^{27} , this being taken as a measure of the fast neutron intensity. The targets were in the form of cylinders, $3/4$ " in diameter x 3" long, placed with the axis perpendicular to the beam and to the plane within which measurements were taken. Detector foils were placed close to the cylinder and in azimuths to catch neutrons ejected forward and at right angles to the beam. After making a small correction for neutrons from the betatron beam which were scattered isotropically in the target, the photoneutrons ejected from the targets were found to be quite asymmetrically distributed, with approximately twice as many coming off at the 90° position as in the forward direction. This asymmetry for fast neutrons is in contrast with the isotropic distribution found in Pb and Fe by Price and Kerst (Phys. Rev. 77, 806 (1950)), who detected the slow neutrons as well. Comparing the total cross section for the fast neutrons with that reported by the above authors for the total neutron yield, it appears that only about one tenth of the total yield has sufficient energy to activate the aluminum detector. Because of the nearly continuous energy distribution in the betatron beam and the poor angular resolution of the detectors used in these experiments, it is difficult to carry the theoretical interpretation beyond noting that the results are consistent with a distribution of the form $A+B\sin^2\theta$, such as would be expected from dipole transitions. This work has been submitted for publication in Physical Review.

(H.L. Poss)

The Capture Cross Sections of Nuclei for Fast Neutrons

The capture cross section of a nucleus for neutrons in the 1-Mev region is proportional to the level density of the compound nucleus with the corresponding excitation. The cross sections can be measured quite accurately in this region with unmoderated fission neutrons (Hughes, Spatz, and Goldstein, Phys. Rev. 75, 1781 (1949)); the results give information on level density which is important for developing the theory of the highly excited states of the nucleus. Neutron capture in nuclei containing 50, 82, or 126 neutrons results in a compound nucleus of low excitation and low level density. Hence, the cross section is extremely low (Hughes and Sherman, Phys. Rev. 78, 632 (1950)). Adding to the many cross sections which have already been measured in this program, nuclei near the magic numbers and some normal nuclei are being measured. The materials have been irradiated at the Argonne National Laboratory and the activities, which are long lived, are being followed at Brookhaven National Laboratory.

New results may be stated as follows: a) Several nuclei containing 100 to 115 neutrons all have normal cross sections of about 150 millibarns. b) Nuclei near the magic numbers, such as those containing 84 and 86 neutrons, have cross sections below the normal value but above the extremely low values characteristic of the magic numbers. c) Since Ru^{102} has a cross section of only 5 millibarns, there seems to be evidence for a closed shell at 58 neutrons.

Arrangements are being made to construct a fast neutron source on top of the reactor which will provide 100 times more intensity than the one previously used at Argonne. This will enable fast neutron work, such as cross-section measurements and studies of gamma rays resulting from neutron capture, to be continued as soon as the reactor is in operation.

(D.J. Hughes, R.C. Garth)

Stationary Properties of the Nuclei

Nuclear Magnetic Resonance of Sb^{121} and Sb^{123}

The failure of earlier attempts to find a magnetic resonance absorption of the Sb nucleus in Sb_2O_3 and SbCl_3 may be attributed to the strong coupling between the electric quadrupole moment of the Sb nucleus and the nonuniform electric field of these two molecules, which might prevent the nucleus from precessing in the applied magnetic field. Therefore, a search was made for resonances with the SbCl_6^- ion in which the Cl atoms are believed to be symmetrically arranged to give a uniform electric field at the Sb nucleus. To obtain this ion, HSbCl_6 was dissolved in HCl. Distinct resonances in a magnetic field of approximately 9700 gauss were obtained in the vicinity of 9800 kc and 5300 kc which could be identified, according to spectroscopic information (Crawford and Bateson, Canadian Jour. Res. 10, 693 (1934)), with Sb^{121} and Sb^{123} , respectively. In a repeated series of readings, the magnetic field was electronically stabilized to 1 in 50,000, and frequencies were standardized against station WWV. The resonance frequencies were then compared with known values of neighboring resonances, that of Na in solid

NaCl for Sb¹²¹, and that of D in D₂O for Sb¹²³. The observed frequency ratios were:

$$\frac{\nu(\text{Sb}^{121})}{\nu(\text{Na}^{23})} = 0.90469 \pm 0.00004$$

$$\frac{\nu(\text{Sb}^{123})}{\nu(\text{D}^2)} = 0.8442 \pm 0.0001$$

Using Bitter's value (Phys. Rev. 75, 1326 (1949)) of the ratio $\nu(\text{Na})/\nu(\text{H}) = 0.26450 \pm 0.01\%$, and using a first-order diamagnetic correction for Sb of 1.00517, and for the H₂ molecule (used by Bitter) of 1.000027, the ratio of the g-values turns out to be:

$$\frac{g(\text{Sb}^{121})}{g(\text{H}^1)} = 0.24052 \pm 0.00003$$

The spectroscopic value of the spin of Sb¹²¹ is 5/2 and the magnetic moment of the proton (Taub and Kusch, Phys. Rev. 75, 1481 (1949)) is $\mu_{\text{H}} = 2.7935 \pm 0.005\%$ nuclear magnetons. Therefore, the magnetic moment of Sb¹²¹ is 3.3595 ± 0.0004 nuclear magnetons. In similar manner, the magnetic moment of Sb¹²³ can be derived from the ratio of the g-values of the deuteron and proton, together with the spectroscopic value 7/2 for the spin of Sb¹²³. One obtains $g(\text{Sb}^{123})/g(\text{H}^1) = 0.13025 \pm 0.00002$, and $\mu(\text{Sb}^{123}) = 2.5470 \pm 0.0003$ nuclear magnetons. The ratio of the g-values of the antimony isotopes is $g(\text{Sb}^{121})/g(\text{Sb}^{123}) = 1.8466$, whereas the value reported from spectroscopic evidence by Bateson and Crawford was 1.82 ± 0.02 . This work has been submitted for publication in Physical Review.

(V.W. Cohen, W.D. Knight, T. Wentink, Jr., W.S. Koski)

High Energy Particle Physics

Meson Production by Primary Cosmic-Ray Protons

In the last quarterly report (BNL 51 (S-5)), results were given of the analysis of nuclear disruptions, or "stars," observed in photographic emulsions exposed, during balloon flights, to the primary cosmic-ray protons at two different latitudes -- a northern latitude, where protons of all energies above about 1 Bev were present, and a southern latitude, where only high energy protons above about 8 Bev were present. The analysis attempted to discern a possible effect of the different energy spectra of the primary protons on the multiplicity of mesons produced in a star, the tracks exhibiting minimum grain density being attributed to relativistic mesons.* However, no change in average multiplicity of the meson tracks appeared above the statistical fluctuations in the samples which had then been analyzed, and it was clear that the multiplicity did not depend strongly upon the proton energy. The results did show, however, that the multiplicity of meson production in heavy nuclei of Ag and Br exceeded that in the light nuclei C, N, and O. This was taken as evidence that mesons are probably pro-

*These tracks cannot yet be identified with absolute certainty with relativistic mesons; they are referred to as meson tracks to simplify the language.

duced singly, or, at most, doubly, at each nucleon-nucleon collision, the cross section for production being nearly independent of the energy, and that the number of such nucleon-nucleon collisions per traversal of the nucleus by the incoming proton is greater in the heavier than in the lighter nuclei.

In more recent analyses submitted for publication in Physical Review, attention has been directed to the variation with latitude, or with proton energy, of the multiplicity of meson tracks appearing in each of two classes of star size -- the small stars with less than 6 heavy prongs, which can be identified with nuclei in the C,N,O group, and the large stars with 9 or more heavy prongs, which can be identified with Ag or Br nuclei. When broken down in this way, the data definitely show that, whereas there is no change of multiplicity of meson production with proton energy in the light nuclei, the average multiplicity in heavy nuclei increases from 3.2 ± 0.4 to 5.2 ± 0.4 in going from the high to the low latitude. These figures apply to proton-induced stars having at least one outgoing relativistic particle. By a subtraction process, one finds that the average multiplicity of mesons produced in the heavy nuclei by protons in the 1 to 8-Bev range is only about half that produced by protons in the range above 8 Bev. Very similar results are obtained if proton-induced stars with no outgoing relativistic particles are included in the count. Since there is no change with latitude in the multiplicity of mesons produced in light nuclei, it is possible to rule against the previously existing possibility that the multiplicity in single nucleon-nucleon encounters might depend upon proton energy. The increase of multiplicity with proton energy in heavy nuclei must then be evidence that there are more meson-producing encounters between nucleons in these nuclei when the energy of the incoming proton is higher. For protons in the 1 to 8-Bev range, the average multiplicity of meson production is the same in both light and heavy nuclei, i.e., about 1.5 per star. This would seem to indicate that the meson producing ability of a proton in this energy range is fully expended even in the light nuclei. It is also noted that the average multiplicities observed are too low to be readily reconciled with other measurements of total meson intensity.

Further evidence, not yet prepared for publication, for the general view that multiplicity of meson production results from multiple collisions between nucleons within the nucleus, and not from a single collision between two nucleons, has been found in a study of the angular distribution of the meson tracks. In the case where single mesons are produced by a high energy proton in collision with a light nucleus (stars produced near the equator with less than 6 heavy prongs), the median angle between the incoming proton and the outgoing meson is about 20° . An angle of this magnitude is consistent with the assumption that a single meson is emitted with random direction in the center-of-mass system of two colliding nucleons, with only enough energy lost in the process to create its mass. When more than one meson is produced, or when a larger number of heavy prongs in the star indicates considerable cascading in a heavy nucleus, the mesons diverge from the direction of the incoming proton by much larger angles, the median in this case being about 40° .

(E.O. Salant, J. Hornbostel, C.B. Fisk, J.E. Smith)

Design of Permanent Magnets for Cloud Chamber Work

For the measurement of the momenta of cosmic rays, a magnetic field can be placed between two cloud chambers. In this arrangement, the air gap of the magnet can be made much smaller without loss of counting rate than when a cloud chamber is mounted between the pole pieces of a magnet; for small gap widths, a permanent magnet is capable of producing a strong magnetic field. Since angular deflections of rays passing through the cloud chambers and the magnetic field are to be measured, the product of the magnetic field intensity H in the gap and the height of the pole faces h should be made as large as possible in order to extend the measurements toward larger momenta. Models of such magnets have been tested in order to determine the optimum amount and distribution of the magnetic alloy.

A simple and approximate calculation shows that, if the variables are chosen appropriately, one single constant can be adjusted so that all the experimental results can be fitted, within a few percent, to a universal function. By means of a simple coordinate transformation of the universal curve, one can then predict field intensities, or determine optimum construction of a large variety of permanent magnets. Reasonable accuracy can be expected as long as the ratio of gap length to linear dimension of the pole faces is less than $1/4$, a condition which will probably always be met in cloud chamber work.

A few examples are calculated, among them the present problem to maximize the product Hh . The field intensity to be expected from a magnet of quite different dimensions constructed by Brode is also checked, and satisfactory agreement is found.

Finally, details on the design of the large magnet constructed at the Laboratory are presented. This work is being submitted to Review of Scientific Instruments for publication.

(R.P. Shutt, W.L. Whittemore)

Neutron Reflection and Diffraction

Coherent Neutron-Proton Scattering by Liquid Mirror Reflection

The experiment to measure the coherent scattering amplitude of hydrogen for slow neutrons, described briefly in the last Quarterly Progress Report (BNL 51 (S-5)), has now been repeated by a somewhat more refined technique, giving a more reliable result, but one which agrees, within the probable errors, with that previously reported. This quantity is important to measure because of its direct bearing upon the range of the neutron-proton force field. In the new experiments, as in the old, the amplitude of hydrogen is compared with that of carbon; the latter is well known from transmission measurements. The method takes advantage of the fact that the neutron index of refraction of a material depends only upon the sum of the coherent scattering amplitudes of its constituents. Since the scattering amplitudes of carbon and of hydrogen are of opposite sign, it is possible to find hydrocarbons in which the carbon and hydrogen roughly balance and

the total amplitude is approximately zero; a relatively inexact measurement of the residual scattering amplitude, combined with an accurate determination of the ratio of C to H, will yield an accurate value of the ratio of the scattering amplitudes. The residual scattering amplitude of such a liquid is determined by measuring the critical angle of reflection from the liquid surface. This gives immediately the index of refraction and the residual scattering amplitude.

This scheme was first used with triethyl benzene ($C_{12}H_{18}$) (Phys. Rev. 77, 291 (1950)), but two improvements have now been effected. The liquid mirror and collimator have been redesigned to increase the reflected intensity by a factor of ten and to give a negative meniscus of the liquid surface, so that no part of the reflected beam is affected by transmission through the mirror material. Also, a method was introduced for determining the ratio of the carbon and hydrogen amplitudes which eliminated the need for any exact knowledge of the neutron spectrum in the beam. The method depends upon finding angles θ_1 and θ_2 at which liquids 1 and 2 reflect with the same intensity. The critical wavelength for a given glancing angle θ is given by

$$\lambda_c = (\pi\theta^2 / \sum n_i a_i)^{1/2},$$

where n_i is the concentration of atoms of type i , and a_i is their scattering amplitude. If $n_H/n_C = R$ and $a_C/a_H = \gamma$, then $\sum n_i a_i = n_C a_C (1 + R/\gamma)$, and:

$$\lambda_c^2 = \pi\theta^2\gamma / n_C a_C (\gamma+R)$$

The intensity of the reflected beam is very sensitive to λ_c . For example, with a Maxwell distribution in which the average λ is small compared with λ_c , the intensity of the reflected beam will vary inversely with the fourth power of λ_c . If the intensity of reflection from liquid 1 at angle θ_1 is equal to that from liquid 2 at angle θ_2 , then the critical wave lengths for these two cases is the same, and:

$$(\gamma+R_1) / (\gamma+R_2) = (\theta_1^2/\theta_2^2)(n_{C1}/n_{C2})$$

Parenthetically, it may be mentioned that it was usually more convenient to plot intensity versus angle, and then interpolate to find the angle for one liquid at which the intensity would be the same as for a known angle of the other liquid. From the above equation, one may solve for γ . The results gave the value $a_H = 3.77 \pm 0.03 \times 10^{-13}$ cm, which differs by less than the probable error from the earlier value of 3.75. However, this value may be altered slightly by a better analysis of the liquids used. Since, in the latest work, a series of wavelengths and several different liquids of varying molecular structure were used with no effect on the result, it is unlikely that the determination is subject to any systematic error.

(D.J. Hughes; M.T. Burgy, G.R. Ringo, Argonne National Laboratory)

Small Angle Neutron Scattering

When a well-collimated beam of neutrons or X-rays is passed through finely divided material, the beam is found to diverge. This is attributed to diffraction and refraction occurring at each individual particle. Much X-ray work has been done in this field, but the interpretation has always been made according to either the theory of Rayleigh-Gans or Guinier (diffraction only), or the theory of Von Nardroff (refraction only). In general, it was found that particles of size $\sim 100-500 \text{ \AA}$ gave results agreeing with Rayleigh-Gans, while particles greater than $\sim 50,000 \text{ \AA}$ agreed with the Von Nardroff theory. Recently, Van de Hulst has shown that, for electromagnetic radiation, both the Rayleigh-Gans and Von Nardroff theories are limiting cases of the correct approach to the problem. The important distinction is the magnitude of the phase change of the radiation while traversing the particle, in comparison to that while traversing the same distance in vacuo. If the relative change $\rho \ll 1$, the Rayleigh-Gans theory is valid, while if $\rho \gg 1$, Von Nardroff's theory is valid. In this new work, which is being prepared for publication in Physical Review, the theory has been extended to cover neutron scattering; experiments have been performed with neutrons from the Oak Ridge reactor to check the theory for all ranges of ρ . In addition, the dependence of the broadening of the beam on the relevant parameters (wave length, particle size, sample thickness, and scattering cross section) were checked. A method was also developed to use small angle scattering in powders to determine the phase of slow neutron scattering and the coherent scattering cross sections.

In developing the theory, the particles are assumed spherical, while the incident neutrons are represented by a plane wave. The index of refraction n of all materials for neutrons is very close to 1, and is represented by $n = 1 - \delta$, where $\delta \sim 10^{-6}$. In traversing the particle, the wave remains essentially plane, but neutrons traversing different chords of the sphere suffer different phase changes. The superposition by Huygen's principle of emergent amplitudes leads to the correct intensity distribution. The deviation of the neutrons in traversing the medium is neglected, since this is a second-order effect. This type of analysis leads to a differential scattering cross section

$$\sigma(\theta) = k^2 \left| \int_0^R [1 - e^{+i\rho(r)}] J_0(k r \sin \theta) r dr \right|^2,$$

where R = radius of particle

ρ = phase change = $k \delta X$,

k = wave number in vacuo, and

X = chord length.

The above method is similar to that used by Fernbach, Serber, and Taylor (Phys. Rev. 75, 1354 (1949)) for high energy neutrons scattered by nuclei, and the method of evaluation of the integral is due to Van de Hulst ("Optics of Spherical Particles," Recherches Astronomiques de l'Observatoire d'Utrecht 11, Part 1, Amsterdam, 1946). For small and large values of ρ , the integral reduces to expressions agreeing, respectively, with the Rayleigh-Gans theory,

which predicts a half-width of the emergent beam proportional to λ/R (λ = wavelength), or with the Von Nardroff theory, which predicts a half-width proportional to δ . In the case of many small particles in a powder sample, coherence between particles must be taken into account; for large particles where $\rho \gg 1$, the particles can be considered completely independent, and the final distribution is Gaussian.

In carrying out the experiments, a neutron beam from the Oak Ridge reactor of half-width of about 1 min was reflected from a mirror set at the critical angle for neutrons of about 2 Å. All neutrons in the Maxwellian distribution from the reactor with wavelength above 2 Å passed through the powder sample. A traveling slit mounted on a vernier in front of a BF³ counter plotted the contour of the beam. The fact that the beam was not monochromatic led to no real complications in the interpretation of the data.

In the refraction range, the broadening as a function of N , λ , δ , and R was checked and found to agree with the Von Nardroff formula:

$$W^2 - W_0^2 = CN \delta^2 \{ \log(2/\delta) + 1 \} ,$$

where W = half width,
 W_0 = half-width of original beam,
 N = number of particles traversed,
 δ = difference of index from 1, and
 C = constant.

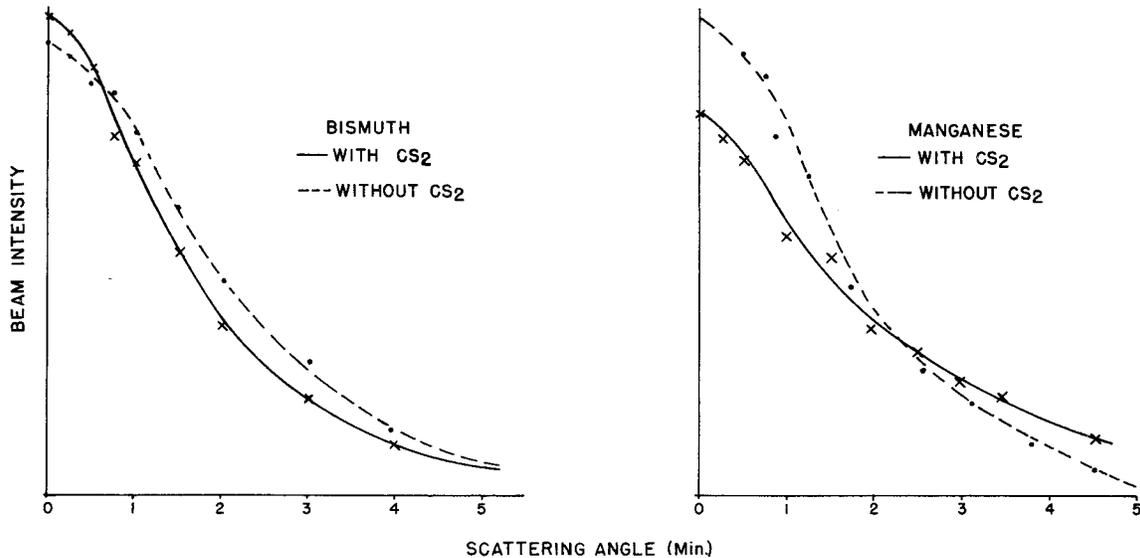
The term $\{ \log(2/\delta) + 1 \}$ contributed little, and was lumped into the constant, giving the approximate form:

$$W^2 - W_0^2 = CN \delta^2$$

The dependence of W on δ was checked, using many different elements for which coherent scattering amplitudes are known, such as Bi, Ti, Mg, Cr, Pd, Cb, SiC, and Ni, keeping the number of particles constant by making the path lengths constant, and using differential mesh grading to restrict the particle size. A straight line was obtained in plotting $\sqrt{W^2 - W_0^2}$ versus δ . The correct dependence of W on N and λ , and its independence of R were shown.

By successive grading of Bi powder, it was possible to obtain a curve in the transition region which showed a slight deviation from Gaussian. In the diffraction range, finely divided carbon black (~ 300 Å) was used. The curves were qualitative, but indicated definitely that refraction theory is not applicable, since the half-width was too small and the shape was not Gaussian. The carbon black was supplied by Columbia Carbon Company through the courtesy of Dr. R. Ladd; grain size was measured by an electron microscope.

The sign of the coherent scattering amplitude was determined by a method suggested by M. Goldhaber. Using particles in the refraction range, the broadening of the beam was first determined for the dry powder sample. The same sample was then immersed in CS₂ and the broadening again noted. If the material has a positive scattering amplitude, the addition of the CS₂, which is also positive, decreases the relative index of refraction and the half-width;



Small angle scattering of neutrons in bismuth and manganese powders, showing the effect of immersion in CS₂. Since both Bi and CS₂ have positive scattering amplitude, the scattering is reduced by immersion, while the reverse is true in Mn, which is negative.

if negative, CS₂ increases the half-width. Curves for Mn (negative) and Bi (positive) are shown in the accompanying figure. The following materials were shown by this method to have positive amplitude: Pd, Cb, Mo, Si, P, Te, and Ru. No new negatives were found, but Ti was confirmed as negative.

The value of the coherent cross section could be determined by measuring the broadening with and without the CS₂, but, as yet, this method is not very accurate.

(R.J. Weiss)

Theoretical Topics

The Self-Energies of Quantum Field Theory

The modification of the usual perturbation theory as applied to quantum field theory, which was recently introduced by Snyder (Phys. Rev. 78, 98 (1950)), has now been applied, in a paper for the same journal, to the calculation of the photon self-energy. Although the theory allows any single ambiguous divergent integral take on any desired finite value, including zero, one must be careful that the assignments of ambiguous integrals appearing in the expressions for different physical quantities are consistent with one another. In the present work, it is shown that, to the order e^2 , both the photon self-energy and the current associated with a mixture of 0-photon and 1-photon states cannot simultaneously be set equal to zero. Finally, it is shown that the requirements of relativistically invariant definitions for a photon and an electron, together with the condition that the true vacuum

state be stationary, imply that both the total photon and the electron self-energies must vanish.

(G. Snow, H.S. Snyder)

Difference Equation Method in Cosmic Ray Shower Theory

In a paper for Physical Review, the recent results of Snyder and Bhabha-Chakrabarty for the cascade theory of cosmic ray showers are shown to be derivable from a general approach involving the use of the Laplace and Mellin transforms and of a general and powerful method, due to Snyder, for solving the resulting difference equations. Boundary conditions are introduced in a natural and automatic way. The accuracy of the solution is limited by the possible ways of evaluating the resulting triple-complex integral.

(W.T. Scott)

Improved Calculations on Cascade Shower Theory

In a study to be published in the Physical Review, the diffusion equations of cascade shower theory are solved by means of a perturbation method. The first approximation is taken to be that solution obtained when the so-called completely screened cross sections are used for the elementary processes of bremsstrahlung and pair production. The correction to this is then calculated, using more refined approximations to the Bethe-Heitler cross sections.

The results, which lend themselves to accurate numerical work only in the case of light elements and high incident energies, indicate: 1) The shower maximum is decreased in height and shifted slightly to greater depths. 2) There is a decrease in the average number of electrons present at small absorber depths, and a correspondingly larger number at large depths. The magnitude of the latter effect is larger than had been previously thought. Numerical results are given, so that the correction to the solution under the assumption of completely screened cross sections can be readily calculated for all light elements when the incident particle is either a single photon or a single electron.

(I.B. Bernstein)

Besides the new research, three compilations have been completed by the Physics Department; they are scheduled for publication in Reviews of Modern Physics.

The first of these, done in collaboration with the University of Wisconsin, is a revision of the summary of neutron cross section data and references originally compiled by Goldsmith, Ibser, and Feld (Rev. Mod. Phys. 19, 259 (1947)). The compilation gives, in chart form, the cross section of an element as a function of neutron energy, bringing this subject up to date as of about May, 1950. It is scheduled for publication in the July issue of Reviews of Modern Physics (R.K. Adair).

A second compilation, done in collaboration with California Institute of Technology and Cornell University, summarizes the literature on the excited states of light nuclei. It brings the previous compilations of Hornyak and Lauritsen (Rev. Mod. Phys. 20, 191 (1948)) and of Lauritsen (NRC Committee on Nuclear Sciences, Preliminary Report No. 5, 1949) up to date as of June, 1950. The range of the survey includes all the light nuclei up to and including the neon isotopes. The compilation is in the form of an annotated bibliography with diagrams showing energy levels and the various reactions involved in their excitation and decay. A table containing the best values for the radioactive constants and the corresponding "ft" values is given at the end of the compilation. This work is scheduled for publication in the October issue of Reviews of Modern Physics. (W.F. Hornyak; T. Lauritsen, W.A. Fowler, California Institute of Technology; P. Morrison, Cornell University).

A third compilation, also scheduled for publication in the October issue of Reviews of Modern Physics, gives the energy levels and processes by which they are excited for isotopes in the range Na₁₁ to Ca₂₀. This work includes a complete list of pertinent references (E.M. Hafner, D.E. Alburger).

INSTRUMENTATION AND HEALTH PHYSICS DEPARTMENT

Electronics Division

For the past three months, the work of the Electronics Division has been concentrated on instrumentation for pulse amplitude and time analysis. Significant progress has been made on the precision timer for S.A. Goudsmit's time-of-flight mass spectrometer. A single-channel and a ten-channel pulse height analyzer have been built and tested. M. Sands has developed and tested a delayed coincidence circuit with a resolving time of less than 2.8×10^{-9} sec. Work has continued on the auxiliary equipment for use with pulse analyzers: improvement of the precision-regulated high voltage supplies and design of a novel nonoverload amplifier. The crystal-growing oven is now in operation. Spectra of the newly discovered liquid scintillators have been recorded.

The other major field of work has been in health physics instrumentation. Special monitoring equipment has been developed for use in the hot lab and around the accelerating machines. Some of the equipment used in the monitoring shacks has been revised and improved.

Miscellaneous instruments reported on include: a circuit for integrating the beam current of the 60" cyclotron or the Van de Graaff accelerator; a monitoring device for civilian defense applications based on a photomultiplier and cold cathode trigger tube; and two photoelectric densitometers for detecting traces of smoke.

Timer for Time-of-Flight Mass Spectrometer

The basic principles of this timer were described in the last quarterly report. The instrument is now about half completed. All fundamental circuits have been developed and tested, except those for modulation of the pulse amplifier. The time standard is a 1-megacycle crystal oscillator. Ring scalars divide this frequency down to a repetition rate which may be 100 or 300 cycles. They also provide gates of 1, 10, 100, or 1000-microsecond duration, conveniently selected by tap switches. Three switch channels select 1- μ sec gates for the pulses which modulate the ion source and for the two sweeps for observing the first and nth revolutions of the ion packet. It is desired to measure the time to 0.01 μ sec, so each 1- μ sec gate will select a fast precision pulse. The latter will be phased relative to the master 1-Mc wave by means of a tapped delay line with 0.1- μ sec steps and a continuously variable line for interpolation. The slow circuits (1 Mc and down) have been constructed and tested. The fast circuits have been designed and tested on breadboard. The scope tubes and high voltage supply are complete. A circuit has been built for calibrating the fast circuits.

Pulse Height Analyzers

Increasing demand for both single and multiple-channel instruments has stimulated a search for more stable and more flexible circuits than have previously existed. In the past, several single-channel instruments were built

here similar to those developed at Los Alamos during the war. A multiple-channel instrument using a conventional cathode-ray tube with photocells, and a ten-channel instrument using a special beam deflection tube, as described by Watkins (Rev. Sci. Inst. 20, 495 (1949)), were also built. The former did not prove at all promising; the latter was not stable enough under test, even though the auxiliary circuits were improved in a number of respects. In this quarter, a ten-channel instrument was built using a circuit developed at Oak Ridge. This includes an expansion amplifier and discrimination anticoincidence circuits using the new type 6BN6 tube. This system has checked out fairly well, the discriminators being constant for several hours to about 1% of the channel width. With the expansion amplifiers, the channels are effectively 1% of the maximum signal. Work is now directed towards improving the whole system, so as to achieve over-all stability consistent with the stability of the analyzer. In fact, it will be possible to prove the stability of the analyzer only after the other components are stable and calibrated.

A different circuit has been developed for a single-channel instrument in which advantage is taken of the sharp and reliable cutoff of crystal diodes. Because of the finite back resistance, it is necessary to drive the crystals from separate cathode followers in this circuit. In spite of provision for convenient calibrating, the stability of this circuit is not yet as high as it should be. This unit is equipped with motor-driven potentiometer, so that curves can be run automatically (P. Prentky).

The interest in pulse height analyzers is project wide. The AEC Instrument Branch has set aside \$10,000 for production of 10 single-channel instruments by a private firm. This contract will be handled through the Laboratory, which will also purchase some units for its own use.

Coincidence Circuits

A fast coincidence circuit has been worked out. The basic idea is one which has been used at M.I.T., Chalk River, and elsewhere. This system was chosen after an analysis of all the currently known systems capable of achieving short resolving times. Stilbene crystals are used, although other scintillation materials may be quite as good for this purpose. The electronic circuit includes 1P21 photomultipliers followed by cathode followers, 100-ohm cable to Hewlett Packard 460A distributed constant amplifiers (rise time of 2.6×10^{-9} sec, and gain of 8), and a 100-ohm cable to the coincidence circuit. The coincidence circuit consists of two 6AH6 tubes with a shorted-line common plate load. The signal across the line would ideally be twice as large for a coincidence as for a single signal. Discrimination is achieved by a diode crystal which charges a condenser. The condenser signal, being slow, is amplified by a conventional amplifier with gain of 1000 and fed into a conventional high level discriminator. Minimum useful signal corresponds to 5 electrons at the photosurface of the multiplier. Care is exercised throughout to minimize capacity and inductance in the fast circuits. The "speeds" of all components -- crystal, photomultiplier, amplifier, and coincidence circuit -- are comparable, and give a measured half-width at half maximum of less than 2.8×10^{-9} sec. The resolving time was measured carefully; optimum conditions were determined with the use of a special pulser and various lengths of coaxial cable. Delays are introduced by varying the length of cable between amplifier and one side of the coincidence

circuit. The pulser makes use of a Western Electric D168479 mercury-contact relay (it is necessary to remove the top of the metal tube and use very direct wiring to the contacts if oscillations are to be avoided). The rise time of the pulser is considerably less than the resolving time of this instrument. A final check was to measure the velocity of coincident gamma rays from Co^{60} . The two crystals were mounted about 10 cm apart, and the source was placed first near one and then near the other. The displacement of the time distribution of pulses gave the speed (M. Sands).

Another coincidence circuit has been designed for a study of the polarization of gamma rays. Four counters will be used. The circuit consists of 4 amplifier channels and 3 coincidence stages. Coincidences are to be taken between pairs of counters, and then between the outputs of the first two coincidence stages. The rise time of amplifiers will be less than 0.1 μsec ; the resolving time will be of the same order of magnitude (M. Sands, P. Prently).

Amplifiers, Power Supplies, and Crystals

To get precise information from pulse height measurements, the stability of amplifiers and power supplies must be pushed to the limit. The stable high voltage supply described in the last quarterly report gave some trouble because of heater cathode leakage in the 2C53 high voltage amplifier tubes. Although the manufacturer rates the tube to stand 300 v between cathode and heater, measurements show that leakage increases from a few μamp to several mils, or even short circuit, in a period of a month. A minor revision of the circuit has eliminated this difficulty. A paper describing this supply is in preparation.

A pulse amplifier has been designed which is highly stable and which recovers instantly from any amount of overload. It has a rise time of 0.2 μsec and a gain of 10,000. The amplifier consists of 3 feedback loops with d.c. coupling throughout, so that there are no capacities which can be charged during overload. To hold the tubes in reasonable operating range, there is also d.c. feedback from the output of the amplifier to the bottom of the input resistor. This feedback is bypassed for the pulse frequencies, and the low frequency cutoff is determined by the constants in this feedback path. Gain stability is provided by the feedback within the loops and by the fact that the operating voltages and currents throughout are held constant by the over-all d.c. feedback. Nevertheless, it was found necessary to regulate the heater voltage, because the feedback factor is not high enough near the upper cutoff frequency, and because G_m of the tubes is a function of the heater voltage -- even when the tube current is held constant. An expansion amplifier has also been developed which is suitable for insertion between this amplifier and a pulse height analyzer (R.L. Chase).

It has been found necessary to regulate the heater voltage in the Brewer nonoverload amplifier, which was developed at the Laboratory last year.

A number of people are exploring the possibility of using various liquid solutions for scintillation counting. Anthracene dissolved in xylene is one promising combination. Addition of mineral oil (Nujol) enhances the effect. The spectra of solutions and solid have been compared to find out whether the

mineral oil increased the light output or shifted the emission bands. Excitation by mercury arc and gamma rays give the same effect. Crystalline anthracene gives two main bands, at 4460 and 4725 Å. The solutions give three bands, at 4500, 4260, and 4020 Å, in order of increasing intensity, regardless of the amount of mineral oil. Addition of the oil increases the light output by about 75%.

The crystal-growing oven is now in operation. Temperature is stable to 0.2°C. The ampule is lowered at the rate of 1" per 20 hr throughout a 6° temperature differential across a 1/2" gap. One good large anthracene crystal has been made, and another is presently being annealed.

Health Physics Instrumentation

At the request of the AEC, the Division has proceeded with the investigation of the possibilities of a scintillation detector for civilian defense applications. Funds have been made available, and a development contract has been placed with Westinghouse for a more rugged, miniature version of the WL-759 trigger tube. First samples of this new tube are now being tested. The design of a suitable vibrator power supply remains as the major problem to be solved before proceeding to package the unit. Funds are being earmarked for the second phase of the development, comprising the packaging and production of prototypes for evaluation.

A continuous monitor has been designed to operate near the target of the cyclotron. The power supply operates on the a.c. mains, and uses the same regulator circuit developed for the high voltage application mentioned above. The monitor consists of a carefully shielded ionization chamber followed by electrometer tube and d.c. feedback amplifier. Full-scale sensitivities, which are selected at the remote meter, are approximately 0.2, 2, and 20 r/hr. The instrument is not sensitive to the magnetic or r.f. fields in the cyclotron vault. A similar meter is being constructed for use in the Van de Graaff room. Experience has indicated that the grid current of the Raytheon 571AX electrometer tube varies widely from tube to tube; it was found wise to select tubes where especially low grid current is important.

A number of Beckman MX-3 radiation meters have been modified for laboratory monitoring purposes. For operating an alarm or "room hot" sign, a sensitive relay (Sigma 5F) is inserted in series with the meter. In other cases, taps are brought out for recording at a remote meter. Fourteen such instruments are being installed in the hot lab. Also, the continuous dust monitor, developed for the area monitoring stations, has been modified to continuously monitor the dustborne activity in the hot lab ventilating exhaust.

The equipment of the area monitoring stations is being constantly serviced and improved. In addition to servicing, 12 indicator panels were revised during this quarter, the charging circuit of the battery-operated rate-meters has been changed so that the storage batteries will be automatically cycled, and a blocking-oscillator high voltage supply is now under test which will replace the high voltage batteries now in use.

Miscellaneous

Two other circuits worth mentioning are a current integrator and smoke densitometer. The current integrator, which is also a current meter, is designed for use with the cyclotron or the Van de Graaff accelerator. The circuit is a d.c. feedback amplifier with very high gain inside the loop. The current to be measured flows through an input resistor, which is selected to give the desired sensitivity. The voltage across the input resistor is read on a 1-ma meter with 1000 ohms resistance. When the instrument is integrating, the meter current, rather than the input current, is passed through a 10-mfd capacitor. When the condenser reaches 100 v, it is discharged, and the same pulse drives a register (Veeder-Root E124804). The register is tapped so that equipment can be turned off after collection of a predetermined quantity of charge. Provision is made for local and remote operation and indication.

Two types of smoke densitometers were developed for the Meteorology Group. In both cases, the smoke is drawn through a light-tight chamber and scatters light from a collimated beam into a photocell. The type for use on the ground uses a 929 phototube and conventional feedback amplifier. The airborne instrument has a light chopper and 931A photomultiplier tube. The chopper also flashes a standardizing light pulse on the photomultiplier for part of each cycle. The output of the photomultiplier is presented on an oscilloscope located on the ground. The unit is powered from the ground and carried aloft by several weather balloons.

Publications

1. "A Monitor for Low Intensity Gamma Rays," J.B.H. Kuper and R.L. Chase, Rev. Sci. Inst. 21, 356 (April, 1950)
2. "A Monitor for Airborne Radioactive Dust," J.B.H. Kuper, E.H. Foster, and W. Bernstein, Nucleonics 6, #4, 44 (April, 1950)

Health Physics Division

Liquid Waste Disposal

Two gaging stations have been completed and put into operation in the stream to which the Laboratory discharges its processed and filtered liquid waste -- one upstream from the discharge point, and one downstream at the site boundary. An automatic sampler has been installed at the exit from the waste processing tanks, and is being tested. A second sampler, located at the point of discharge to the stream, has been completed, but requires modification before it will operate satisfactorily.

Considerable difficulty has been experienced in obtaining automatic sampling devices for monitoring liquid wastes from operating laboratories, because of the highly variable flow rate, pH, and solid content. A "Proportioneer" used for this purpose at the Chemistry Department semi-hot laboratory has been returned to the factory for servicing. A second such unit has been installed at the new biology laboratory, and is being tested. A much simpler sampler

has been designed by the Architectural Planning and Plant Maintenance Department; it will be tried out as a part of the waste system for the cyclotron building. A homemade sampler for use in neutralizing tanks has been constructed, and works satisfactorily. Further development of this device is planned.

The Laboratory liquid waste effluent had a daily average activity of less than 10^{-14} curies per cc on all but three days, when activities of about 10^{-13} c/cc were noted as a result of emptying of Chemistry Department hold-up tank. This discharge is still negligible when compared with the 3-month average limit of 3×10^{-12} c/cc agreed to by the AEC.

Building Survey Operations

In addition to the usual laboratory surveys, special studies have been made of the Chemistry Department Van de Graaff accelerator, the Biology Department electron microscope, and the rectifier tubes in the 60" cyclotron. In the case of the Chemistry Van de Graaff, it appears that the shielding is adequate with respect to the direct beam, but that sufficient scattered radiation finds its way out into the laboratory room to make some additional shielding desirable.

Determinations of sensitive volume and counting efficiency have been made for some BF_3 counters for neutron surveys. Also, a special ion chamber, capable of evacuation, has been constructed for assaying air for soft beta emitters. A similar chamber with an open end has proved useful for direct assay of liquid waste samples. Both chambers are designed to be used with a standard "Minometer."

A beta-gamma counting setup has been constructed for "Precipitron" samples. Its counting efficiency has been determined for various energies of radiation. A series of film calibrations have been made at very high dosages, using a 2-curie Co^{60} source. These calibrations will be useful in connection with various irradiation experiments.

Area Monitoring

A number of difficulties with equipment in the area monitoring stations have developed as a result of continuous operation over the past year and a half. Steady improvements are being made in servicing and preventive maintenance. Better photographic records of the data are being obtained as a result of modifications in lighting and camera adjustments. The dynamic condenser electrometers have been given a major overhaul. Improvements are being made in the power supplies of the battery-operated ratemeters. An analysis of area monitoring station performance for the month of April showed an over-all operating efficiency of 82%. This is an average figure for all stations and all types of equipment, efficiency being the fraction of the time during which reliable data is obtained with a given apparatus.

Measurements were made of the effect of the 16-curie Co^{60} source used for field irradiations by the biologists on radiation levels at the nearest site boundary. Values approximating the agreed limit of 0.5 mr/day were found. A study is being made of possible conflicts between use of this field and operation of the reactor.

Personnel Monitoring

Approximately 2400 film badges and somewhat fewer pairs of pocket chambers are being processed each month. Neutron films are included in about 100 of these badges.

All personnel monitoring equipment showed less than the weekly limit of 300 mr except in one case where an exposure of 550 mr was indicated by a film badge. The origin of this indicated exposure is in doubt, since the individual is unable to explain an exposure of this magnitude. Exposures during civilian defense simulated disasters were all less than 75 mr.

Improvements in the Weston Model 877 densitometer which result in greater accuracy and good reproducibility of readings were described in Ra-Det (April, 1950, p. 36).

Training

Preliminary editing of the papers given at the training course for representatives of casualty insurance companies in February has been completed. Final editing and publication will be done in Washington.

A 5-week course in civilian defense against atomic attack was given for 15 representatives from 10 states, Puerto Rico, and the District of Columbia. The program included 47 lectures, 17 laboratory experiments, and 3 field exercises. The climax of the course was a simulated disaster, "Operation Tombstone." For this, a wrecked building was contaminated with 2 curies of pile-activated KBr, and high levels of radiation were provided by use of 15 curies of carefully hidden Co^{60} . The trainees were organized into headquarters and field groups, with appropriate radiological and communication equipment, for a detailed survey of the area. Very pure KBr was used; there is less than 1 μc total of residual long-lived activity. A somewhat similar field exercise was conducted for the New York AEC emergency monitoring team.

Transcripts of papers by outside speakers at the civilian defense training course have been edited, and will be distributed to the trainees and other training centers after approval by the authors.

Five AEC fellows, having completed course work at the University of Rochester, are now at the Laboratory for 10 weeks of experience in health physics operations.

Each member of the Reactor Operations Division has been given 2 days' experience in health physics survey activities.

ACCELERATOR PROJECT

Cosmotron

The method of constructing the vacuum chamber has been decided upon; thus, the last major decision with regard to over-all design has been made. Accordingly, the attention of the engineering staff is now concentrated mainly on construction and details of design. In addition, considerable testing of materials and prototypes is going on, since the complexity of this instrument demands the simultaneous performance of a great many components. The design of critical components is examined by constructing at least one prototype which is then thoroughly tested; if any modifications are indicated, they are incorporated into the final unit.

Examples of components for which prototypes were constructed and tested are:

1. The 20" diffusion pump stations.
2. The vacuum chamber (a short section).
3. All important parts of the r.f. system, with the exception of the last amplifier stage.
4. The magnet coil (a corner section).

The construction is progressing smoothly, and, although the project may be a little behind previous estimates, no single component is lagging seriously. It still appears that the major components will all exist physically sometime this fall.

To facilitate the design and construction of the instrument, its various components have been made the responsibility of various staff members in the project. What follows is a progress report for most of these components submitted by the staff member in charge.

Power

The unit substation has been connected and energized. It is now feeding the Cosmotron Group with power at 120/208, 440, 2400, and 13,800 volts. A total of 6500 kva is available; this includes, conservatively, 1500 kva of power for experimental work in addition to power necessary to run the machine.

The Westinghouse power supply for the magnet has been received and installed. Almost all wiring is complete. Final leveling of the large motor-generator set is proceeding. Because the foundation settled and worked slightly, leveling was halted for a month to let the foundation stabilize. The large ignitrons have been outgassed and tested at East Pittsburgh before shipment. They appear to operate satisfactorily at their rated voltage, but final performance on load must await the completion of the magnet coil.

(G.K. Green, A. Wise)

Controls

The general control scheme for the machine has been outlined. Most circuit schematics have been drawn tentatively. A steel multi-channel wireway for carrying all the wiring has been designed and ordered. The first portion has been received. The first extensive electrical wiring is now in progress on the diffusion pump frames, where 15 electrical control units are under fabrication in the test shack.

(G.K. Green, R.R. Kassner, F.J. Seufert, Jr.)

Magnet

The magnet steel has been fully installed. All blocks have been leveled to an accuracy of the order of 0.010". The position of each block has also been established in relation to bench marks, in order to determine changes in position which might occur during operation.

Spreader bars have been installed in the gap between the quadrants to improve the alignment of the upper and lower pole faces and to prevent bowing of the end plates of the magnet under magnetic stress.

The steel parts of the magnet, as a result of careful fabrication and installation, so far appear to have come up to expectations in every way.

(W.H. Moore, L.D. Stoughton)

Magnet Coil

Machining, brazing, testing, and insulation of the complete set of conductors for the first magnet quadrant is complete; the conductors for the second quadrant are nearly complete. Installation of the conductors in the first quadrant has begun.

The work of installation was delayed until a full-scale end structure of the coil was constructed in prototype and tested for voltage breakdown to ground. The final design withstood test voltages up to 40 kv. This is to be compared with the normal voltage to ground of 3 kv.

(J.A. Kosh)

Magnetic Field Tests

For making magnetic field measurements near injection time, a full-scale model was constructed of 11 surplus magnet blocks. With this model, the magnetic field index n was measured throughout the gap to show that the entire vertical aperture and about 23" of radial aperture are usable. The position of vertical magnetic symmetry, "the median plane," was examined and found to be constant within 1/4" throughout the usable radial aperture. However, it was found that a tilt in the exciting coil can shift this position radically, due to eddy currents induced in the copper. Measurements on the magnet itself will determine whether sufficient tilt of the coil exists to need correction.

Sample sections of vacuum chamber components, inserted in this model, were studied to determine their influence on the magnetic field. Satisfactory values of the field index were obtained for saw cuts in the top and bottom sections with 3" azimuthal and 3/8" radial separations. The median plane position is affected, however, by a tilt in the backwall as small as $0^{\circ}10'$. Again, final measurements will show whether such a tilt, consistent throughout a whole quadrant, exists.

A series of measurements, also for injection values, was made in this model to determine the influence of pole-face windings for correction of the field index and the position of the median plane, or for extension of the radial aperture, should any of these seem desirable.

In the quarter-scale, 12-block magnet model, measurements of the magnetic effects of an all-metal vacuum chamber showed that a metallic skin of only 0.008" Inconel still distorts the field enough that correction windings will be necessary. To determine the effect of the spreader bars which have been inserted in the straight sections of the magnet, a model of the spreader bars, half-length in extent, was added to the end of the magnet model. The effect at injection time is almost negligible. At higher fields, the spreader bars concentrated sufficient stray field to saturate the legs of a model of the ferrite core which had been placed between them. Further measurements are in progress with "de-gaussing" windings on the spreader bars.

(M.H. Blewett, J.M. Kelly, W.H. Moore, L.W. Smith)

Radio-Frequency System

During the past three months, the master oscillator has been constructed in final form, together with its associated temperature controls and power supplies. The final control system which makes the oscillator frequency track the magnetic field, and which includes integrator, analog computer (diode network), control amplifier, and initial clamping circuits, is about 80% complete. Of the 4 stages of the high level power amplifier, two are complete and tested; the third is almost ready for test, and the fourth is under construction. Enough ferrite material for construction of the final accelerator unit has been delivered and is in the process of assembly.

(J.P. Blewett, M. Plotkin, A. Pressman, J.C. Logue, L.C.L. Yuan)

Vacuum Chamber

A vacuum chamber design for the proton synchrotron has been decided upon, based on the following considerations: The maximum pressure in the chamber should not be greater than 10^{-5} mm Hg, with a desirable operating pressure of 5×10^{-6} mm Hg; the vertical aperture of available magnetic field should be as large as possible, consistent with other design factors; under no conditions should there be ferromagnetic material in the gap; the vacuum chamber materials should be so arranged that induced eddy current effects will be minimized.

With the above factors in mind, a fabricated vacuum chamber of gasketed and bolted design is being made. This will consist of four 90° curved sec-

tions, joined with four straight sections. The straight sections will contain injection, ejection, r.f., and probe apparatus, and will be essentially of welded stainless steel construction, since they are out of the main magnetic field. The curved sections will be rectangular in cross section; each one will be made up of vertical inner and outer continuous stainless steel walls 1" thick, bent to the proper arc. Three manifolds will be welded in the outer wall to connect to the pumping apparatus. To the inner and outer walls will be bolted ledges made of stainless steel strip, upon which will rest insulated 3/8" thick horizontal stainless steel plates, slotted from either side with saw cuts which do not quite meet at the vertical centerline of the chamber. This leaves a continuous backbone running the full length of the quadrant. Vertical rods placed in the gaps between magnet blocks will have one of their ends fastened into this continuous strip, the other ends fastened to the outer upper and lower surfaces of the magnet blocks, and will serve to prevent the grids from having large deflections under conditions of evacuation. Over the grid plates will be placed a skin, preferably made of a nonconducting material. This skin will be bolted and gasketed at its periphery to form a vacuum-tight structure. Tests have been performed on various plastic materials with the result that a polymer of trifluorochloroethylene appears to have practically all the qualities desired. The ends of the chambers will be flanged stainless steel boxes bolted to the inner and outer steel walls and insulated from them.

Steel and most of the other material is on order for the curved sections of the chamber, which should be under intensive fabrication by August 1 of this year.

(I. Polk)

Vacuum System

Assembly of the fifteen 20" diffusion pump stations has been started. The basic mechanical assembly is complete. Eleven refrigeration units for the baffles are installed and ready to be connected to the baffles. One prototype and one production wiring assembly have been completed and checked out. One of the 300-cfm Kinney forepumps has been uncrated. A prototype power and control circuit has been made and checked out on that pump.

In running a prototype 20" diffusion pump, it was observed that the original baffles supplied with these pumps were rather ineffective in preventing backstreaming of oil from the jets. A new baffle was designed and built which is far more dense optically than the original baffle. Speed tests are now in progress to determine the comparative effect of the new design on the pump speed. Final connection of the refrigeration units in the pumping stations has been held up for this reason.

Apart from actual assembly of the pumping components described above, some progress has been made in the design of the structural components which go to make up the complete vacuum system. The basic vacuum chamber is discussed elsewhere. Aside from the basic chamber itself, there is the problem of the valving system and the transition, or plenum, sections which join the chamber proper to the large valves and pumping stations. The design of the large 16" valve was completed; the drawing was released to the shops for the

construction of one prototype. Construction of this prototype is about 75% complete. Sufficient experience has been gained to justify the placing of orders for major components for the balance of the valves.

The design of the transition sections or plenum chambers is complete. Steel has been ordered for construction of a prototype.

(C. Lasky)

Cosmotron Injector

The Van de Graaff injector for the Cosmotron, which is being built by High Voltage Engineering Corp., Cambridge, Mass., is nearing completion. Final testing is under way. Delivery and installation are expected to start in about one month.

The machine has been operated with a pulsed ion beam of about 200 μ amp at voltages up to 3.8 Mev. The principal remaining jobs are:

1. Getting the source output up to the desired value of about 1 milliamper.
2. Checking out the corona feedback energy control system.
3. Looking at the beam focus and position stability at a distance of 50' from the machine.

(C.M. Turner, G.J. Hoey)

60" Cyclotron

During the past quarter, the 60" cyclotron installation and assembly were completed. The vacuum system has been apart and together numerous times to repair internal and external vacuum and water vapor leaks; the system is now reasonably tight, with a base pressure of 0.8×10^{-6} mm of Hg.

The radio-frequency oscillator has been up to the 60-kw level; some 110 hours of oscillator running for chamber outgassing has taken place.

Numerous insulator breakdowns due to cathode concentrations and plate output arcing have been, to some extent, brought under control by redesign of the cathode feedback and plate output feedthrough systems. The initial probe target and controls have been completed and tested. The hunt for inside beam is in prospect as soon as a value somewhat higher than the present 12-kv dee voltage is reached.

(C.P. Baker, W.W. Merkle)

General Electric Electrostatic Accelerator

The G.E. electrostatic accelerator has not yet reached its design rating of 3.5 Mev. The voltage limitation is set principally by the accelerating and differential pumping tubes. The use of large (6" ID) vacuum tubes to

attain high pumping speed has led to a difficulty in which spontaneous electron loading appears at a voltage threshold which rises with increasing tube pressure. Studies are under way which show promise of an early solution to this problem. A large number of mechanical and engineering defects in the machine have come to light during the course of testing.

Physics experiments have been started in a very preliminary way in the voltage range available with the machine. The experiments planned for the machine remain essentially the same as reported previously.

A designer and machinist have been assigned to the group recently to speed up work.

(C.M. Turner, J.G. Cottingham)

CHEMISTRY DEPARTMENT

The following collection of research reports describes investigations carried out in the Chemistry Department which have reached such a stage in the past quarter that it is felt worthwhile to present the results obtained. The individual investigations discussed, sixteen in number, fall under the general categories of a) general chemistry of various substances, b) chemical studies with isotopes, c) nuclear problems. Certain portions of the work have been carried out in collaboration with members of other Departments of the Laboratory, other portions with persons not members of the Laboratory staff; such collaboration is indicated.

One phase of the study of the chemistry of the heavy elements is the investigation of the absorption spectra of their salts in solutions fluid at low temperatures. Preliminary observations on the spectrum of UCl_4 solutions are reported. The general character of reactions in such systems is also being surveyed; new observations on reactions of propene with iodine at liquid air temperature are described.

Tracer investigations on reaction kinetics and mechanisms which are reported include: new data for the ferrous-ferric electron transfer exchange reaction, a radiochemical determination of the dissociation constant of ferriin, observations on the exchange of hydrocarbons with deuterium under Fischer-Tropsch synthesis conditions, a check of a proposed mechanism for the change in configuration about carbon atom C-2 in glucose (epimerization), a study of some features of the mechanism of the Willgerodt reaction, the thermal decomposition of N_2O . The infrared spectra of isotopically substituted N_2O have been measured; force constants of the molecule have been calculated; and partition function ratios for isotopic exchange reactions have been calculated.

In connection with the mass-spectrometric investigation of isotopic molecules, a knowledge of the effect of isotopic substitution on mass-spectral patterns is important; an approximate method for calculating this effect and some experimental tests of it are reported. The relative efficiencies for the collection of positive ions of different e/m in a Nier-type mass spectrometer have also been studied.

Two studies of an analytical nature are included, one on a spectrophotometric method for the determination of $CeIV$, and one on a new test for traces of organic matter in water.

The nuclear problems reported on include the recoil following neutrino emission in Be^7 , the half life of I^{129} , and the genetic relationship of the isomers of Ag^{110} .

ABSORPTION SPECTRUM OF URANIUM TETRACHLORIDE IN FLUID SOLUTION AT 77°K

S. Freed and K.M. Sancier

Anhydrous uranium tetrachloride purified by repeated sublimation in a vacuum was dissolved in a solvent consisting of 10% n-propyl alcohol, about 45% propane, and 45% propene.

The spectrum of the solution at 77°K consisted of groups of lines suggesting the characteristic spectra of rare earths. There were some bands present which were not resolved into discrete structure. However, it was observed that the spectrum of the anhydrous crystals at 77°K also contained diffuse bands, which may perhaps be resolved at still lower temperatures. The lines in the spectrum of the solution were broader than those from the crystals at 77°, but sharper than the crystals exhibited at room temperature.

A continuum began rather abruptly at about 3000 Å and extended to the optical limit of the equipment, about 2100 Å. When radiation in this spectral region was absorbed, a photochemical transformation took place. The solution, originally pale green, became intensely red. When the solution was warmed to about 220°K, the red color disappeared and a pale green color returned which, however, had characteristics in its spectrum not present in that of the original green solution. Another sign of irreversibility was furnished by the attempt to regain the red solution by irradiating again with ultraviolet light. The photochemical yield was much less than before; only a pale red solution was obtained after long irradiation.

It is supposed at present that the red color originates in a reduction of the tetrachloride to the trichloride, which is known to be red. However, there are features in the spectra which are not accounted for by so simple an interpretation. Further work is needed for definitive identification of the photochemical products.

EXPERIMENTS ON COMPOUND FORMATION
IN SOLUTIONS AT LOW TEMPERATURES. PROPENE AND IODINE

S. Freed and K.M. Sancier

It is to be expected that compounds may form and persist at low temperatures which would not be formed in detectable amounts in a mixture of the reactants at higher temperatures. Thus, the lower temperatures may make possible the observation of weakly bonded substances, and may also permit interruption at an intermediate stage of reactions requiring activation energy. Phenomena of this character have been observed in a preliminary study of the reactions between propene and iodine at low temperatures.

The color of solutions of iodine in organic solvents ranges from violet to brown, the latter color being especially characteristic of aromatic hydro-

carbon solvents. Benesi and Hildebrand¹ have shown that the brown solutions exhibit an intense absorption peak in the ultraviolet and that this peak can be ascribed to a 1:1 complex between iodine and the aromatic compound. They regarded such a complex as a salt composed of the acid, iodine, and base, e.g., benzene, according to the general classification of G.N. Lewis. Mulliken² viewed the intense absorption peak in the ultraviolet as a forbidden transition between energy levels in the conjugated double bond system made "allowed" by the presence of iodine; he concluded that iodine probably lay in a plane parallel to that of the aromatic structure.

Our experiments were undertaken to see whether propene formed an addition compound with iodine at low temperatures. The absorption spectra of solutions of iodine in propane, in propene, and in propane-propene mixtures were observed and furnish definite evidence for a propene-iodine compound.

The color of iodine in propane is violet with an absorption peak at 5200 Å at 230°K, while its solution in propene is amber with a peak of 4800 Å. At 77°K, the colors of both solutions are about the same with peaks at 4400 Å. The area under the absorption band of iodine-propane remained approximately unchanged with variation in temperature, but that of iodine-propene increased about threefold on changing the temperature from 230°K to 77°K. In the ultraviolet region, the propane solution exhibited virtually no structure save for two weak peaks at 2500 Å and 2550 Å, but the propene solution showed an extremely intense band at about 2750 Å. The intensity of this peak was about ten times as great as the peak in the visible. Both the intensity and wavelength of this ultraviolet absorption match those of the aromatic compounds with iodine; and there seems no doubt that it arises from a corresponding propene-iodine compound.

However the bond between the propene and iodine is very weak as is witnessed by the fact that when propene was added to a solution of iodine in propane, the amount of propene required for the appearance of the characteristic absorption was thirty times the molar amount of iodine present.

It was found that the reaction required activation energy. Little if any reaction occurred at 77°K. Above the temperature of dry ice, it seemed rapid. At 230°K, our highest temperature, a chemical reaction occurred, after a time, which consumed iodine, that is, it removed the characteristic absorption peak. It is possible that di-iodo propane is formed.

It seems best to postpone interpretation of the character of the "intermediate" propene-iodine compound and of the origin of the color until more data are obtained. However, it seems clear at this point that no conjugated double bond system is necessary for the formation of the substances exhibiting the ultraviolet peak; and it does not seem likely to us that a proper description of this absorption is that of a forced transition between energy levels of the hydrocarbon component. The great intensity of the absorption, which in both the present system and in the case of aromatic hydrocarbons,¹ has an extinction coefficient of about 10,000 moles⁻¹ cm², speaks rather strongly

¹H.A. Benesi and J.H. Hildebrand, J. Am. Chem. Soc. 71, 2703 (1949)

²R.S. Mulliken, J. Am. Chem. Soc. 72, 600 (1950)

against this. Furthermore, a match in energy levels between substances such as benzene and propene seems unlikely.

It is to be expected that activation energy is required for a reaction in which a double bond acts as a base, according to Lewis's classification, so that, at present, we do not see any inconsistency with this description of the formation of the addition compound.

THE FERROUS-FERRIC EXCHANGE REACTION

J. Silverman and R.W. Dodson

The study of the ferrous-ferric exchange reaction described in the previous progress report has been continued, with improvements in the experimental technique, measurements at 0°C, and determination of the reaction order. Experiments thus far indicate that the reaction is first order with respect to both the ferrous and the ferric species. The rate constant at $0.00 \pm 0.05^\circ\text{C}$, $\mu = 0.540$, $(\text{HClO}_4) = 0.540$ f, has been found to be 1.34 ± 0.05 moles⁻¹-liter-sec⁻¹.

The ferrous perchlorate used in these experiments was obtained by recrystallizing $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ from 8-f HClO_4 . The product gave negative tests for chloride and sulfate.

The ferric perchlorate stock solution was prepared from an HCl solution of high specific activity Fe^{55} . This was subjected to successive precipitations with NH_4OH and resolution in HClO_4 until the washings of the ferric-hydroxide precipitate gave negative tests for chloride, sulfate, and ammonium ions. The purified $\text{Fe}(\text{OH})_3$ precipitate was dissolved in HClO_4 . The resulting solution also gave negative tests for chloride and sulfate.

The procedure employed is basically the one described previously. The reactants are brought to the desired temperature and mixed. Aliquots of the reaction mixture are removed at selected time intervals. Immediately upon withdrawal of an aliquot, the reaction is quenched by the rapid successive addition of α' dipyridyl and sodium acetate solutions. The ferric species is then precipitated with NH_4OH . Because of the low concentration of the reactants, ferric carrier is added to increase the mass of the precipitate. Also, an aliquot of a fine suspension of diatomaceous earth is added to aid the filtration of the $\text{Fe}(\text{OH})_3$. This precipitate is filtered, washed, dried, and counted.

The data obtained thus far are summarized in the accompanying table.

All the runs were done at $0.00 \pm 0.05^\circ\text{C}$, $\mu = 0.540$, $(\text{HClO}_4) = 0.540$.

These results are in disagreement with the data for essentially similar systems obtained by Van Alten and Rice¹ and by Kierstead,² who employed a

¹L. Van Alten and C.N. Rice, J. Am. Chem. Soc. 70, 883 (1948)

²H.A. Kierstead, J. Chem. Phys. 18, 7, 6 (1950)

<u>Ferrous-Ferric Exchange</u>			
$(\text{Fe}^{++}) \times 10^4$	$(\text{Fe}^{+++}) \times 10^4$	$T_{\frac{1}{2}}$ (sec)	k ($\text{mole}^{-1}\text{-liter-sec}^{-1}$)
1.98	1.05	1670	1.37
2.96	1.06	1315	1.31
3.93	1.08	1045	1.32
3.95	2.10	850	1.35
3.97	3.11	730	1.34
3.88	4.25	647	1.32

diffusion method to separate the exchanging species and reported long half-lives for the reaction. The discrepancy between their results and those herein reported has not been resolved. The present results are, however, consistent with the findings of Linnenbom and Wahl,³ who, also using a diffusion separation, observed complete exchange in 1 to 2 hr.

³V.J. Linnenbom and A.C. Wahl, J. Am. Chem. Soc. 71, 2589 (1949)

DETERMINATION OF THE DISSOCIATION CONSTANT OF FERROIN

C.M. Cook, Jr., and F.A. Long*

Abstract

A radiochemical method for determining the dissociation constant of complex ions is described. It is based on measuring the concentration of the uncomplexed metal ion in solution with the aid of a radioactive tracer, and requires that shifts in the complex equilibrium be slow compared with the time required to separate the free ion from the complex species. The method has been successfully applied to a determination of the dissociation constant of ferriin, the tri-orthophenanthroline complex of ferrous ion. Results in good agreement with a literature value determined by other methods, were obtained.

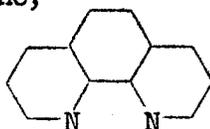
A coordination complex, MeA_x^{n-xm} , of a metal ion, Me^{+n} , with the anion, A^{-m} , of a weak acid should be expected to undergo a partial dissociation in acid solutions, due to the removal from solution of the ion, A^{-m} , as the undissociated acid, and the resultant shifting of the equilibrium $\text{MeA}_x^{n-xm} \rightleftharpoons \text{Me}^{+n} + x\text{A}^{-m}$ to the right. If a solution of MeA_x^{n-xm} of known acidity is allowed to equilibrate and the concentration of Me^{+n} ion is then determined, the dissociation constant, $[\text{Me}^{+n}][\text{A}^{-m}]^x/[\text{MeA}_x^{n-xm}]$, of the complex can be

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computed from these data and knowledge of the ionization constant of the weak acid. The concentration of the Me^{+n} ion can be determined by isotopically labeling the Me in the complex, and then, after the solution of complex has equilibrated in acid solution, adding a known portion of inactive Me^{+n} ion to the solution and separating the excess Me^{+n} from the MeA_x^{n-xm} complex. The concentration of the Me^{+n} ion originally in the solution due to dissociation of the complex will be proportional to the radioactivity of the final Me^{+n} ion solution. This method of determining the equilibrium Me^{+n} concentration will be in error unless the Me^{+n} and Me^{+n} ions undergo complete mixing before any recomplexing with A^{-m} occurs, and unless the exchange between excess Me^{+n} ion in solution and complexed Me^* is negligible, or at least measurably slow.

This report deals with the application of this radiochemical method to the determination of the known dissociation constant of the coordination complex ferroin. This work was undertaken to provide a check upon the accuracy of the radiochemical method, which appears to be applicable to a wide variety of coordination complexes. It has been used previously by the authors for the determination of the dissociation constant of the nickel-ethylenediaminetetraacetic acid complex, whose exchange kinetics are being investigated.

Orthophenanthroline, which we will represent as Ph, reacts with ferrous iron to form an intensely red colored complex, ferroin, FePh_3^{++} , which is widely used as an oxidation-reduction indicator and in the colorimetric determination of iron. Phenanthroline,



is an organic base which, presumably because of steric effects, combines with only one hydrogen ion in acid solution. Lee, Kolthoff, and Leussing¹ determined the acid dissociation constant of the resulting phenanthrolium ion, HPh^+ , to be 1.1×10^{-5} .

These authors have studied the stability of the complexes FePh^{++} , FePh_2^{++} , as well as ferroin, FePh_3^{++} , and have found² that the latter is sufficiently more stable than the first two so that the complexes FePh^{++} and FePh_2^{++} , which would complicate study of the FePh_3^{++} if they were present in any amount, will exist in appreciable quantities only in the presence of excess Fe^{++} . Using a colorimetric method, these authors¹ found the dissociation constant of FePh_3^{++} to be 5×10^{-22} .

Procedure

A stock solution of active ferroin was prepared by mixing a Fe^{55} -labeled ferric sulfate solution of known strength with a slight excess over the stoichiometrical quantity of orthophenanthroline monohydrate. The solution was then treated with hydroxylamine sulfate and with sulfur dioxide to effect reduction to ferroin. The ferrous phenanthroline complex is stable to the

¹T.S. Lee, I.M. Kolthoff, and D.L. Leussing, J. Am. Chem. Soc. 70, 2348 (1948)

²I.M. Kolthoff, D.L. Leussing, and T.S. Lee, J. Am. Chem. Soc. 72, 2173 (1950)

atmosphere. Samples of the stock solution were mixed with known quantities of sulfuric acid in volumetric flasks and diluted to the mark; the air above the solution was flushed out with nitrogen; and the solution was allowed to stand at 25° for two or more days. It was then mixed with a large excess of inactive Fe⁺⁺, and the FePh₃⁺⁺ was removed by precipitation with excess CdI₄⁼ and the filtration. The filtrate containing ferrous ion was acidified; its radioactivity was determined in a solution counter of fixed geometry.

Computations

Let C be the total concentration of Fe* as Fe⁺⁺ and Fe*Ph₃⁺⁺ in the solution before the addition of the large excess of inactive Fe⁺⁺, i.e., C would be the concentration of Fe*Ph₃⁺⁺ that would exist in solution if no dissociation took place. Let α be the fractional dissociation of the original Fe*Ph₃⁺⁺ complex.

The dissociation constant of HPh⁺ is taken as $\frac{[H^+][Ph]}{[HPh^+]} = 1.1 \times 10^{-5}$.

Define the dissociation constant of FePh₃⁺⁺ as $K_d \equiv \frac{[Fe^{++}][Ph]^3}{[FePh_3^{++}]}$.

The following relations hold in the equilibrium solution (concentrations being denoted by parentheses and activities by brackets):

$$(Fe^{++}) = \alpha C$$

$$(FePh_3^{++}) = (1-\alpha)C$$

$$(Ph) = \frac{3C\alpha}{F(H)}, \text{ where } F(H) \equiv 1 + \frac{(H^+) \gamma_{H^+}/\gamma_{HPh^+}}{1.1 \times 10^{-5}},$$

$$\text{since } 3(Fe^{++}) = (Ph) + (HPh^+) = (Ph) + \frac{[H^+][Ph]/\gamma_{HPh^+}}{1.1 \times 10^{-5}}$$

$$\cong (Ph) \left(1 + \frac{(H^+) \gamma_{H^+}/\gamma_{HPh^+}}{1.1 \times 10^{-5}} \right), \text{ assuming } (Ph) = [Ph].$$

$$\text{Thus, } K_d = \frac{27 C^3}{F(H)^3} \frac{\alpha^4}{1-\alpha}, \text{ assuming } \gamma_{Fe^{++}} = \gamma_{FePh_3^{++}}.$$

In this expression the quantities C and F(H) are determined by the conditions of the experiment, while $\alpha = \frac{\text{counts/sec of Fe}^{++} \text{ separated from solution}}{\text{counts/sec of original Fe*Ph}_3^{++}}$ corrected for such effects as the difference in density of the two solutions.

In computing F(H), the assumed values of the ratio of the activity coefficients $\gamma_{H^+}/\gamma_{HPh^+}$ were interpolated from data given in the work of Lee et al.¹ The hydrogen ion concentrations in the solutions were computed using values of the apparent second dissociation constant of H₂SO₄ as a function

of ionic strength taken from the work of Klotz and Eckert.³

Results

The accompanying table summarizes the results of eight runs carried out at various H_2SO_4 and FePh_3^{++} concentrations:

<u>Summary of Results</u>						
Run No.	Initial Conc. of H_2SO_4 (M)	Initial Conc. of FePh_3^{++} (M)	Observed α	Conc. of H^+ (M)	$\frac{\gamma_{\text{H}^+}}{\gamma_{\text{FePh}_3^{++}}}$	$K_d \times 10^{22}$
1	0.400	0.50×10^{-2}	0.439	0.427	1.5	11.3
2	0.300	1.00 "	0.178	0.325	1.35	5.2
3	0.250	0.50 "	0.271	0.275	1.3	7.4
4	0.250	0.25 "	0.410	0.275	1.3	5.9
5	0.100	1.00 "	0.094	0.1174	1.15	12.5
6	0.050	0.50 "	0.094	0.0623	1.1	12.0
7	0.050	0.25 "	0.144	0.0626	1.1	8.7
8	~ 0.001	0.50 "	~ 0.007	~ 0.001	1	~ 110

Not counting Run No. 8, which was run at a low acid concentration for the purpose of checking on the magnitude of such effects as exchange or incomplete separation of FePh_3^{++} , these data show an average value of $K_d = 9.0 \times 10^{-22}$.

In their determination of K_d , Lee et al.¹ used a means of calculating H^+ ion concentration based upon individual ion activity coefficients. If values of H^+ concentration derived from their data are substituted in the table, the average value of K_d determined therefrom is lowered to 7.8×10^{-22} . This appears to be a satisfactory check with the 5×10^{-22} value found previously by Lee et al.

³I.M. Klotz and C.F. Eckert, J. Am. Chem. Soc. 64, 1878 (1942)

REACTION OF DEUTERIUM WITH HYDROCARBONS OVER A COBALT-THORIA FISCHER-TROPSCH CATALYST

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Abstract

The isotopic nature of the products of exchange reactions between deuterium and protium methane, ethane, propane, n-butane,

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and isobutane on a cobalt-thoria-magnesia-kieselguhr Fischer-Tropsch catalyst has been determined under conditions used for the synthesis of hydrocarbons from carbon monoxide and hydrogen. In all cases except that of isobutane, the exchanged hydrocarbons showed a nonstatistical distribution of deuterium, in the sense that a high degree of deuterization is favored. The isotopic nature of the deuteromethanes formed by cracking deuterization was also determined. The results are interpreted in terms of radical fragments on the catalyst surface. It is suggested that in some cases the results may be accounted for in terms of reactions of the completely dehydrogenated carbon skeleton with a limited local pool of adsorbed protium and deuterium atoms.

Introduction

Taylor^{1,2} and coworkers established that paraffin hydrocarbons, methane to propane, undergo exchange with deuterium on nickel at 65 to 180°C, with the production of not only deuterated hydrocarbons but also of methane. A. and L. Farkas³ demonstrated that propane, butane, n-hexane, and cyclohexane also exchange on platinized platinum. The isotopic nature of the deuterocompounds was not established. These findings were interpreted to indicate that the chemisorption of the hydrocarbon molecule on the surface was of the dissociative type, leading to the production of hydrocarbon radicals and hydrogen atoms on the catalyst surface.^{4,5}

As a part of the mechanism studies of the Fischer-Tropsch synthesis being carried out in this Laboratory, an investigation was made of the interaction of deuterium with hydrocarbon gases over a cobalt-thoria-magnesia-kieselguhr catalyst under synthesis conditions. Two objectives were sought: to determine the stability of the hydrocarbon gases toward exchange, and to gain some insight as to the types of radicals present on the catalytic surface from the isotopic character of the exchanged products.

Procedure

The catalyst was a cobalt-thoria-magnesia-kieselguhr preparation.⁶

The hydrocarbon gases were C.P. grade Matheson Company products. The propane, however, was Phillips Company research grade gas. The deuterium was 99% isotopically pure; it was obtained from the U.S. Atomic Energy Commission.

¹K. Morikawa, W.S. Benedict, and H.S. Taylor, J. Am. Chem. Soc. 58, 1445, 1795 (1936)

²K. Morikawa, N.R. Trenner, and H.S. Taylor, J. Am. Chem. Soc. 59, 1103 (1937)

³A. and L. Farkas, Trans. Faraday Soc. 35, 917 (1939); 36, 522 (1940)

⁴H.S. Taylor and J. Turkevich, J. Am. Chem. Soc. 56, 2254 (1934)

⁵M.M. Wright and H.S. Taylor, Can. J. Research B27, 302 (1949)

⁶B.R. Anderson, A. Krieg, B. Seligman, W.E. O'Neill, Ind. Engr. Chem. 39, 1548 (1947)

The catalyst (4.6 g) was reduced by recycling the deuterium gas (1 liter) over the catalyst at 400°C at a space velocity 2000 per hour. The gas was changed every half hour by partial evacuation of the reactor and recycle pump and recharging them to atmospheric pressure with pure deuterium gas. After a reduction schedule of 3 hours, the temperature was lowered to 183°C and the system was kept at this temperature in an atmosphere of deuterium. The deuterium-hydrocarbon mixture was prepared in a 3-liter flask at 2 atmospheres pressure and in a mole ratio of 6 to 1, as determined by manometric measurements. Immediately before each run, the catalytic chamber was evacuated and the gas allowed to flow at a space velocity of 140-150/hr at 183°C and 1 atmosphere pressure. The products were collected in bulbs placed in the line of flow, and were analyzed in a General Electric Company mass spectrometer.

Experimental Results

A quantitative evaluation of the nature and extent of the exchange reactions involves the conversion of the positive ion currents of the mass spectra into numbers representing the abundances of the various isotopic molecular species in the sample. This has been carried out by assuming that the mass spectra of the various deuterated hydrocarbons can be calculated from the corresponding protium hydrocarbons on a purely statistical basis, i.e., assuming the equality of the ease of removal of hydrogen or deuterium from a hydrocarbon molecule. This approach has been taken before for lack of a better, unified treatment of the mass spectra of deuterocarbons.⁷ In the following, the results obtained with the individual hydrocarbons are discussed from this point of view.

Methane

Under Fischer-Tropsch synthesis conditions, there was no exchange between methane and deuterium as revealed by infrared analysis. A Baird double-beam infrared spectrometer was used to examine the 4.6 μ C-D band; this method is capable of detecting about 2% exchanged methanes. When a gas mixture of 6 parts deuterium and 1 part methane was allowed to stand for 17 hr in contact with the catalyst at 183°C, about 11% of the total sample underwent exchange to form deuteromethanes: 1.7% CD₄, 0.1% CD₃H, 9% CH₃D, and 89% CH₄. Morikawa, Benedict, and Taylor¹ found, on a nickel catalyst, 17% of the molecules exchanged in 25 hr with a one-to-one hydrocarbon-deuterium mixture.

Ethane

Under synthesis conditions, 5.8% of the ethane molecules underwent exchange revealed by the following analysis of a typical run: 2.4% C₂D₆, 0.4% C₂D₅H, 0.3% C₂D₄H₂, 2.7% C₂D₂H₄, and 94.2% C₂H₆. The original ethane contained less than 1% C₂H₄ as revealed by infrared analysis, and was subjected to bromine treatment before use. Mass spectrometric analysis revealed also the presence of 1% of deuteromethanes, with the following isotopic composition: 41% CD₄, 10% CD₃H, and 49% CH₃D. These results may be interpreted in the fol-

⁷J. Turkevich, L. Friedman, E. Solomon, and F.M. Wrightson, J. Am. Chem. Soc. 70, 2638 (1948)

lowing way: At least 5.8% of the ethane in the reaction zone dissociated, when adsorbed on the surface, into radicals and hydrogen atoms.⁸ Since there was a large excess of deuterium present on the surface, the hydrogen atoms were replaced by deuteriums. The hydrocarbons that desorb from the surface thus have become deuterated to the extent that they previously lost hydrogens. Analysis of the deuterocarbons should, therefore, give insight into the type of radicals present on the surface. Simple calculations indicate that 100 moles of ethane, dissociated on the surface, produced the following amounts of free radicals: $41C_2$, $6.8C_2H$, $5.1C_2H_3$, $46.1C_2H_4$, and small amounts of C_1 , CH , and CH_3 .

Propane

Of the propane, 6% exchanged with deuterium to form deuteropropanes: 4.7% C_3D_8 and 1.4% C_3D_7H . The deuterium also reacted to form 1-2% methanes: 64% CD_4 , 12.4% CD_3H , 7% CD_2H_2 ; 2.5% CDH_3 , and 14% CH_4 . The general picture of the association of the propane with the surface appears to be similar to that prevailing with ethane. A large part of the propane on the surface was in the form of C_3 aggregates and C_3H complexes. About 5-10% underwent carbon scission to form methane. The formation of CH_4 may have resulted from a $C_3H_8 \rightarrow C + 2CH_4$ reaction proposed by Morikawa, Trenner, and Taylor.^{1,2} Otherwise, the methane was highly deuterated, indicating a marked tendency of the isolated methyl radicals also to lose their hydrogens.

n-Butane

n-Butane underwent extensive exchange with deuterium, forming 7.9% C_4D_{10} , 11.8% C_4D_9H , 10.6% $C_4D_8H_2$, 8.9% $C_4D_7H_3$, 2.7% $C_4D_6H_4$, 0.6% $C_4D_5H_5$, and 58.2% C_4H_{10} . The amount of methane formed varied with the space velocity from 6.9%, for a space velocity of 75/hr to 2%, for one of 150/hr. The isotopic composition of the methane was the same for both space velocities: 48% CD_4 , 38% CD_3H , and 14% CD_2H_2 . Again, the association of the butane with the surface resulted in a predominant rupture of carbon hydrogen bonds and the preservation of the carbon-carbon bonds.

In contrast to the deuteropropanes, the deuterobutanes showed a wider distribution of number of deuteriums, from C_4D_{10} to $C_4D_5H_5$. This might be interpreted to mean the existence of radicals from C_4 to C_4H_5 on the surface. It should be realized, however, that this distribution may be due also to the fact that the active catalytic area on the surface may not have obtained sufficient deuterium atoms from the gas phase to avoid back hydrogenation of the C_4 radical by protium atoms.

Thus, in the above case, one can account qualitatively for the distribution of the deuterobutanes by assuming that a molecule of butane loses all its protium atoms in the adsorbed phase of a pool of deuterium atoms, that complete mixing takes place, and that the desorbed deuterobutanes are in the ratio of probabilities of removing the appropriate amounts of H and D from the combined pool.

⁸C. Kemball and H.S. Taylor, J. Am. Chem. Soc. 70, 345 (1948)

Isobutane

About 50% of the isobutane molecules underwent exchange, as revealed by the following analysis:* 0.4-0% C₄D₁₀, 0.6-1.5% C₄D₉H, 6.1-3.5% C₄D₈H₂, 4.7-6.0% C₄D₇H₃, 5.5-8.6% C₄D₆H₄, 11.0-11.1% C₄D₅H₅, 10.2-10.0% C₄D₄H₆, 6.0-5.0% C₄D₃H₇, 3.0-1.5% C₄D₂H₈, 2.0-1.5% C₄DH₉, and 48.1-48.9% C₄H₁₀.

The percentage of methane formed was low, about 0.2%, and was analyzed as 6% CD₄, 18% CD₃H, 35% C₂D₂H₂, 33% CDH₃, and 8% CH₄.

It is clear from the above results that the association of isobutane with the cobalt thoria catalyst is different from that of the straight chain hydrocarbons. This difference expresses itself in the statistical distribution of the deuterium not only in the isobutanes, but also in the methanes formed and in the small amount of cracking that takes place. The behavior of isobutane is in many ways similar to that observed by Beeck⁹ and coworkers⁹ on the exchange of this compound with water on aluminum chloride.

*The first figures in the analysis were obtained on the assumption that in the exchange the hydrogen always prefers the tertiary carbon atom; the second figures are based on the assumption that the deuterium atom prefers that position.

⁹C.D. Wagner, O. Beeck, J.W. Otvos, D.P. Stevenson, J. Chem. Phys. 17, 419-20 (1949)

THE EPIMERIZATION OF GLUCOSE-1-C¹⁴

A.A. Bothner-By and M. Gibbs*

The mechanism (or mechanisms) by which the epimerization of glucose proceeds in alkaline solution is not clearly established, the commonly accepted intermediate formation of an enediol being inconsistent with the results of the investigations of Fredenhagen and Bonhoeffer¹ concerning the conversion of glucose to fructose in heavy water. A rearrangement of the carbon chain of glucose during the course of the reaction has not been excluded by any earlier work and could conceivably occur. Such a rearrangement would be detectable using glucose-1-C¹⁴ which has recently become available.² We have performed this experiment, and our results indicate that no rearrangement takes place.

Experimental

1.3 mg of glucose-1-C¹⁴ having a specific activity of 120 mμc/mg** was

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¹Fredenhagen and Bonhoeffer, Z. physik. Chem. A181, 392 (1938)

²Sowden, Science 109, 229 (1949)

**The glucose-1-C¹⁴ was most generously furnished us by Prof. J.C. Sowden.

diluted with 30 mg of inactive glucose and dissolved in 0.2 ml of saturated calcium hydroxide solution. The solution was kept at 70° for 2 hours,³ then chilled and passed over 1 g each of Amberlite IR-100-H and IRA-400 ion exchange resins. The volume with washings was 6 ml. The mixed sugars were diluted with 25 mg inactive glucose, and were degraded by the method of Wood, Lifson, and Lorber.⁴ The specific activities obtained were: for the glucose carbon atoms 1 and 6, 4.4 mμc/mg of carbon; carbon atoms 2 and 5, 0.1 mμc/mg; carbon atoms 3 and 4, 0.09 mμc/mg. A similar distribution of label in the lactic acid was obtained by degrading glucose-1-C¹⁴ which had not been epimerized.⁵

³DeBruyn and Van Ekenstein, Rec. trav. chim. 14, 203 (1895)

⁴Wood, Lifson, and Lorber, J. Biol. Chem. 159, 475 (1945)

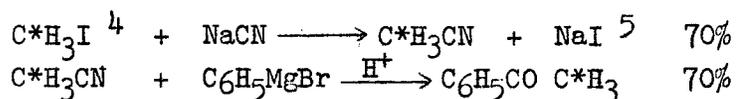
⁵Gibbs, Dumrose, Bennett, and Bubeck, J. Biol. Chem. (in press)

THE MECHANISM OF THE WILLGERODT REACTION

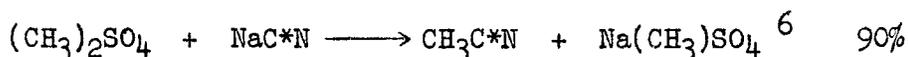
E. Cerwonka, R.C. Anderson, in collaboration with
E. Brown of Fordham University

Carbon isotopes have been employed by two groups^{1,2} in the investigation of the Willgerodt reaction mechanism. With acetophenone as the starting material, the Willgerodt reaction yields two products, phenylacetamide and phenylacetic acid. Both groups agree that the phenylacetamide retains the carbon skeleton of the original acetophenone. However, Dauben announced the untoward result that the phenylacetic acid had a rearranged skeleton. The evidence was not conclusive, and a subsequent publication³ has not settled the issue decisively.

The present work was undertaken to resolve this problem. To this end, acetophenone-(carbonyl)-C¹⁴ and acetophenone-(methyl)-C¹⁴ have been prepared via the following sequence(s) of reactions.



and



¹Shantz and Rittenberg, J. Am. Chem. Soc. 68, 2109 (1946)

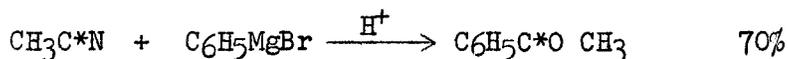
²Dauben, Reid, Yankwich, Calvin, J. Am. Chem. Soc. 68, 2117 (1946)

³Dauben, Reid, Yankwich, Calvin, J. Am. Chem. Soc. 72, 121 (1950)

⁴Prepared by H.C. Prosser of the Brookhaven staff according to Melville et al., J. Biol. Chem. 169, 419 (1947)

⁵Kilmer and du Vigneaud, J. Biol. Chem. 154, 247 (1944)

⁶The best yields of the acetonitrile are obtained by this method. Walden, Berichte 40, 3214 (1907)



In both syntheses, the Grignard addition to the nitrile was accomplished by using a 4:1 ratio of starting materials.⁷ The Willgerodt reactions were run according to the procedure of Carmark and Spielman,⁸ in which the ketone was treated with sulfur, ammonium hydroxide, and pyridine in a sealed tube at 170°C for 12 hours. The products, phenylacetamide and phenylacetic acid, were recovered according to Dauben's procedures.^{2,3}

For the determination of the isotopic carbon positions, the compounds were combusted by a modified Van Slyke-Folch reagent, and the evolved CO₂ trapped in NaOH solution. The NaOH·Na₂CO₃ solution was then acidified and the CO₂ finally trapped in Ba(OH)₂·BaCl₂ solution. All the counts reported are on BaCO₃ precipitates at infinite thickness for 1 cm².

The carbonyl carbon in the phenylacetamide was obtained by a Hoffman degradation. The BaCO₃ was reprecipitated in this case. The carboxyl carbon in phenylacetic acid was obtained by decarboxylation using copper chromate catalyst in quinoline at reflux temperature. The CO₂ evolved was trapped in NaOH solution and handled as above. Yields of CO₂ were 65-75%

Results of the Assays on C ₆ H ₅ COC*H ₃	
Compound	cpm/cm ² as BaCO ₃
1. Total C ₆ H ₅ COC*H ₃	75
2. Total C ₆ H ₅ CH ₂ C*ONH ₂	75
3. Total C ₆ H ₅ CH ₂ CO ₂ H	74
4. CO ₂ from Hoffman	600
5. CO ₂ from decarboxylation	487:500
6. Theory of ratio of 4/2	8:1
7. Theory of ratio 5/3	8:1

The phenylacetamide and phenylacetic acid from C₆H₅C*O CH₃ have been obtained but not assayed.

The results thus far do not significantly differ from those of Dauben. However, it is felt that a rearrangement as postulated is not a necessary conclusion from these results. More likely, the possibility exists that the decarboxylation procedure used here and by Dauben suffers from not being clean. If some of the toluene resulting on decarboxylation were oxidized, the dilution of the carboxyl CO₂ activity is explicable. To establish this point the phenylacetic acid obtained will be converted to the acid chloride and then aminated to give phenylacetamide, which in turn will be subjected to a Hoffman degradation. If this indicates no rearrangement in the carbon side chain, the point at issue will be completely settled. In addition, the use of the acetophenone-(carbonyl)-C¹⁴ will serve to complement to above results.

⁷Shriner and Turner, J. Am. Chem. Soc. 52, 267 (1930)

⁸Carmark and Spielman, Organic Reactions, Vol. III, (1946)

THE THERMAL DECOMPOSITION OF $N^{15}N^{14}O$

L. Friedman and J. Bigeleisen

Abstract

The mechanism of the thermal decomposition of nitrous oxide is discussed in the light of measurements on the isotopic composition of N_2 resulting from the decomposition of mixtures of $N^{15}N^{14}O^{16}$ and $N^{14}N^{14}O^{16}$. It was found that the product N_2 is formed from N_2O without rupture of the N-N bond. Hence, previously proposed mechanisms involving N-N bond rupture are considered untenable. The results are consistent with a mechanism involving dissociation into N_2 and O, followed by reactions of the oxygen atoms with N_2O and with each other.

Several mechanisms have been proposed for the thermal decomposition of nitrous oxide. A combination of quasi-unimolecular reactions have been assumed to account for the experimentally observed variation of half-time with initial pressure.¹ It has been shown that an atomic chain mechanism of 1.5 order also fits the experimental data.² We have investigated the thermal decomposition of $N^{15}N^{14}O$ in order to obtain additional information on the mechanism of this reaction.

$N^{15}N^{14}O$ was prepared by the thermal decomposition of samples of $N^{15}H_4NO_3$ obtained from the Eastman Kodak Company according to a method described previously.³ The N_2O so obtained was transferred to a quartz reactor fitted with a break seal. Decompositions were carried out by heating the N_2O at approximately 750°C for two hours in the sealed quartz tube. Runs were made with initial pressures of approximately 80 mm at 25°C. The composition of the product gas was determined by mass spectrometric analysis with a 60° sector type spectrometer. The absence of appreciable ion currents in the $m/e=44$ region, above the normal background of CO_2 , was taken as good evidence for the completeness of the decomposition.

Samples of N_2O containing approximately 7.5 and 60% excess $N^{15}N^{14}O$ were decomposed. The 7.5% sample contained approximately 0.37% $N^{14}N^{15}O$ and 0.03% $N^{15}N^{15}O$ resulting from the 0.4% natural abundance of N^{15} in the nitrate ion in the source ammonium nitrate. In the case of the 60% sample, 0.16% $N^{14}N^{15}O$ and 0.24% $N^{15}N^{15}O$ were the expected "isotopic impurities."

Several mechanisms have been considered previously for the path of the decomposition. Hinshelwood and Burk⁴ first proposed a bimolecular collision

¹C.N. Hinshelwood, *The Kinetics of Chemical Change*. Oxford University Press, New York, 1945. pp. 131-6.

²R.N. Pease, *Equilibrium and Kinetics of Gas Reactions*. Princeton University Press, Princeton, 1942. pp. 128-34.

³L. Friedman and J. Bigeleisen, Brookhaven National Laboratory Progress Report, January-March, 1950 (BNL 51(S-5)). p. 33.

⁴C.N. Hinshelwood and R.E. Burk, *Proc. Roy. Soc. London* A106, 284 (1924).

process in which two molecules of nitrogen and one molecule of oxygen are formed directly from two molecules of N_2O . A second possibility is the decomposition according to the scheme:



This mechanism leads to a complex order of the reaction which is dependent on the relative magnitudes of k_2 and k_3 and lies between 1 and 2. Pease² has proposed a chain mechanism which leads to a 1.5-order reaction



Pease proposed this mechanism primarily because the data of Hunter⁵ could be fitted by a rate law of order $3/2$. The $3/2$ -order rate law resulted in a single activation energy, in contrast to two activation energies in different pressure ranges from a first-order rate law. Musgrave and Hinshelwood⁶ found a catalytic effect of NO on the reaction, and also found that NO is present to a small extent in the products of the uncatalyzed reaction. Pease considered this as evidence for a mechanism involving NO as an intermediate.

From some qualitative considerations of the force constants in the N_2O molecule, one might expect reaction (1) to be more favorable energetically than reaction (4).

It has been shown that molecular nitrogen does not come to isotopic equilibrium in a quartz vessel at $750^\circ C$ in a period of 40 hours contact time,⁷ so that an equilibrium distribution of isotopic nitrogen molecules is expected only for a decomposition mechanism involving the rupture of N-N bonds. The results obtained in two experiments in which a mixture of $N^{14}N^{14}O$ and $N^{15}N^{14}O$ were decomposed are presented in the accompanying table. The results of the decomposition of 7.5% excess $N^{15}N^{14}O$ are perhaps consistent with the chain processes of the type suggested in reaction (4-7) occurring simultaneously with a quasi-unimolecular reaction. However the possibility of traces of nitric oxide in the decomposition products and of background in the mass spectrometer at $m/e=30$ could easily account for the deviation of the ratio 30/29 which was found from that expected for a process in which the isotopic isomerization equilibrium of the nitrogen atoms is not established. The experiment using 60% excess N^{15} was much more conclusive. The results are in good agreement with the isotopic distribution estimated for a non-chain dissociation process. The slightly high experimental value of $m/e=30$ can be completely accounted for by the assumption of small amounts of $N^{14}O^{16}$. This assumption is supported by the observation of ions of $m/e=31$ which can only be $N^{15}O^{16}$.

⁵E. Hunter, Proc. Roy. Soc. London A144, 386 (1934).

⁶F.F. Musgrave and C.N. Hinshelwood, Proc. Roy. Soc. London A135, 23 (1932).

⁷G.C. Joris and H.S. Taylor, J. Chem. Phys. 7, 893 (1939).

<u>Mass-Spectrometer Analysis of the Products</u> <u>of the Decomposition of N¹⁵N¹⁴O₁₆ and N¹⁴N¹⁴O₁₆ Mixtures</u>				
m/e =	28	29	30	31
	N ¹⁴ N ¹⁴	N ¹⁴ N ¹⁵	N ¹⁵ N ¹⁵ + N ¹⁴ O ₁₆	N ¹⁵ O ₁₆
Expt. 1) (7.5% N ¹⁵ N ¹⁴ O ₁₆)	92.35	7.55	0.096	-
Calc. 1) N-N bonds do not rupture	92.34	7.60	0.03	
Calc. 2) Isotopic equilibrium be- tween N atoms in N ₂	92.57	7.10	0.147	
Expt. 2) (60% N ¹⁵ N ¹⁴ O ₁₆)	37.9	61.66	0.44	0.15
Calc. 1)	37.7	62.0	0.26	-
Calc. 2)	48.8	42.5	9.77	-

Two possibilities exist for the formation of N¹⁵O₁₆ in this reaction mixture. It can be formed in the dissociation and rearrangement of N¹⁵N¹⁴O, reactions of nitrogen atoms with N₂O, or oxygen atoms with N₂O to give NO. Reactions which consume N¹⁵O are ones between NO, and N₂O and N nitrogen atoms, respectively. In the case of the reaction between oxygen atoms and N₂O, one would expect 30% N¹⁵O and 70% N¹⁴O from a starting mixture containing 60% N¹⁵N¹⁴O. A reasonable value of the relative abundance of N¹⁴O may be obtained by subtracting the value of N¹⁵N¹⁵ calculated for no equilibration of nitrogen atoms from the total intensity of the m/e=30 peak. On this basis, the ratio of N¹⁵O/N¹⁴O is approximately 3/4, rather than 3/7. In view of the rather small concentrations of N¹⁴O and N¹⁵O, we are not certain whether any significance may be attached to this difference.

In conclusion, it is evident that, from the studies on the decomposition of N¹⁵N¹⁴O, the mechanism suggested by Pease is untenable, and any mechanism involving the rupture of N-N bonds should be eliminated from consideration. The results are consistent with the quasi-unimolecular reaction outlined in equations (1), (2), and (3), essentially the mechanism proposed by Hinshelwood and Hunter.¹ They also indicate that the excellent agreement between the kinetic data of Hunter and the chain mechanism proposed by Pease was fortuitous.

THE INFRARED SPECTRA OF $N^{15}N^{14}O^{16}$ AND $N^{14}N^{15}O^{16}$.
SOME THERMODYNAMIC PROPERTIES OF THE ISOTOPIC N_2O MOLECULES

J. Bigeleisen and L. Friedman

Abstract

The three fundamental frequencies of $N^{15}N^{14}O^{16}$ have been studied in the infrared. One stretching frequency and the bending frequency in $N^{14}N^{15}O^{16}$ have been similarly investigated. The bending frequencies in $N^{15}N^{14}O^{16}$ and $N^{14}N^{15}O^{16}$ are found to be in good agreement with calculations from the product rule. Some slight changes are made in the force constants for the stretching vibrations in N_2O . The stretching frequency ω_3 in $N^{14}N^{15}O^{16}$ provides a good independent check on the force constants.

The partition function ratios for isotopic exchange reactions involving nitrogen and oxygen in N_2O are calculated. The isomerization equilibrium $N^{15}N^{14}O^{16} = N^{14}N^{15}O^{16}$ has been calculated over the temperature range 273.16-1000°K. A correlation is drawn between the structures of the isotopic isomers, $N^{15}N^{14}O^{16}$ and $N^{14}N^{15}O^{16}$, and the isomerization equilibrium.

Introduction

In the course of an investigation of some aspects of the controlled thermal decomposition of ammonium nitrate into nitrous oxide and water, we prepared a sample of nitrous oxide enriched in N^{15} exclusively in the end position.¹ The availability of such a sample afforded the opportunity of determining its infrared spectrum with the expectation of improving the potential function for the vibrations of nitrous oxide. In a concurrent and independent investigation, Richardson and Wilson² have described the preparation of a sample of nitrous oxide containing 60% N^{15} in the end position, and the infrared spectrum of this molecule in the fluorite and rock salt regions of the spectrum. They have also evaluated the stretching force constants in the potential functions:

$$2V = f_1 \Delta r_1^2 + f_2 \Delta r_2^2 + 2 f_{12} \Delta r_1 \Delta r_2 \quad (1)$$

We have measured the shift in the three fundamental vibrational frequencies of N_2O on substitution of N^{15} for N^{14} in the end position, and in two of the fundamental vibrations on N^{15} substitution in the center. The measurements on the $N^{14}N^{15}O^{16}$ afford an independent check on the force constants in equation (1), and confirm Richardson and Wilson's force constants. A slight

¹L. Friedman and J. Bigeleisen, Brookhaven National Laboratory Progress Report, January-March, 1950 (BNL 51(S-5)). p. 33.

²W.S. Richardson and E.B. Wilson, Jr., J. Chem. Phys. 18, 694 (1950)

improvement of their force constants results from the combination of our measurements on $N^{15}N^{14}O_2$ and theirs, as evidenced by a better agreement with the product rule and the spectrum of $N^{14}N^{15}O_2$. The potential function (1) and the product rule have been used to calculate the vibrational frequencies of $N^{14}N^{14}O_2$. From the vibrational frequencies, the partition function ratios of the various isotopic N_2O molecules can be calculated. The partition function ratio f , $N^{14}N^{15}O_2/N^{15}N^{14}O_2$, is just the equilibrium constant for the isomerization equilibrium



Thus, we can calculate the equilibrium between a pair of isotopic isomers. The results of the measurements and calculations are presented below.

Experimental

The preparation of a sample containing 7.5% N^{15} in the end position has been described previously.¹ A sample of N_2O containing 31.4% N^{15} in the center position and 0.4% N^{15} in the end position was prepared from 31.4% $N^{15}-HNO_3$ as a starting material. The nitric acid was obtained from the Eastman Kodak Company. Five millimoles of the enriched nitric acid were titrated with ordinary ammonium hydroxide to the stoichiometric end point; brom-phenol blue was used as an external indicator. The solution was evaporated to dryness and the solid ammonium nitrate was decomposed to give N_2O by the method described previously.¹ It has been shown^{1,2} that the decomposition of $N^{15}H_4N^{14}O_3$ yields $N^{15}N^{14}O$ exclusively. Therefore, the decomposition of a sample of ammonium nitrate enriched in N^{15} in the nitrate ion yields N_2O enriched in N^{15} in the middle position.

The spectra were measured with a Baird Associates, Inc., Model B infrared recording spectrophotometer. The shifts in the ν_1 and ν_3 bands, 1285.4 and 2224.1 cm^{-1} , respectively, in $N^{14}N^{14}O_2$ were measured with a rock salt prism; those in the ν_2 band were measured with a KBr prism. The cells were 5 cm long and equipped with KBr windows. A sample of tank N_2O was used in the reference cell. The shifts were measured from experiments in which the pressure in the reference cell was equal to the total pressure of N_2O in the sample cell. The shutter in front of the mirror in the sample beam was adjusted to give roughly 50% transmittance in a spectral region of no absorption. Under these conditions, an excess transmittance, negative absorption, appears at the absorption frequencies of $N^{14}N^{14}O_2$ corresponding to the amount of absorption for one of the N^{15} -substituted molecules at its corresponding frequency. This negative absorption provides an internal wavelength calibration of the instrument. The wavelength shift was determined using the dispersion of the instrument as furnished by the manufacturer. The frequency shift over a small spectral region is given by the relation:

$$\Delta\nu = -\bar{\nu}^2 \Delta\lambda, \quad (3)$$

where $\bar{\nu}$ is the average of the frequency determined by Plyler and Barker³ and the corresponding N¹⁵-substituted frequency, and is easily calculated to a higher precision than the present experimental measurements. Determinations of the wavelength shifts were made by measurements of recorded spectra as well as point-by-point manual scanning of the spectrum. The latter gave better precision and reproducibility because of the fact that the response time of the bolometer and recording system is not negligible in comparison with the time to scan an absorption peak.

The above procedure for measuring small frequency shifts was checked by measuring the separation of close absorption lines in the ammonia spectrum. The separations measured in this way were compared with the precise grating measurements of Barker.⁴ No systematic deviations were found; the accuracy of our determinations was limited by the precision to which the wavelength shift could be measured. The corresponding errors in the shifts in the N₂O spectrum on N¹⁵ substitution are indicated along with the experimental results.

Results

The shifts in the bending frequency ν_2 were easily resolved by the KBr optics, and were determined from the separation of the pronounced Q branches. In accord with expectations, no shift could be found in the low stretching frequency ν_1 for the N¹⁴N¹⁵O¹⁶ molecule. In the case of the N¹⁵N¹⁴O¹⁶ molecule, the shifts in ν_1 in both the P and R branches were clearly resolved and measured. In the measurement of the ν_3 shift in N¹⁵N¹⁴O¹⁶, the R branch of the N¹⁵N¹⁴O¹⁶ molecule was complete unresolved from the P branch of the N¹⁴N¹⁴O¹⁶. The separation between the R branch of N¹⁴N¹⁴O¹⁶ and the P branch of N¹⁵N¹⁴O¹⁶ was measured. The shift in the band origin was calculated from this measured separation; the value of 28 cm⁻¹ was estimated for the P-R separation.^{3,5} The shift in ν_3 in the N¹⁴N¹⁵O¹⁶ molecule was sufficiently large so that the P and R branches of both the N¹⁴N¹⁴O¹⁶ and N¹⁴N¹⁵O¹⁶ molecules appeared distinctly. The experimentally determined frequency shifts are given in the accompanying Table I.

I. Frequency Shifts on N ¹⁵ Substitution in N ₂ O (cm ⁻¹)				
Designation	N ¹⁴ N ¹⁴ O ¹⁶ ^a	N ¹⁴ N ¹⁴ O ¹⁶ -N ¹⁵ N ¹⁴ O ¹⁶ ^b	N ¹⁴ N ¹⁴ O ¹⁶ -N ¹⁵ N ¹⁴ O ¹⁶	N ¹⁴ N ¹⁴ O ¹⁶ -N ¹⁴ N ¹⁵ O ¹⁶
ν_1	1285.0	17.5	16.1 ± 1.4	-
ν_2	588.8	-	4.2 ± 0.3	12.9 ± 0.2
ν_3	2223.5	22.5	29 ± 4	46.5 ± 2.0

^aMeasurements of Plyler and Barker³ reduced to vacuum.⁶
^bRichardson and Wilson.²

³E.K. Plyler and E.F. Barker, Phys. Rev. 38, 1827 (1931)

⁴E.F. Barker, Phys. Rev. 55, 657 (1939)

⁵C.P. Snow, Proc. Roy. Soc. A128, 294 (1930).

⁶G. Herzberg, Infra-Red and Raman Spectra of Polyatomic Molecules. D. Van Nostrand Co., Inc., New York, 1945. p. 278.

The shifts determined for the $N^{15}N^{14}O^{16}$ agree with the measurements made by Richardson and Wilson within the limits of the experimental errors of both measurements. As will be shown below, their shift in ν_3 is undoubtedly more accurate than ours as a result of their use of a fluorite prism to measure this shift.

The experimental zero-order stretching frequencies are tabulated in the accompanying Table II. The zero-order frequencies for $N^{14}N^{14}O^{16}$ are those calculated by Herzberg⁶ from the observed fundamentals, combination, and overtone bands. The zero-order frequencies for $N^{15}N^{14}O^{16}$ and $N^{14}N^{15}O^{16}$ have been calculated from the ones for $N^{14}N^{14}O^{16}$, the observed shifts in Table I, and the approximate relations introduced by Dennison:⁷

$$\omega_j = \nu_j(1 + \alpha_j) \quad (4)$$

$$\omega_j^i \approx \nu_j^i \left[1 + \alpha_j (\nu_j^i / \nu_j) \right] \quad (5)$$

The zero order bending frequencies are given in the accompanying Table III.

The first check that can be made on the isotopic zero order frequencies is by means of the Teller-Redlich product rule.⁸ For the linear XYZ molecule, this rule states:

$$\frac{\omega_1 \omega_3}{\omega_1^i \omega_3^i} = \left(\frac{m^i}{m} \cdot \frac{M}{M^i} \right)^{\frac{1}{2}} \quad (6)$$

$$\frac{\omega_2}{\omega_2^i} = \left(\frac{m^i}{m} \cdot \frac{M}{M^i} \cdot \frac{I}{I^i} \right)^{\frac{1}{2}}, \quad (7)$$

where the superscript i refers to the isotopically substituted molecule, m is the mass of the isotopically substituted atom, M is the mass of the molecule, and I is the moment of inertia of the molecule. The bending vibrations ω_2^i have been calculated from equation (6), with the value of ω_2 calculated from Plyler and Barker's data.⁶ The moments of inertia of $N^{14}N^{14}O^{16}$, $N^{15}N^{14}O^{16}$, and $N^{14}N^{15}O^{16}$ have been determined by microwave spectroscopy.^{9,10} The experimentally determined microwave frequencies were used directly, since $I \propto 1/\nu$. The moment of inertia of $N^{14}N^{14}O^{18}$ was calculated using 1.126 Å and 1.191 Å for the N-N and N-O bond distances,⁹ respectively. The values of ω_2 calculated from the product rule are compared with experiment in Table III. The agreement between the observed and calculated frequencies is satisfactory. The deviations can be ascribed to experimental error, and the reduction of the observed frequencies to zero-order frequencies by Dennison's approximation.

⁷D.M. Dennison, Rev. Mod. Phys. 12, 175 (1940)

⁸See Ref. 6 pp. 112, 231, ff.

⁹D.K. Coles, E.S. Elyash, and J.G. Gorman, Phys. Rev. 72, 973 (1947).

¹⁰D.K. Coles and R.H. Hughes, Phys. Rev. 76, 178 (1949).

II. Zero-Order Stretching Frequencies for the Isotopic N ₂ O Molecules (cm ⁻¹)											
N ¹⁴ N ¹⁴ O ¹⁶				N ¹⁵ N ¹⁴ O ¹⁶				N ¹⁴ N ¹⁵ O ¹⁶			N ¹⁴ N ¹⁴ O ¹⁸
Designation	Observed	Calc. from Force Constants A Table IV	Calc. from Force Constants C Table IV	Observed R & W	Observed this Re-search	Calc. from Force Constants A Table IV	Calc. from Force Constants C Table IV	Observed	Calc. from Force Constants A Table IV	Calc. from Force Constants C Table IV	Calc. from Force Constants C Table IV
ω_1	1299.8	1298.8	1299.8	1281.9	1283.3	1283.0	1283.5	-	1296.2	1298.6	1256.2
ω_3	2276.5	2277.1	2276.5	2252.9	2246.2	2252.3	2252.6	2227.8	2228.8	2228.1	2270.8

III. Zero-Order Bending Frequencies for the Isotopic N ₂ O Molecules (cm ⁻¹)		
Molecule	ω_2 Observed	ω_2 Calculated (Product Rule)
N ¹⁴ N ¹⁴ O ¹⁶	596.5	-
N ¹⁵ N ¹⁴ O ¹⁶	592.2	592.9
N ¹⁴ N ¹⁵ O ¹⁶	583.2	582.8
N ¹⁴ N ¹⁴ O ¹⁶	-	591.9

The product rule check for the stretching frequencies is given in the accompanying Table IV. It is clear from the product rule check that Richardson and Wilson's value for ω_3 for $N^{15}N^{14}O^{16}$ is to be preferred to ours. The best agreement with the product rule is obtained by using their value for ω_3 and our value for ω_1 for $N^{15}N^{14}O^{16}$, together with Plyler and Barker's measurements on $N^{14}N^{14}O^{16}$. This combination gives for the ratio of the product of the stretching frequencies 1.0235, in perfect agreement with the product rule. There is no other reason to prefer our measurements for ω_1 over those of Richardson and Wilson. Therefore, we have chosen as the best set of values for the zero-order frequencies for $N^{15}N^{14}O^{16}$ their value for ω_3 , and the average of their value and ours for ω_1 .

IV. Force Constants ^a and Product Rule Check for the Stretching Frequencies in N_2O				
Quantity	A	B	C ^b	Product Rule
	Richardson and Wilson	$N^{15}N^{14}O^{16}$ (This Research)		
f_1	18.98	22.22	18.71 ₇	
f_2	11.50	10.31	11.66 ₁	
f_{12}	1.43	3.56	1.31 ₂₇	
$\frac{\omega_1\omega_3}{\omega_1^i\omega_3^i}$	1.0246	1.0265	1.0240	1.0235

^aForce constants in units of 10^5 dynes/cm.
^bCalculated from $\omega_3(N^{15}N^{14}O^{16})$ from Richardson and Wilson, and $\omega_1(N^{15}N^{14}O^{16})$ from the average of R and W and this research

The force constants in the potential function (1) can be calculated from the zero-order frequencies by the use of the following relations:

$$\lambda_1 + \lambda_3 = (\mu_x + \mu_y) f_1 + (\mu_y + \mu_z) f_2 - 2 \mu_y f_{12} \quad (8)$$

$$\lambda_1 \lambda_3 = (\mu_x \mu_y + \mu_x \mu_z + \mu_y \mu_z) (f_1 f_2 - f_{12}^2) \quad (9)$$

where $\lambda = 4\pi^2\omega^2$ and $\mu_k = 1/m_k$. Equations (8) and (9) have been solved for the force constants from the zero-order frequencies of $N^{14}N^{14}O^{16}$ and $N^{15}N^{14}O^{16}$. Three sets of force constants are listed in table IV corresponding to three sets of frequencies for $N^{15}N^{14}O^{16}$. The force constants in column A are those calculated by Richardson and Wilson; those in Column B are calculated from our measurements on $N^{15}N^{14}O^{16}$; those in column C are calculated from Richardson and Wilson's value for ω_3 , and the average of their value and ours for ω_1 . Our value of ω_3 leads to an unsatisfactory set of force constants. The resulting

value of f_1 , corresponding to N-N stretching, is higher than the force constant in the nitrogen molecule, which seems unreasonable. The interaction constant f_{12} is also rather large. There is little difference between the force constants in column C and those in column A. As has been pointed out by Richardson and Wilson, the interaction constant is most sensitive even to the slight changes which we have introduced in Richardson and Wilson's values for the frequency shifts.

The stretching frequencies in the molecules $N^{14}N^{14}O^{16}$, $N^{15}N^{14}O^{16}$, $N^{14}N^{15}O^{16}$, and $N^{14}N^{14}O^{18}$ have been calculated from the force constants in Table IV. They are compared with experiment in Table II. The only independent check on the force constants is afforded by the measured value of ω_3 for $N^{14}N^{15}O^{16}$. The agreement of both force constant sets A and C is well within the limits of the experimental error. Set C gives a slightly better agreement than does set A. Either set of force constants can be used to calculate the stretching frequencies of any one of the isotopic N_2O molecules to a few tenths of a wave number.

Thermodynamic Properties

The vibrational frequencies for $N^{14}N^{14}O^{16}$, $N^{15}N^{14}O^{16}$, $N^{14}N^{15}O^{16}$, and $N^{14}N^{14}O^{18}$ in tables II and III can be used to calculate nitrogen and oxygen exchange equilibria involving N_2O . The equilibria are most readily calculated with the aid of the tables published for calculating partition function ratios.¹¹ The partition function ratios, f values,¹¹ for nitrogen and oxygen substitution in N_2O are given in the accompanying Table V. The stretching frequencies used in the calculations were those calculated from force constants C in Table IV; the bending frequencies were those calculated in Table III. The conversion factor hc/k was taken as 1.43847.¹²

The partition function ratio f , $N^{14}N^{15}O^{16}/N^{15}N^{14}O^{16}$, is the equilibrium constant for the isomerization reaction (2). This can readily be seen from the definition of f .¹³ The values for the equilibrium constant are about as large as most of the ones which arise from the exchange of nitrogen atoms between different chemical species.¹⁴ This may appear surprising and counter to the expectation that isotopic isomerization equilibrium constants should be smaller than equilibrium constants for exchange between different kinds of molecules. The large equilibrium constant in the present case can be understood from the nature of the normal modes of vibration and the product rule. The shift in the stretching frequencies on N^{15} substitution is distributed between the modes corresponding to ω_1 and ω_3 . In the mode ω_1 , the central nitrogen atom is virtually at rest; therefore, N^{15} substitution in the central position puts almost all of the shift in the high frequency ω_3 . This makes a large contribution to f by virtue of the larger values of both the factor

¹¹J. Bigeleisen and M.G. Mayer *J. Chem. Phys.* 15, 261 (1947). See equation (11a) and Table I

¹²Selected Values of Chemical Thermodynamic Properties. National Bureau of Standards, June 30, 1948

¹³See Ref. 11, equation (7)

¹⁴H.C. Urey, *J. Chem. Soc.* 1947, 562

V. Partition Function Ratios and Exchange Equilibria Involving N ₂ O						
T°K	f	f	f = K	f	K	
	$\frac{N^{15}N^{14}O^{16}}{N^{14}N^{14}O^{16}}$	$\frac{N^{14}N^{15}O^{16}}{N^{14}N^{14}O^{16}}$	$\frac{N^{14}N^{15}O^{16}}{N^{15}N^{14}O^{16}}$	$\frac{N^{14}N^{14}O^{18}}{N^{14}N^{14}O^{16}}$	$\frac{N^{14}N^{14}O^{18}}{N^{14}N^{14}O^{16}}$	$\frac{H_2O^{16}}{H_2O^{18}}$
273.16	1.0915	1.1401	1.0445	1.1127	1.0359	
298.16	1.0814	1.1246	1.0399	1.0916	1.0233	
300	1.0808	1.1235	1.0395	1.0908		
400	1.0541	1.0827	1.0271	1.0586	1.0116	
500	1.0388	1.0595	1.0199	1.0408	1.0056	
600	1.0291	1.0449	1.0154	1.0299	1.0023	
700	1.0226	1.0350	1.0121	1.0227		
800	1.0180	1.0280	1.0098	1.0179		
900	1.0147	1.0229	1.0081	1.0144		
1000	1.0122	1.0190	1.0067	1.0118		

G(u) and also Δu . The bending mode, which is doubly degenerate, also has a larger shift on N¹⁵ substitution in the center, rather than on the end, because of the fact that the center atom is very close to the center of gravity of the molecule.

The oxygen exchange equilibrium constant between gaseous N₂O and H₂O is also included in Table V. The partition function ratios for the water molecules are taken from Urey's tabulation.¹⁴ This equilibrium has been calculated previously by Rosenthal,¹⁵ who obtained the value 1.056 at 0°C. The discrepancy between Rosenthal's calculations and those in table V arises from the fact that her stretching frequencies for N¹⁴N¹⁴O¹⁸ were calculated from a potential function based entirely on the spectrum of N¹⁴N¹⁴O¹⁶.

Acknowledgement

We wish to thank W.S. Richardson and E.B. Wilson, Jr., for sending us a copy of their manuscript on the infrared spectrum of N¹⁵N¹⁴O prior to publication.

¹⁵J.E. Rosenthal, J. Chem. Phys. 5, 465 (1937)

THE EFFECT OF ISOTOPIC SUBSTITUTION ON THE MASS SPECTRAL PATTERNS OF MOLECULES

O.A. Schaeffer

Abstract

The effect of isotopic substitution on the mass spectral patterns of simple molecules is discussed. A general approximate method for predicting this effect is presented. It is assumed that bond rupture occurs through independent harmonic vibrations of the individual bonds. The probability of a particular mode of fragmentation is calculated from the vibrational wave functions of the molecule and from values of the critical separation of the two atoms, the latter numbers being estimated from the known mass spectral pattern of an isotopic molecule. Predictions are compared with experiment for a number of cases. Agreement within the limits of experimental error is found, although experimental errors obscure sharp test of the predictions.

There have been a number of determinations¹ of the effect of isotopic substitution on the mass spectral pattern of a molecule. Except for the case of hydrogen, no theoretical calculations which explain these effects quantitatively appear in the literature.

When a molecule is ionized by electron impact in a mass spectrometer, a number of products are formed because of the breaking of one or more bonds in the molecule. The nature of this process has been understood for some time.² The first step is the removal of one or more electrons by the impinging electron, sometimes accompanied by excitation of the remaining electrons. This process takes place in a time so short that the nuclei can be considered at rest. The effect on the nuclei is that they suddenly find themselves in a new potential field, that of the smaller number of electrons. Depending on the configuration of the nuclei at the time of impact, the molecule will decompose or remain intact.

Two kinds of information are required for a prediction of the probability for breaking a given bond or set of bonds. These are 1) a knowledge of which configurations of the nuclei lead to the rupture of the given bond or set of bonds, and 2) the probability of finding the nuclei in a given configuration. The latter is obtained easily from the ground state vibrational wave functions. Vibrational wave functions are available for most simple molecules from analysis of spectral data. The former type of information can be deduced from appropriate potential functions for the various ionized states. Such potential functions are, in general, however, not available.

Because so little is known about the potential surfaces of molecular ions,

¹See, for example, J. Turkevich, L. Friedman, E. Solomon, and F.M. Wrightson, J. Am. Chem. Soc. 70, 2638 (1948)

²W. Bleakney, E.U. Condon, and L.G. Smith, J. Phys. Chem. 41, 197 (1937)

these ideas have been applied only to a calculation of the relative yields of molecular and atomic ions from hydrogen.³ For hydrogen, the potential function of the ions as well as accurate wave functions are known. The agreement between this calculation and recent experimental results⁴ shows that the essential ideas on which the theory is based are valid. It is the purpose of this report to describe an approximate method which allows a calculation of the change in mass spectral pattern on isotopic substitution without a knowledge of the potential surfaces of the ionic states.

The General Method

The potential energy of a molecule or molecule ion can be approximated by the form:

$$V = \frac{1}{2} \sum_j k_j R_j^2, \quad (1)$$

where R_j is the j^{th} internal coordinate. This form neglects the coupling terms of the form $k_{ij} R_i R_j$ and all anharmonic terms. Such a potential does give reasonable agreement between calculated and observed vibrational frequencies for polyatomic molecules.⁵ Then for each bond i in a given molecule ion, there will be some distance R_{ci} such that, when R_i , the bond length, is less than R_{ci} , the potential energy of the bond will be larger than the energy required to break the bond.

It will be assumed that, for a given arbitrary displacement of the nuclei, those bonds and only those bonds will break for which:

$$R_i < R_{ci} \quad (2)$$

This assumption is the basis for the application to polyatomic molecules. It states, in effect, that the bonds are independent. That is, if one bond possesses a large amount of potential energy, it will dissociate rather than distribute its potential energy among the other bonds.

The assumption certainly is valid for diatomic molecules, where only one bond is involved. The application to diatomic molecules will furnish no test of this hypothesis, but will serve as a check on the correctness of the approximations used.

The problem now is to evaluate the various R_{ci} 's, which would be a relatively easy matter if the appropriate potential functions for the molecule ion were available. In place of such information, the R_{ci} 's can be considered as parameters to be evaluated by inserting values for the probabilities for breaking the bonds. The bond breaking probabilities may be determined from the mass spectral pattern of one of the isotopic molecules. For example, the probability of breaking the bond in the molecule X-X would be given by

³D.P. Stevenson, J. Chem. Phys. 15, 409 (1947)

⁴O.A. Schaeffer and J.M. Hastings, J. Chem. Phys. (in press)

⁵See for example, G. Herzberg, Infrared and Raman Spectra. D. Van Nostrand Co., 1945

$X^+/(X^+X_2^+)$. The R_{ci} values are invariant to an isotopic substitution. As defined, they depend on the potential surface of the molecule ion which is negligibly influenced by an isotopic substitution for one of the nuclei. The mass spectral patterns of the other isotopic molecules can then be obtained by the use of the R_{ci} 's and the known vibrational wave functions. In effect, the calculation allows an estimate of the pattern of a molecule if the pattern of an isotopic molecule is available.

The vibrational wave function for the harmonic oscillations of a polyatomic ion or molecule can be written:

$$\psi(Q) = e^{-\frac{\alpha_1}{2} Q_1^2} \cdot e^{-\frac{\alpha_2}{2} Q_2^2} \cdot \dots \cdot e^{-\frac{\alpha_n}{2} Q_n^2}, \quad (3)$$

where Q represents the totality of the normal coordinates, Q_i being a particular one, and:

$$\alpha_i = \frac{2\pi(m_i k_i)^{\frac{1}{2}}}{h} \quad (4)$$

The other symbols have their usual significance. The normal coordinates can be expressed in terms of internal coordinates R by:

$$Q_k = \sum_i J_{ki} R_i \quad (5)$$

In terms of internal coordinates, the wave function becomes:

$$\psi(R) = e^{-\frac{\alpha_1}{2}(J_{11}R_1 + J_{12}R_2 + \dots + J_{1n}R_n)^2} \cdot e^{-\frac{\alpha_2}{2}(J_{21}R_1 + J_{22}R_2 + \dots + J_{2n}R_n)^2} \cdot \dots \cdot e^{-\frac{\alpha_n}{2}(J_{n1}R_1 + J_{n2}R_2 + \dots + J_{nn}R_n)^2} \quad (6)$$

Let P_k be the probability of breaking the k^{th} bond and no other bonds, and let $P_{k,j}$ be the probability of breaking the k^{th} and j^{th} bonds simultaneously and no other bonds, and so forth for other combinations of bonds.

Then according to the previously stated assumption (2):

$$P_k = \int_{R_k=0}^{R_{ck}} \int_{R_i \neq k = R_{ci}}^{\infty} \psi^2(R) dR \quad (7)$$

and

$$P_{kj} = \int_{R_k=0}^{R_{ck}} \int_{R_j=0}^{R_{cj}} \int_{R_i \neq k \text{ or } j = R_{ci}}^{\infty} \psi^2(R) dR, \quad (8)$$

with similar expressions for the other P values. Since values for the Q's, i.e., the J's, and for the α 's can be determined by a normal coordinate analysis of the molecule, the values of the R_{gi} 's are uniquely determined, in principle, by relations of the type (7) and (8), together with values of the P's obtained from the mass spectral pattern.

The determination of the P's from the mass spectral data involves certain approximations which need further discussion. It would be a simple matter to evaluate the P's accurately if only one electronic state of the ion were involved. But for most work reported in the literature, the data were obtained at relatively high accelerating voltages, in the neighborhood of 50 v. For electrons of 50-v energy, molecules will be excited to a number of ionic states, so that the measured ratio $X^+/(X_2^++X^+)$, for example, will not represent P for a single state, but rather will be an average value of P over several states.

To evaluate how large such effects may be, the numbers in the accompanying Table I were calculated. The body of the table lists values of $X^+/(X_2^++X^+)$ for the isotopic molecule whose α is 1.1 times the α of the normal molecule.

I. Calculated Ion Ratios $X^+/(X_2^++X^+)$ of Isotopic Diatomic Molecules for Various Types of Electronic States					
Assumed Experimental Ratio for the Normal Molecule	One Bonding Ionic State	Two Bonding States		One Bonding, One Repulsive State c	All X^+ from Repulsive States
		a	b		
0.050	0.042	0.043	0.045	0.046	0.050
0.100	0.089	0.090	0.094	0.092	0.100
0.200	0.189	0.190	0.195	0.190	0.200

^aFor half the X^+ ions coming from each state, 1/3 the X_2^+ from one state, and 2/3 the X_2^+ from the other.
^bFor all the X^+ ions coming from the same state, half the X_2^+ coming from each state.
^cFor half the X^+ ions coming from each state, all the X_2^+ coming from the same state.

The range of $X^+/(X_2^++X^+)$ listed in Table I is that encountered in most molecules. The calculation based on a single state does not deviate appreciably from the value if two states are involved, both of comparable $X^+/(X_2^++X^+)$ ratio; however, it does deviate appreciably from the true value if one of the states either contributes no X^+ and a large fraction of the X_2^+ , or if a large amount of the X^+ comes from the repulsive states. An interesting point to note is that, in this range of $X^+/(X_2^++X^+)$, the largest isotope effect is obtained if the X^+ all comes from a single bound state.

For experimental data which are determined at low electron voltages, there will be negligible amounts of ions contributed from repulsive states.

However, there will not necessarily be negligible amounts of undissociated ions contributed from states having low probability of fragmentation. The assumption of only one state as responsible will lead to an upper limit for the isotope effect.

Comparison with Experimental Data

Nitrogen

The mass spectral pattern of a mixture of $N^{14}N^{14}$, $N^{14}N^{15}$, and $N^{15}N^{15}$ has been obtained using 50-v electrons.⁷ From this pattern and that of a sample of natural abundance nitrogen, it was possible to obtain values of X^+/X_2^+ for all three isotopic molecules. These are listed in the accompanying Table II, along with a set of values calculated by the preceding method, assuming that all the ions originate from a single state.

II. X^+/X_2^+ Ratios for the Nitrogen Molecules		
Molecule	Observed ⁷ X^+/X_2^+	Calculated X^+/X_2^+
N ¹⁴ N ¹⁴	0.067	(Used to evaluate R_c) 0.065 0.063
N ¹⁴ N ¹⁵	0.067	
N ¹⁵ N ¹⁵	0.061	

The agreement between the experimental data and the calculated values is satisfactory. The ratios listed by Mohler and coworkers were obtained by subtracting a number of contributions to the 14 and 15 mass peaks, a procedure which tends to increase the error. The observations were made by electrostatic scanning, which requires a correction for discrimination. Discrimination will reduce the apparent isotope effect and make the observed values approach the calculated ones. On the other hand, there are known low-lying states of N_2^+ whose R_c values are so small that the states would lead to negligible fragmentation.

Carbon Monoxide

For carbon monoxide, Dibeler and coworkers⁸ have obtained the ratios $C^{13+}/C^{13}O^{16+}$ and $C^{12+}/C^{12}O^{16+}$ from a C^{13} -enriched sample. The comparison of these observations with a calculated $C^{13+}/C^{13}O^{16+}$ ratio appears in the accompanying Table III. Here again, the agreement is better than one would expect, as the same sort of errors are involved as discussed before for nitrogen.

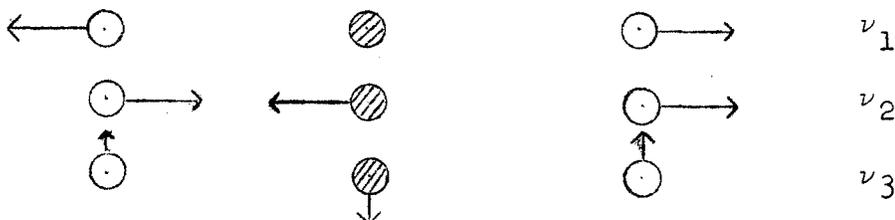
⁷V. Dibeler, F. Mohler, R. Reese, J. Chem. Phys. 18, 156 (1950)

⁸V. Dibeler, E. Wells, Jr., and R. Reese, Bull. Am. Phys. Soc. 25, #3, 32, Abstract N8 (April, 1950)

III. C^+/CO^+ Ratios for Carbon Monoxide		
Molecule	Observed ⁸ C^+/CO^+	Calculated C^+/CO^+
$C^{12}O^{16}$ $C^{13}O^{16}$	0.054 0.051	(Used to evaluate R_c) 0.052

Carbon Dioxide

A particularly interesting case which will test the assumption of the independence of the bonds is that of the ratios $C^{13+}/C^{13}O_2^{16+}$ and $C^{12+}/C^{12}O_2^{16+}$ from carbon dioxide. The normal modes of carbon dioxide are represented below.



The bending mode can be neglected as there are never any large repulsive terms in its motion. The only mode capable of yielding C^+ is ν_1 , to the approximation discussed before. Since for ν_1 , m equals the mass of O^{16} , the value of α for $C^{13}O_2^{16}$ and $C^{12}O_2^{16}$ will be the same. Hence, the observed ratios $C^{13+}/C^{13}O_2^{16+}$ and $C^{12+}/C^{12}O_2^{16+}$ should be the same. Dibeler and coworkers⁸ have reported the values $C^{13+}/C^{13}O_2^{16+} = 0.0542$ and $C^{12+}/C^{12}O_2^{16+} = 0.0564$. Since it seemed that this non-equality might have been caused by a discrimination error by the mass spectrometer used, this point was investigated, by redetermining the values at high accelerating voltages and with magnetic scanning, at this Laboratory. The ratios are listed in the accompanying Table IV for several electron voltages.

IV. C^+/CO_2^+ Ratios from $C^{12}O_2^{16}$ and $C^{13}O_2^{16}$		
Electron Voltage*	$C^{12+}/C^{12}O_2^{16+}$	$C^{13+}/C^{13}O_2^{16+}$
35	0.0121	0.0123
40	0.0216	0.0220
50	0.0318	0.0328
60	0.0392	0.0400
68	0.0412	0.0418
*Not corrected for contact potential		

These data show the C^+/CO_2^+ ratio to be the same from $C^{12}O_2^{16}$ and $C^{13}O_2^{16}$, within 2%. The agreement is within the experimental error.

From the results given in Tables II, III, and IV, one can conclude that the proposed method of calculation, with its necessary approximations, leads to reasonable agreement with the experimental results available at present. It must be admitted that the inaccuracies inherent in the available experimental data prevent a sharp comparison with theory. The data of Mohler, Dibeler, and coworkers,^{7,8} undoubtedly suffer from discrimination errors introduced by the method of scanning employed. Our data, likewise, may be in error from discrimination caused by the source magnet.⁹

⁹Brookhaven National Laboratory Progress Report, January-March, 1950 (BNL 51 (S-5)) p. 32

ON THE RELATIVE EFFICIENCIES FOR THE COLLECTION OF
POSITIVE IONS BY A 60°-SECTOR MASS SPECTROMETER

O.A. Schaeffer

Abstract

The discrimination effect in a 60°-sector type mass spectrometer has been studied with electrostatic scanning and with magnetic scanning. It is found that electrostatic scanning causes serious discrimination errors in relative abundance measurements, which, however, can be practically eliminated by scanning at high ion accelerating voltages, 4000-5000 v. Magnetic scanning, on the other hand, yields ratios free from discrimination at voltages from 750 to 5000 when the ions have initially only thermal energy. For ions which are formed by rupture of bonds and possess appreciable kinetic energy, only magnetic scanning at voltages in excess of 4000 gives a pattern free from major discrimination errors.

The relative abundances of positive ions of different e/m ratios formed in the source of a mass spectrometer by electron impact are not necessarily the same as the relative abundances of these same positive ions received on the collector plate and recorded. The effect of preferentially collecting ions of certain e/m is usually called discrimination. One of the consequences of discrimination is that the mass spectral patterns of molecules or mixtures of isotopes vary with the particular magnetic and ion accelerating field chosen to focus the various ions on the collector.¹ For a given method

¹This is particularly evidenced by the patterns reported in the American Petroleum Institute Research Project 44, National Bureau of Standards Catalog of Mass Spectral Data. If one compares the patterns obtained with a relatively low accelerating voltage and magnetic scanning with those patterns obtained at higher voltages using electrostatic scanning, one finds that differences as large as a factor of two are not uncommon among the lighter fragments.

of scanning, the patterns are closely reproducible. As a result, discrimination errors can be eliminated from the analytical applications of mass spectrometry by the use of proper internal standards. However, this effect is of concern in some other aspects of mass spectrometry, such as the determination of isotope abundances and the interpretation of differences in mass spectral patterns of isotopic molecules. In the former case, discrimination may introduce a systematic error far exceeding the precision available. In the latter case, one may ascribe a change in pattern wholly to the effect of isotopic substitution, when indeed the effect, in certain cases, might be predominantly a discrimination effect. It has been calculated² that, for a simplified ion source, the collimating slit may cause the measured abundance ratio of Ne^{20} to Ne^{22} ions to differ from the true value by about 1% if the ions are brought into focus at a fixed magnetic field by varying the ion accelerating voltage. The seat of the effect is that the differences in the random initial velocities of the ions (thermal motion) with different masses cause the different masses to have different efficiencies in traversing the slits in the ion source. This same calculation indicates that magnetic scanning should eliminate the effect.

More recently, experimental data have been presented³ for the difference in the pattern of n-butane using either magnetic or electrostatic scanning, and also for the variation of different peak heights with accelerating voltage. Here also, the cause of the effect was believed to be differences in the initial velocities of the ions, resulting in this case from differences in the recoil momenta of the various fragments. It was found that neither electrostatic scanning nor magnetic scanning at 1200 v gave a pattern free from discrimination.

Bainbridge⁴ has pointed out that, in order to maintain identical trajectories for the various e/m ions in a spectrometer with a fixed source magnetic field, the masses must be scanned by varying the ion accelerating field. For this reason, one would favor electrostatic scanning over magnetic scanning. This conclusion is at variance with that suggested by Coggeshall's calculation and also with the results of the following investigation.

It is thus evident that differences in the initial velocities of the ions can cause a discrimination effect. However, the remedy for this effect is not as evident; while magnetic scanning will eliminate the discrimination due to different velocities, it may introduce an error due to different trajectories of the ions. This investigation was directed at the questions as to how large such effects are and how they can be minimized in measured ratios.

Experimental

All the data were obtained with the 60° -sector type mass spectrometer described elsewhere.⁵ The only difference was that the magnet current was

²N.D. Coggeshall, J. Chem. Phys. 12, 19 (1944)

³H. Washburn and C. Berry, Phys. Rev. 71, 559 (1946); C. Berry, Phys. Rev. 78, 597 (1950)

⁴K.T. Bainbridge, Rapports et Discussions sur Les Isotopes. R. Stoops, Brussels, 1948. pp. 83, 97

⁵O.A. Schaeffer and J.M. Hastings, J. Chem. Phys. (in press)

supplied by a regulated electronic power supply with a sweep circuit which slowly increased the magnetic field. The source magnet was positioned to obtain a maximum ratio of trap current to total emission current, then repositioned slightly to give maximum ion beam current without reducing the trap current to emission current ratio. The spectrometer was operated with an emission current of 120 μ amp, a trap current of 50 μ amp, and 40-v electrons. The sample pressure behind the leak was adjusted so that the pressure in the mass spectrometer tube was about 1×10^{-6} mm of Hg.

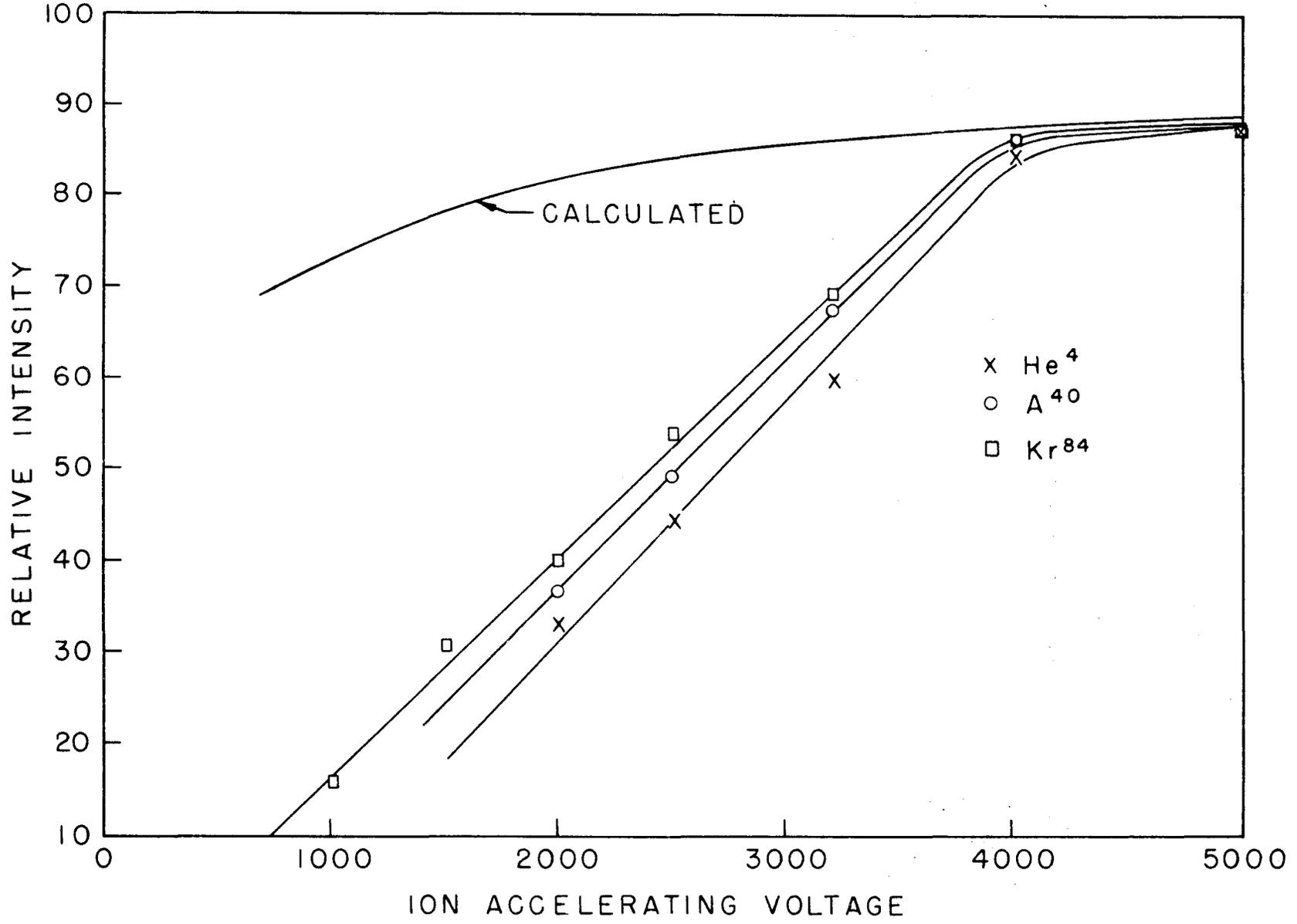
The ion source voltages were readjusted for each scan of the magnet. For krypton, mass 84 was focused, and then masses 78 to 86 were scanned. It was observed that when mass 84 was properly focused, all the krypton isotopes were also focused. For the other rare gases, the ion source voltages were adjusted so that each mass was in proper focus. The propane data were obtained by focusing on mass 29 and then scanning the masses 12 to 45. It was found that this procedure gave proper focus conditions, except for the lowest masses, which could be increased in intensity by roughly 10% by refocusing. While the method of scanning used introduces roughly 10% error in the absolute ratios of the lowest masses to mass 44, it introduces a comparatively smaller error in the trend of the ratios with accelerating voltage.

Electrostatic scanning was accomplished by manually varying the ion acceleration field with a voltage divider network, keeping the ions in proper focus by readjusting the ion source voltages for each mass.

The krypton sample was obtained from a tank supplied by Linde. The rare gas samples of A and He were Matheson tank gases. The propane was Phillips research grade. All the gases were used without further purification.

Effect of Discrimination on Isotope Abundance Measurements

In order to evaluate the nature of voltage effects on measured isotope abundances, a set of curves was obtained which represent the variation in ion intensity with ion accelerating voltage for Kr^{84} , A^{40} , and He^4 . These are presented in the accompanying figure along with a calculated curve. The experimental curves in the figure have been plotted in such a way that at 5000 v all curves have the same value, i.e., the intensities, in recorder divisions, of the experimental points for each curve have been divided by a number which makes the 5000-v value the same as on the calculated curve. The calculation was made on the basis that the decrease in intensity as the voltage is lowered is due to the thermal motion of the ions in the source; it was similar to Coggeshall's calculation,² except that it was made in terms of the geometry of the ion source used here. For the calculation, it was assumed that the wide top slits and the first narrow slit had no effect, and that all the discrimination was caused by the second narrow slit, which was the one just before the magnetic analyzer. It was further assumed that the slit immediately before the collector also had no discrimination effect. The basis for the last assumption was the fact that this slit was opened to several times its usual width for these experiments. It was found that the slit could then be closed appreciably without diminishing the peak heights, which could only be the case if the beam were focused by the magnet to a size smaller than the slit. With the slit this wide, it was still possible to resolve completely the



Variation of ion intensities with accelerating voltage.

krypton isotopes, as evidenced by the fact that the ion current dropped to zero between the various krypton peaks.

It is quite evident that the calculated curve does not approximate the experimental curves, except possibly for the region from 4000 to 5000 v. The difference is that the experimental voltage effect is much larger than the calculated one. The focusing efficiency of the ion source increases with voltage; also, the high voltage can penetrate further into the ionizing region and collect ions over a larger volume. Both of these effects have been neglected in the calculation. The curves also show, however, that the collection efficiency is not solely a function of the ion accelerating voltage, but depends also, to some extent, on the e/m of the ion being focused. This is evidenced by the fact that the curves for He^4 , A^{40} , and Kr^{84} are not parallel over the entire voltage range. The dependence of e/m can be ascribed to the fact that the various e/m ions do not traverse the same trajectory because of the fixed source magnetic field. Because of the rather steep slope of these curves, it is apparent that electrostatic scanning of a mixture of isotopes at voltages below 4000 would lead to erroneous abundances.

It has been observed that, quantitatively, this behavior is dependent on the positioning of the source magnet, and that for certain positions the voltage effect will be different from that illustrated in the figure. However, the qualitative features remain, namely: that there is a several-fold enhancement in using 4000 over 1000-v ion accelerating potential, that there is a relatively small additional enhancement in going to 5000 v, and that the various mass curves are not parallel. The curves in the figure are typical of what is considered an optimum source magnet position using the criteria discussed in the experimental section of this article. That the position of the source magnet affects the collection efficiency is reasonable, since any movement of the source magnet causes a corresponding movement of the electron beam and, hence, a movement of the region in which the ions are formed.

From the results, one would conclude that the best scanning conditions with this type of instrument would be high accelerating voltage and magnetic scanning. The mass effect is not very large; the data show that in traversing a 10% range in mass, as is the case for most isotopes, one would introduce less than a 1% error by using magnetic scanning, even at low voltages.

To determine the effects for an actual case, the relative abundances of the krypton isotopes were determined by scanning the masses magnetically at several ion accelerating voltages from 750 to 5000 v, and by electrostatic scanning at low voltages and at high voltages. The data are presented in the accompanying Table I. Each set of values represents the average of from one to three individual determinations. There are no evident systematic trends in the magnetically scanned values with voltage. However, the electrostatically scanned value at low voltages deviates quite considerably from any of these values, while the one scanned at high voltages does not deviate from the magnetically scanned values beyond the experimental error of about 1% for a single determination.

The electrostatically scanned values are what one would predict from curves similar to those in the figure. The additional information obtained from the magnetically scanned results is that, for the mass range covered by krypton, the mass effect is less than experimental error.

I. <u>Isotope Abundances of Krypton with Different Scanning Methods</u>									
Mass	Magnetic Scanning							Electrostatic Scanning	
	750 v	1000 v	1500 v	2000 v	3000 v	4000 v	5000 v	H ₁ ^a	H ₂ ^b
78	0.337	0.334	0.338	0.340	0.344	0.341	0.345	0.38	0.35
80	2.21	2.22	2.22	2.23	2.27	2.26	2.25	2.46	2.30
82	11.49	11.50	11.48	11.42	11.42	11.46	11.45	11.90	11.51
83	11.45	11.51	11.48	11.41	11.42	11.46	11.45	11.58	11.60
84	56.80	56.97	57.00	57.14	57.03	56.94	57.03	56.85	56.97
86	17.70	17.46	17.50	17.46	17.51	17.53	17.47	16.83	17.27

^aMagnetic field such that mass 78 is focused at 1700 v.
^bMagnetic field such that mass 78 is focused at 4500 v.

The magnetically scanned results for krypton were averaged and then corrected for fractionation caused by the leak employed.⁵ The values are compared with those of previous investigators in the accompanying Table II. The results of the present work, when uncorrected for fractionation, agree well with those of Thode,⁶ while the corrected values deviate slightly and agree more nearly with Nier's⁷ corrected values. Thode⁶ used a capillary type leak, and it is difficult to understand that such a leak does not require any correction for fractionation.

II. <u>Comparison of Various Isotopic Krypton Abundances</u>					
Mass	This Research		Lounsbury, Epstein and Thode ⁶	Nier ⁷	Dibeler, Mohler and Reese ⁸
	Uncorrected	Corrected for Fractionation			
78	0.34	0.35	0.34	0.34	0.36
80	2.23	2.28	2.23	2.26	2.25
82	11.47	11.61	11.50	11.50	11.57
83	11.45	11.51	11.48	11.50	11.44
84	57.00	56.94	57.02	56.95	57.14
86	17.53	17.31	17.43	17.41	17.24

The agreement of this present result based on magnetic scanning and the previous results which used electrostatic scanning at relatively low voltages

⁶M. Lounsbury, S. Epstein, and H.G. Thode, Phys. Rev. 72, 517 (1947)

⁷A.O. Nier, Phys. Rev. 52, 933 (1937); private communication to H.G. Thode, see Ref. 6

⁸V.H. Dibeler, F.L. Mohler, and R.M. Reese, J. Research Nat. Bur. Standards 38, 617 (1947)

seems anomalous at first glance. This apparent anomaly means only that the large voltage effect found for the spectrometer used here was not present in the spectrometers of Thode⁶ or Nier.⁷ That this should be the case is not hard to understand, because the spectrometers of these investigators do not have the same type electrostatic lens system as that used in our spectrometer. This indicates that the large voltage effect is to be associated with the particular type electrostatic focusing used in our spectrometer. In support of this contention is the fact that both the Consolidated-Nier and the General Electric analytical mass spectrometers, which have ion sources similar to ours, show the same large voltage effect. Previous results³ on the Consolidated Model 102 spectrometer with an ion source like that used by Thode⁶ and Nier⁷ do not show as large a voltage effect. Recent results on a 60°-sector type spectrometer⁹ similar to the one used for this research show the same large voltage effect.

The conclusion to be drawn from these results is certainly not that all electrostatically scanned values of previous investigators are in error. Rather, it is that, for spectrometers which have an ion source design similar to the one in our spectrometer, electrostatic scanning gives correct results only at relatively high voltages, while magnetic scanning gives correct results over a wide range of ion accelerating voltages.

Voltage Effect on Mass Spectrometric Patterns of Polyatomic Molecules

There still remains the interesting point of the effect of a change of scanning conditions in the pattern of a polyatomic molecule. This is of particular interest in those isotope abundance measurements which are made on ion fragments of polyatomic molecules and in the evaluation of the question to what extent observed isotope effects on bond rupture may be instrumental.

For this study, the mass spectral pattern of propane was recorded by magnetic scanning at various ion accelerating voltages. The results are listed in the accompanying Table III, where the magnetically scanned mass spectral patterns of propane are given for 750, 2000, 4000, and 5000-v ion accelerating potentials. Here one sees that there is a marked variation in pattern with voltage in contradistinction to the case of the rare gases. The only difference between comparing the ratio of two rare gas ions and comparing that of two ions of comparable e/m from the pattern of a polyatomic molecule is that the initially formed rare gas ions will have only thermal energy, while the corresponding ions from the polyatomic molecule will have, in addition, some kinetic energy acquired on the rupture of the chemical bonds. The variation in pattern can be ascribed to the initial kinetic energy of the ions.

It might seem from previous data³ that, because of the wide variation in initial kinetic energies encountered in the different ion fragments of a polyatomic molecule, no method of scanning could hope to approximate a true measure of the relative abundances of those fragments as present in the ion source. However, the data in Table III for the magnetic scans at 4000 and 5000 v show

⁹G. Careri and G. Nencini, J. Chem. Phys. 18, 897 (1950)

III. Mass Spectral Pattern of Propane as a Function of Ion Accelerating Voltage Using Magnetic Scanning				
Mass	750 v	2000 v	4000 v	5000 v
12	*	.12	.08	.11
13	.22	.25	.29	.22
14	.87	1.52	1.58	1.48
15	4.8	8.58	8.90	8.49
24	.07	.09	.08	.11
25	.65	.64	.78	.75
26	16.4	16.9	18.7	18.3
27	94	104	111	112
28	149	173	175	175
29	242	276	278	279
30	5.54	6.16	6.47	6.31
36	*	.05	.08	.08
37	3.17	3.34	3.61	3.58
38	9.5	9.0	9.61	9.55
39	55.5	53.1	57.2	57.3
40	8.5	8.7	9.27	9.25
41	44.1	43.2	44.2	43.9
42	19.2	19.0	19.8	19.6
43	80.9	79.6	79.2	78.2
44	100	100	100	100
45	3.29	3.30	3.33	3.32

*Too small to be detected

such good agreement that one is led to the conclusion that, even in the case of a molecule as complex as propane, one can get a true pattern if one scans magnetically at relatively high voltages. This means that measured isotope effects which are determined by magnetic scanning at high accelerating voltages should not be instrumental effects. On the other hand, isotope effects measured by electrostatic scanning or at low ion accelerating voltages will require a correction for voltage discrimination, a conclusion which is independent of the type ion source used. The data of Barry³ show that even for a simplified ion source in a 180° instrument the collection efficiency changes markedly with ion accelerating voltage for ions with initial energy in excess of thermal motion.

SPECTROPHOTOMETRIC DETERMINATION OF CERIU (IV)

A.I. Medalia and B.J. Byrne*

Abstract

A method has been developed for the determination of Ce(IV) based on spectrophotometric measurements at the peak of its absorption at 320 m μ in the ultraviolet. The recommended procedure is more than ten times as sensitive as a previous procedure using a blue filter in the visible. In the persulfate oxidation to Ce(IV), it is important not to use too large an amount of persulfate or of ammonium ion, because of the absorption of residual persulfate and of nitrate (formed by oxidation of ammonium ion) at 320 m μ . Interference by several elements was studied.

The familiar yellow color of the ceric ion in acid medium has been made the basis for a colorimetric procedure, in which cerous ion is oxidized with persulfate in boiling 1 N sulfuric acid with silver ion as a catalyst.¹ If the intensity of the yellow color is determined visually, the sensitivity is approximately 10 gamma of cerium per square centimeter; the photometric sensitivity with a blue filter is 0.5 gamma, according to the definition of Sandell.¹ A spectrophotometric study in the visible² has established that the absorption of ceric sulfate increases continuously up to 480 m μ (the lower limit of the study). As pointed out by Sandell,¹ increased sensitivity would be expected to result from use of monochromatic violet light.

Absorption Spectrum of Ceric Ion

The absorption spectra of ceric sulfate in sulfuric acid of various concentrations are shown in the accompanying Figures 1 and 2. These spectra, covering the range 260-400 m μ , were obtained with a Cary recording spectrophotometer, with a cell length of 10.0 cm, using 2.22×10^{-5} M solutions of ceric sulfate prepared by fresh dilution of a standardized solution (0.0888 N) of G.F. Smith ceric sulfate. In 1 N acid, the absorption maximum occurs at 322 m μ ; in 6 N acid, at 314 m μ ; and in 0.1 N acid, at 319 m μ . The molar extinction coefficients found in these solutions at the maxima are 4.84×10^3 , 4.70×10^3 , and 5.16×10^3 , respectively. A photometric sensitivity of 0.029 gamma can thus be realized; that is, according to the definition of Sandell,¹ this amount of Ce(IV) in a column of 1 cm² cross section will give an extinction of 0.001.

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¹E.B. Sandell, Colorimetric Determination of Traces of Metals. Interscience Publishers, New York, 1944

²C.T. Kasline and M.G. Mellon, Ind. Eng. Chem., Anal. Ed. 8, 463 (1936)

Development of Procedure

It was first attempted to determine cerium according to the procedure of Sandell,¹ with the modification that the absorption was measured at 320 m μ using a Beckman DU spectrophotometer with a 1-cm silica cell. In this procedure, 10 ml of solution are made 1 N in sulfuric acid; 0.2 g of ammonium persulfate and 0.5 mg of silver nitrate are added. The solution is boiled for 5 min, cooled, and diluted to 10 ml, and the transmittance is then measured. This procedure gave erratic results when the measurements were made at 320 m μ . Further study revealed two principal sources of error: first, absorption of light at 320 m μ by any persulfate remaining after boiling, and, second, absorption by the nitrate ion formed by oxidation of the ammonium ion by persulfate. An absorption spectrum of 0.0010 M ammonium persulfate in 1 N sulfuric acid, measured in the 10-cm cell of the Cary, with 1 N sulfuric acid as the blank, is shown in the accompanying Figure 3a. The absorption increases continuously as the wavelength is decreased; this is also seen from the curves of Figures 3b and 3c, which were obtained with 0.010 and 0.10 M persulfate, respectively. An absorption spectrum of potassium nitrate is shown in Figure 4; the location of the maximum at 301.5 m μ has been established previously.³

Both of the above sources of error can be made negligible by using 1/10 the amount of persulfate recommended by Sandell.¹ While satisfactory results are obtained with this amount of ammonium persulfate, it is evident that potassium persulfate is to be preferred.

The solutions are stable after oxidation for 10-20 min if water of good quality is used throughout; however, with water containing traces of organic matter, rapid fading has been found.

Recommended Procedure

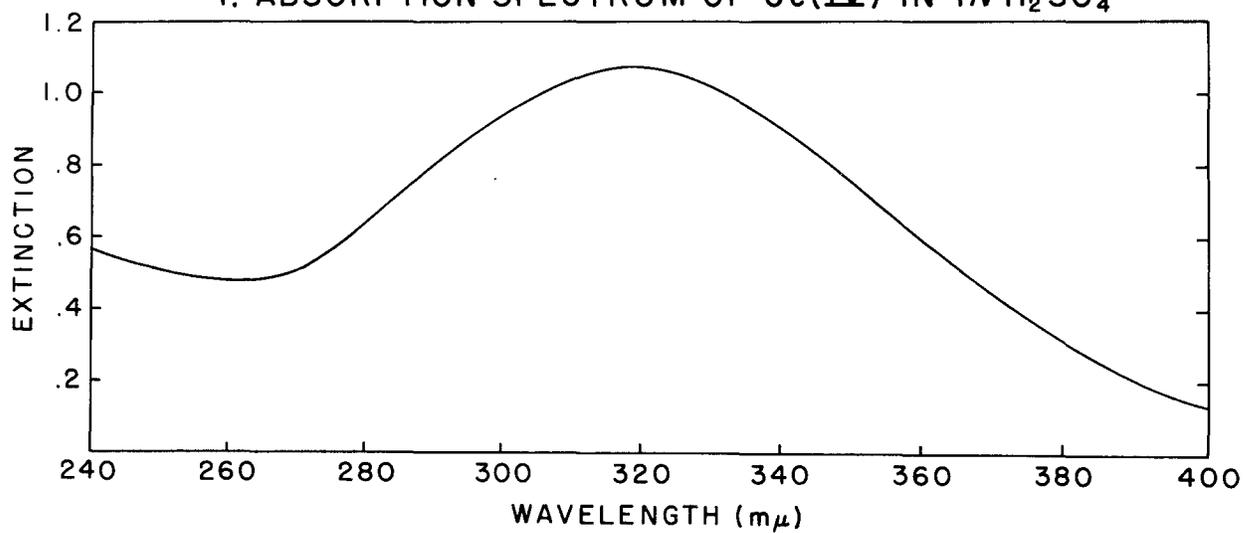
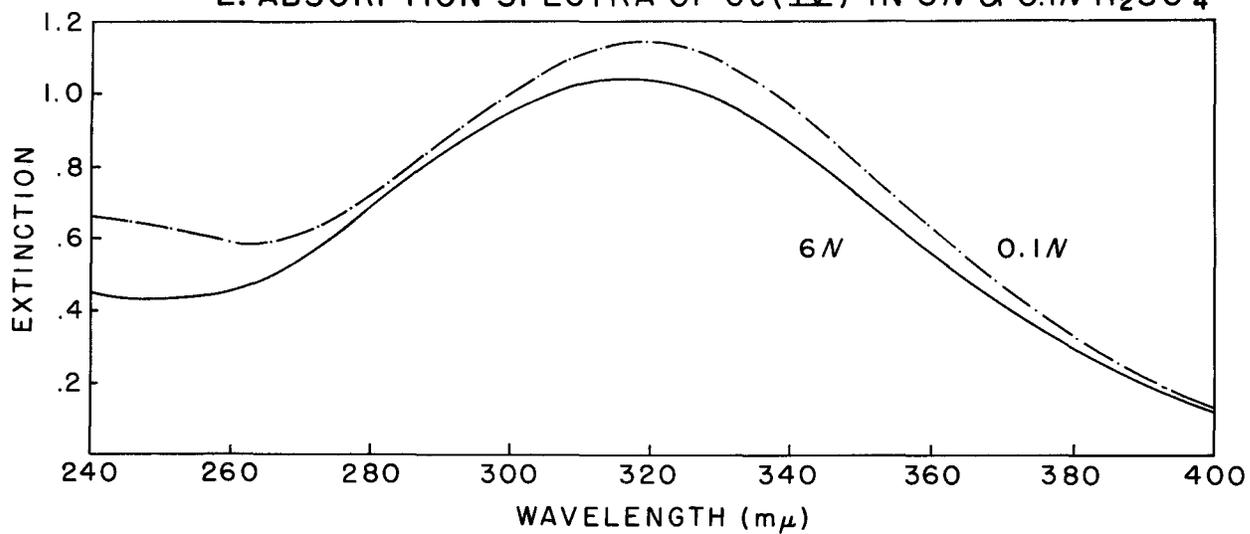
The amount of cerium taken should be between 0.04 and 0.20 mg, for maximum accuracy (although as little as 0.003 mg can be detected without undue care), in 10 ml of 1 N sulfuric acid in a 30-ml beaker. To this solution is added 0.5 mg of silver nitrate (0.2 ml of a 0.25% solution) and 24 mg of potassium persulfate (1.0 ml of a 2.4% solution). A small carborundum chip is added to promote even boiling; the beaker is covered; and the solution is boiled for 5-10 min, water being added, if necessary, to maintain a volume of 6-10 ml. The beaker is placed in cold (15 $^{\circ}$) water for 5 min, and the solution is then transferred to a 10-ml volumetric flask and made up to volume. The extinction is measured at 320 m μ in a silica cell; the concentration of cerium is determined from a calibration curve.

Results Obtained with Recommended Procedure

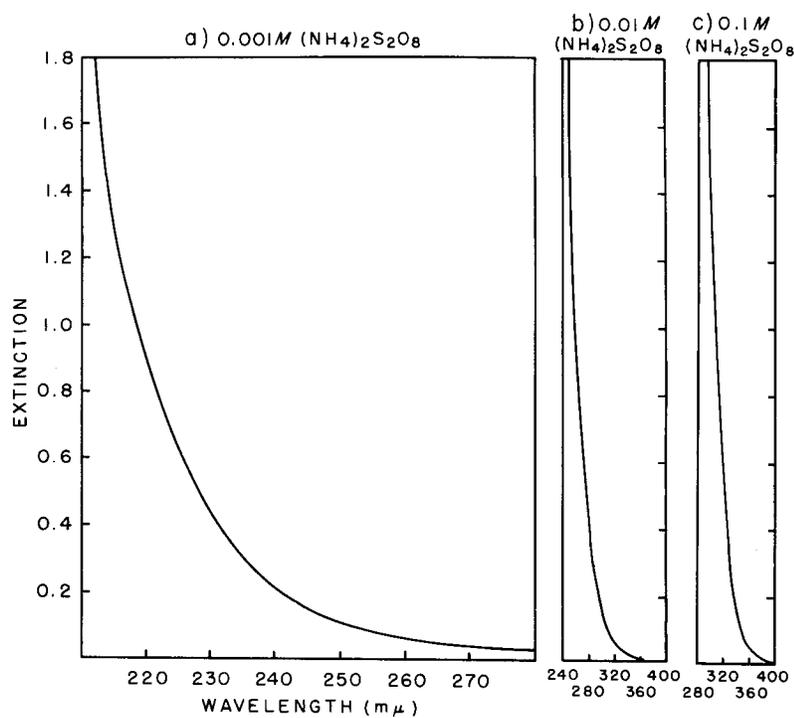
Construction of Calibration Curve

To 5.00 ml of ceric sulfate (0.0888 N) was added 0.1 N hydrogen peroxide

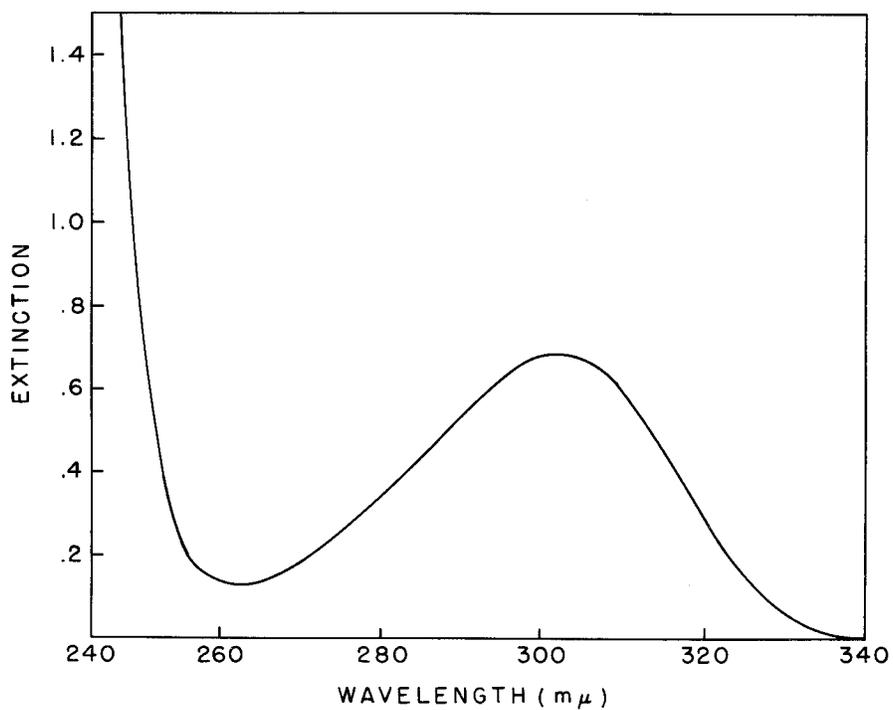
³G. Kortum, Z. Physik. Chem. B43, 418 (1939); G. Scheibe, Ber. 59, 1321 (1926)

1. ABSORPTION SPECTRUM OF Ce(IV) IN 1N H₂SO₄2. ABSORPTION SPECTRA OF Ce(IV) IN 6N & 0.1N H₂SO₄

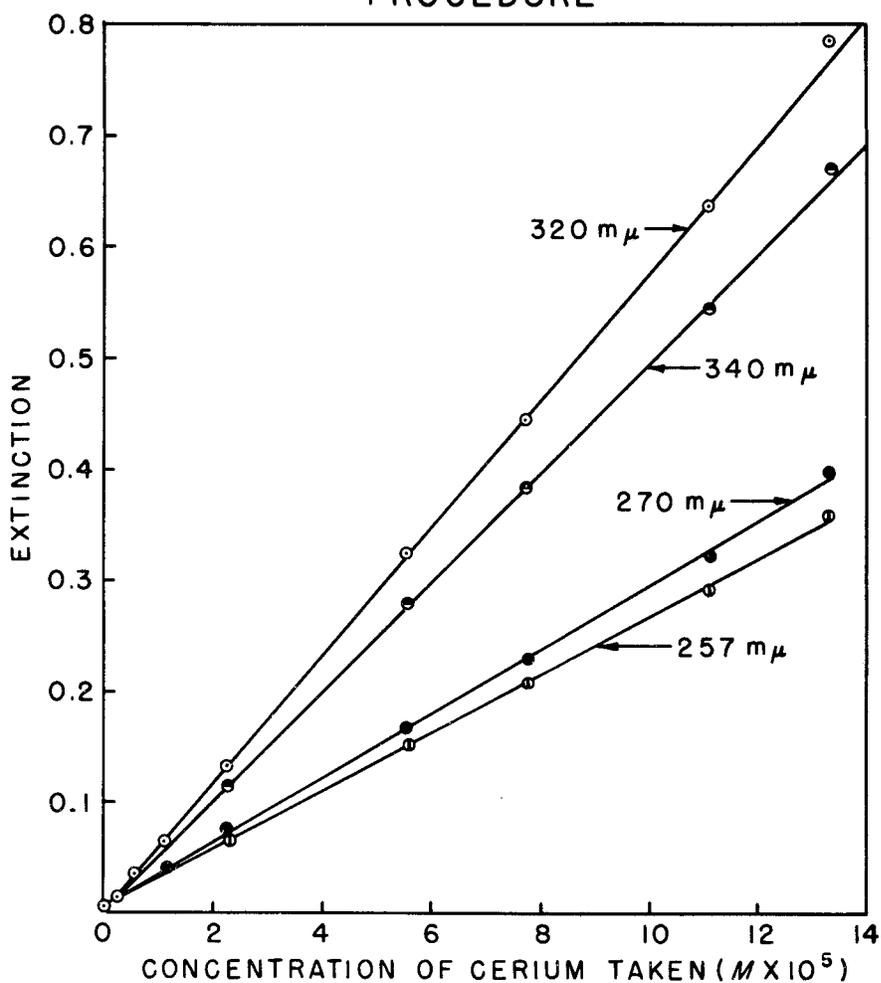
3. ABSORPTION SPECTRA OF AMMONIUM PERSULFATE IN 1*N* H₂SO₄



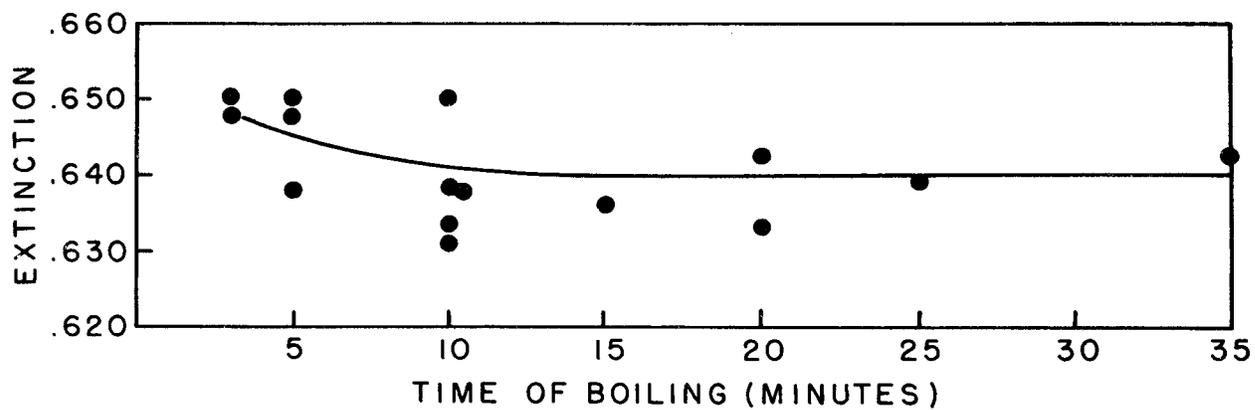
4. ABSORPTION SPECTRUM OF POTASSIUM NITRATE (0.0101*M*)



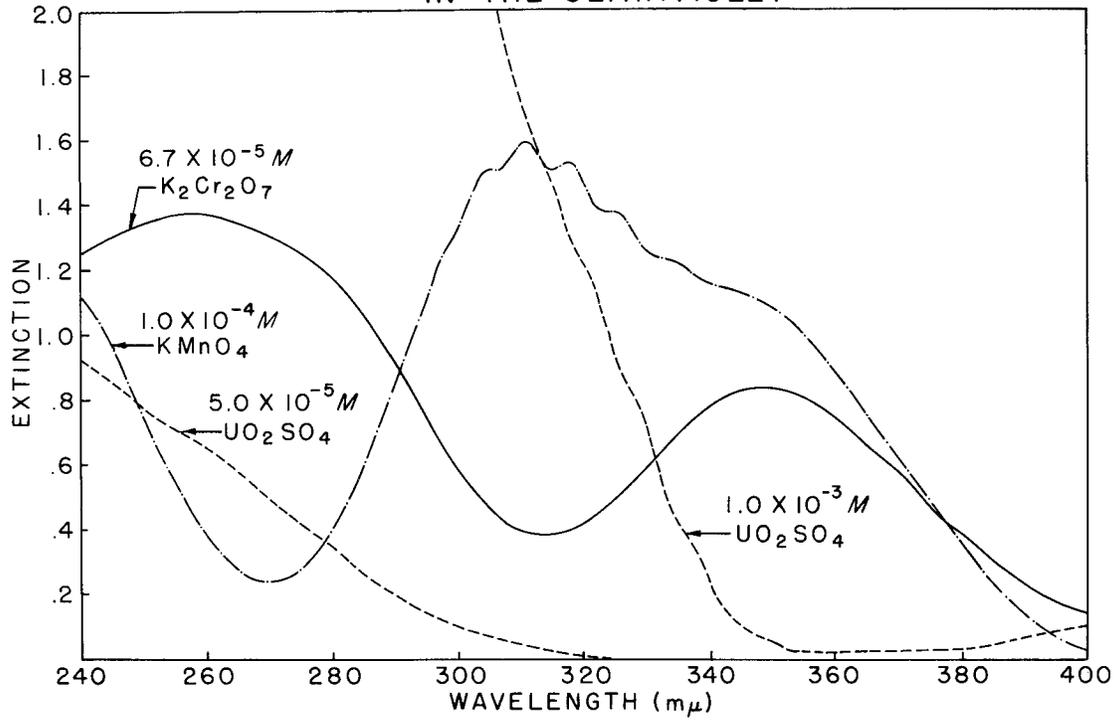
5. EXTINCTION VS. CONCENTRATION OF CERIUM TAKEN IN RECOMMENDED PROCEDURE



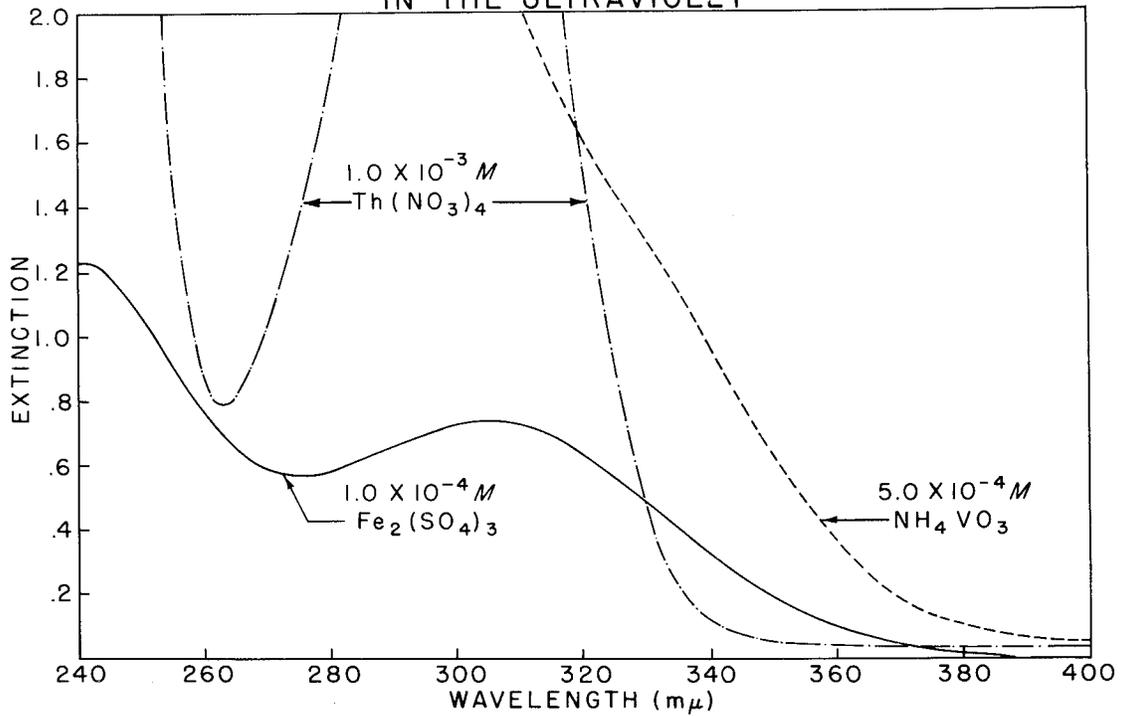
6. EXTINCTION AT 320 $m\mu$ VS. TIME OF BOILING



7. ABSORPTION SPECTRA OF VARIOUS COMPOUNDS IN THE ULTRAVIOLET



8. ABSORPTION SPECTRA OF VARIOUS COMPOUNDS IN THE ULTRAVIOLET



until the solution was colorless. From this was prepared, by successive dilutions, a solution 1.11×10^{-4} M in cerous ion, in 1 N sulfuric acid; aliquots of this solution were treated by the above procedure, and the extinctions were measured in a 1-cm cell with a Beckman DU spectrophotometer (hydrogen lamp, 0.34-mm slit width). The results are shown in the accompanying Figure 5. Beer's law is followed closely over the range studied; the extrapolated blank (0.003) is virtually negligible. Similar curves obtained at other wavelengths than 320 m μ are also shown in Figure 5; Beer's law is followed at these wavelengths also, although the sensitivity is, of course, not as great.

Variations in the Recommended Procedure -- Time of Boiling

Extinctions measured of solutions initially 1.11×10^{-4} M in cerous sulfate, oxidized according to the above procedure with various times of boiling, are shown in the accompanying Figure 6. Satisfactory results are found with between 5 and 35 min of boiling.

Amounts of Persulfate and Silver Nitrate

The effects of variations in the amounts of these ingredients are shown in the accompanying Table I. Satisfactory results are obtained with the recommended amounts of silver and persulfate, or with as little as 1/4 these amounts.

<u>I. Recommended Procedure with Varying Amounts of Silver Nitrate and Potassium Persulfate</u> (all with 155 gamma Ce(III); boiled 10 min)		
AgNO ₃ (mg)	K ₂ S ₂ O ₈ (mg)	Extinction (320 m μ)
0.50	24	0.640
0.12	24	0.648
None	24	0.598
2.50	24	0.660
0.50	6.0	0.640
0.50	96	0.666

Effect of Ammonium Ion

Oxidation of ammonium ion to nitrogen and nitrate ion by persulfate in the presence of silver ion (at 25°) has been reported by Marshall and subsequent workers.⁴ Results obtained under the conditions of the present procedure are given in the accompanying Tables II and III.

⁴H. Marshall, Proc. Roy. Soc. Edinburgh 23, 163 (1900); H. Marshall and J.K.H. Inglis, ibid. 24, 88 (1902); D.M. Yost, J. Am. Chem. Soc. 48, 374 (1926); C.V. King, ibid. 49, 2689 (1927); 50, 2080 (1928); C.V. King and F.L. Griswold, ibid. 52, 1493 (1930)

II. Oxidation of Ammonium Ion to Nitrate Ion in the Absence of Cerium (solutions boiled 10 min, then made up to 10 ml)					
$S_2O_8^{2-}$ ($M \times 10^2$)	NH_4 ($M \times 10^2$)	$AgNO_3$ (mg)	H_2SO_4	Extinction (320 $m\mu$)	NO_3^- Formed ^a ($M \times 10^2$)
8.9 ^b	-	-	-	0.054	-
8.9	17.8	0.50	-	0.079	1.8
8.9	17.8	0.50	1 \underline{N}	0.017	0.2
8.9	17.8	-	1 \underline{N}	0.008	0.0
0.89 ^c	1.78 ^c	0.50	-	0.023	0.4
0.89	1.78	0.50	1 \underline{N}	0.005	0.1
0.89	1.78	-	1 \underline{N}	0.004	0.0
0.89	200.	0.50	1 \underline{N}	0.054	1.2
0.89	20.	0.50	1 \underline{N}	0.005	0.1

^aCalculated from extinction at 301 $m\mu$, corrected for blank (boiled without ammonium sulfate).
^bUnboiled; extinction due to persulfate.
^cThese amounts correspond to 20 mg of ammonium persulfate (equivalent to 24 mg of potassium persulfate).

III. Oxidation of Ammonium Ion to Nitrate Ion in the Presence of Cerium (all solutions 1 \underline{N} in sulfuric acid, with 0.50 mg $AgNO_3$, 24 mg $K_2S_2O_8$, and 155 gamma cerous or ceric cerium; solutions boiled 10 min, then made up to 10 ml)			
NH_4 ($M \times 10^2$)	Cerium	Extinction (320 $m\mu$)	NO_3^- Formed ^a ($M \times 10^2$)
-	Cerous	0.640	-
-	Ceric	0.643	-
200	Cerous	0.870	4.2
20	Cerous	0.665	0.4
2	Cerous	0.635	0.0
200	Ceric	0.837	3.2

^aCalculated from extinction at 301 $m\mu$, corrected for blank.

From the data of Table II, it is seen that the persulfate-ammonia reaction leads to the formation of much more nitrate in initially neutral solution than in 1 \underline{N} sulfuric acid; this effect of acid is in agreement with the observations of Marshall and Inglis.⁴ In 1 \underline{N} acid, the amount of nitrate formed from ammonium persulfate in the amount used by Sandell¹ is sufficient to give a significant extinction at 320 $m\mu$, even in the absence of cerium. With the recommended amount of potassium persulfate, and 2 \underline{M} ammonium ion (added as ammonium sulfate), the amount of nitrate apparently formed is greater

IV. Interference by Various Metals in the Determination of Cerium
 (All extinction coefficients are those of the individual compounds;
 extinctions are those of the indicated mixtures with 1.11×10^{-4}
 \underline{M} cerium (III) carried through the recommended procedure with
 20 mg of $(\text{NH}_4)_2\text{S}_2\text{O}_8$)

Compound Taken	Molar Extinction Coefficient (ϵ ; $\text{cm}^2/\text{millimole}$)			Amount Taken (\underline{M})	Extinction	
	320 $\text{m}\mu$	340 $\text{m}\mu$	270 $\text{m}\mu$		320 $\text{m}\mu$	340 $\text{m}\mu$
$\text{Ce}_2(\text{SO}_4)_3$ alone	4.83×10^3	4.11×10^3	2.26×10^3	1.11×10^{-4}	0.640	0.550
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	-	-	2.8×10^1	1.0×10^{-2} 1.0×10^{-1}	0.639 0.676	0.550 0.556
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ or $\text{Fe}_2(\text{SO}_4)_3^a$	6.3×10^2	3.3×10^2	5.8×10^2	2.0×10^{-5} 1.0×10^{-4}	0.684 0.920	- -
$\text{K}_2\text{Cr}_2\text{O}_7$	6.3×10^2	1.2×10^3	2.0×10^3	6.9×10^{-6} 3.3×10^{-5} 1.3×10^{-4}	0.642 0.653 0.707	- - -
KMnO_4	1.5×10^3	1.2×10^3	2.4×10^2	1.0×10^{-5} 4.0×10^{-5}	0.634 0.641	- -
NH_4VO_3	3.2×10^2	1.9×10^2	-	2.0×10^{-5} 1.0×10^{-4}	0.639 0.661	- -
$\text{UO}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$	1.2×10^2	2.3×10^1	1.0×10^3	1.0×10^{-5} 1.0×10^{-4}	0.653 0.758	0.556 0.574
$\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$	1.6×10^2	1.2×10^1	1.0×10^2	1.0×10^{-5} 1.0×10^{-4}	0.636 0.660	0.552 0.563
KNO_3	3.0	-	1.9	1.0×10^{-2} 1.0×10^{-1}	0.675 0.980	0.556 0.562

^aFerric sulfate taken for determination of extinction coefficient; ferrous sulfate used in analytical procedure.

than would correspond stoichiometrically to the amount of persulfate taken. The significance of this is not clear at present.

In the presence of 155 gamma of cerium (III), the extent of formation of nitrate is several fold higher than in the absence of cerium. Thus, with the recommended amount of persulfate, the initial presence of 0.2 M ammonium ion causes a significant error in the cerium determination, although the corresponding blank (Table II) is negligible. However, with 0.02 M ammonium ion, which is slightly greater than the amount of ammonium ion present in 20 mg of ammonium persulfate (corresponding to the recommended amount of potassium persulfate), no error is found. When cerium is present initially in the quadrivalent, rather than the trivalent, state, the amount of nitrate formed (from 2 M ammonium ion) is considerably greater than in the absence of cerium, indicating that the cerium acts here principally as a catalyst, rather than by an induced reaction.

Effects of Various Metal Ions

A number of metal ions, of such a nature as would be expected to either occur together with cerium in nature, or to interfere with the cerium determination, have been studied according to the following plan. First, the absorption spectra of solutions of C.P. compounds in 1 N sulfuric acid were determined in the ultraviolet, with the Cary instrument (10-cm cell). The extinction coefficients at 320 m μ were calculated; on this basis, various amounts of each substance were taken, together with a known amount of cerium (III), for analysis according to the above procedure, with ammonium persulfate (20 mg) as reagent. With many metals, it was evident from the absorption curves that the interference could be greatly reduced, at comparatively slight cost in sensitivity of cerium determination, by working at 340 m μ , rather than at 320 m μ . The results are given in the accompanying Table IV and Figures 7 and 8. Data for potassium nitrate are also included.

The molar extinction coefficients at 320 m μ of the majority of the compounds of Table IV are of the order of 10% of that of cerium (IV). For this reason, separations must be made from a larger number of elements than if the color of the cerium (IV) is measured in the violet portion of the visible spectrum. On the other hand, the interference due to copper, particularly at 340 m μ , is so slight that it is possible to determine cerium accurately in a strong blue solution. The interference found with iron was higher than expected on the basis of its extinction coefficient; with manganese, on the other hand, less interference was found than expected.

A TEST FOR TRACES OF ORGANIC MATTER IN WATER

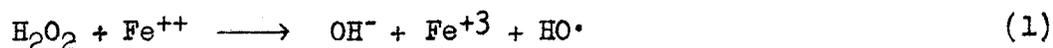
A.I. Medalia

Abstract

A method is described by means of which traces of organic matter in water can be detected with greater sensitivity than by the customary permanganate test. The new method is based on the induced air oxidation of ferrous iron accompanying the reaction between ferrous iron and hydrogen peroxide, in the presence of organic compounds. The sensitivity of the method varies from about 0.1 ppm to 10 ppm.

Detection of small amounts of organic contaminants in water is of importance from the standpoints of potability, industrial use, or use as a solvent for reaction studies at high dilutions. While specific methods are available for certain classes of organic matter, such as hydrocarbons¹ and phenols,² the only general test in current use is the reduction of permanganate in hot acid solution. Many classes of organic compounds are, however, quite stable toward permanganate under these conditions; on the other hand, reaction of permanganate with compounds which are readily attacked gives rise to the formation of manganese dioxide, which catalyzes the decomposition of permanganate,³ thus apparently magnifying the extent of the reaction between permanganate and these compounds. Even motes of pyrex or silica have been reported to catalyze this decomposition.⁴ Doubtless connected with this autocatalytic decomposition of permanganate is the occurrence of blanks (with purified water) which may be sufficiently large and irreproducible to mask the effect of traces of organic matter.

Recently it was found⁵ that the reaction between ferrous iron and hydrogen peroxide can initiate a chain reaction in which dissolved organic compounds react with dissolved molecular oxygen, with the formation of organic peroxides. If the amount of ferrous iron taken is in excess of that of hydrogen peroxide, then these organic peroxides oxidize a portion of the excess ferrous iron, so that the net observed result is an induced oxidation of ferrous iron. The following reaction sequence may be taken as typical:



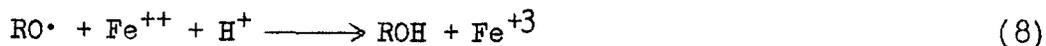
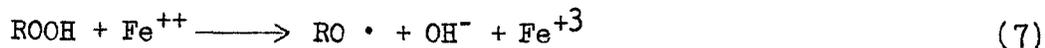
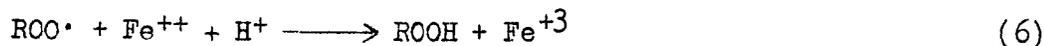
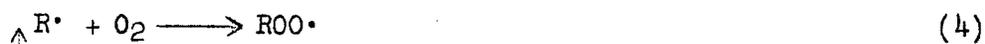
¹H.D. Kirschman and R. Pomeroy, *Anal. Chem.* 21, 793 (1949)

²M.B. Etinger and C.C. Ruchhoft, *Anal. Chem.* 20, 1191 (1948)

³M.N. Morse, A.I. Hopkins, and M.S. Walker, *Am. Chem. J.* 18, 401 (1896)

⁴C.B. Taylor, *Nature* 160, 56 (1947)

⁵I.M. Kolthoff and A.I. Medalia, *J. Am. Chem. Soc.* 71, 3784 (1949)



In the above mechanism, whatever the path or chain length, the oxidation of two ferrous ions by the induced reaction corresponds to the reduction of one oxygen atom (to water) and the insertion of another oxygen atom in the organic compound. That is, for each oxygen molecule which enters into the reaction, one oxygen atom oxidizes two ferrous ions, and the other oxygen atom is consumed by the organic compound. For the sake of comparison with the permanganate method, therefore, we may express the results obtained in terms of the amount of oxygen consumed, calculated on the basis of one equivalent (8 g) of oxygen per equivalent of ferrous iron oxidized by the induced reaction.

Since the hydroxyl radical is an extremely strong oxidizing agent, even the most stable organic compounds are attacked; high sensitivity is afforded by virtue of the chain nature of the autoxidation. The reaction is carried out at room temperature, so that the difficulties inherent in the use of hot solutions of strong oxidizing agents are avoided.

Procedure

Reagents

Ceric sulfate, 0.005 N, in 1 N sulfuric acid: prepared fresh daily by dilution of standardized 0.1 N ceric sulfate. Ferrous sulfate, 0.02 M, in 1.2 N sulfuric acid: add 8 ml of concentrated sulfuric acid to 200 ml of water; then add 1 g of a good grade of $FeSO_4 \cdot 7H_2O$. Hydrogen peroxide, 0.005 M: dilute 0.1 ml of 30% hydrogen peroxide (reagent grade, inhibitor-free) to 200 ml with water. Ferrous phenanthroline (ferroin) indicator, 0.006 M.

The ceric sulfate and ferroin solutions can be made up in ordinary distilled water; the ferrous sulfate and hydrogen peroxide should be made up in water which has been distilled from alkaline permanganate, then from 0.1 M sulfuric acid.

Standardization: 10.00 ml of the ferrous solution is diluted with about 20 ml of water; 0.2 ml of ferroin is added, and the mixture titrated with ceric solution. Similarly, 10.00 ml of hydrogen peroxide is mixed with 15 ml of water and 5 ml of 6 N sulfuric acid; 0.2 ml of ferroin is added, and the mixture titrated with ceric solution to a colorless end point (complete disappearance of orange color). The indicator blank is found by adding 0.20 ml of indicator to 120 ml of water containing 2 ml of 6 N sulfuric acid, then titrating to a colorless end point.

Procedure

To 100 ml of the sample of water, in a 250-ml Erlenmeyer flask 10.00 ml of ferrous solution is added from a pipet, with swirling; followed by* 10.00 ml of hydrogen peroxide solution, with swirling. The mixture is allowed to stand 15 min at room temperature; then 0.2 ml of ferroin is added, and the ferrous iron is titrated with ceric solution to a completely colorless end point. A blank is run with water which has been distilled from permanganate, then from acid. The blank should correspond to less than 0.05 ml of ceric solution (calculated as below).

Calculations

Let F, H, and B be the titer (in ml of ceric solution) of the ferrous solution (10 ml), the hydrogen peroxide solution (10 ml), and the blank, respectively; let I be the indicator correction as determined experimentally. The corrected blank B-I should be within 0.05 ml of F-H.

Let S be the titer of the sample of water by the above procedure; let N be the normality of the ceric solution. Then the number of milliequivalents of ferrous iron oxidized by the induced reaction is given by

$$(B - S) N$$

and the number of milligrams of oxygen consumed per liter of water sample is:

$$(80)(N)(B - S)$$

Results

The above procedure has been tested using water to which was added known amounts of various typical organic compounds. The blank on the pure water was satisfactory in all cases. The organic compounds were the purest available; in view of the small amounts used of the individual compounds, further purification did not appear necessary. The benzene (reagent grade) and pentane (Phillips Petroleum Co. 99% mol purity) were added as filtered, saturated aqueous solutions.

For comparison, tests were also carried out by the reaction with permanganate, according to the procedure given in Scott's Standard Methods of Chemical Analysis (5th ed.), Vol.2, p.2053. Solutions of volatile compounds were heated in screw-capped bottles. Results obtained with both methods are given in the accompanying Table I, expressed throughout as milligrams of oxygen consumed per liter of solution, corrected for the blank.

In comparing the results obtained with the two methods, it must be borne in mind that the titrations are more precise, and that the blanks are lower

*The hydrogen peroxide must be added after the ferrous solution, not before, to avoid error due to induced decomposition of the hydrogen peroxide; cf. A.I. Medalia, Ph.D. Thesis, University of Minnesota, June, 1948.

I. Comparison of Ferrous Iron - Hydrogen Peroxide Test with Permanganate Test, with Solutions of Various Organic Compounds

(A dash (-) indicates that the oxygen consumption was equal to or less than that of the blank; a blank space indicates that the corresponding experiment was not carried out)

Compound	Concentration (M)	Oxygen Consumption (mg/liter)	
		Fe ⁺⁺ -H ₂ O ₂	Permanganate
Ethanol	2x10 ⁻⁵	0.22	0.17
	1x10 ⁻⁴	0.98	0.83
Acetone	2x10 ⁻⁵	0.04	-
	1x10 ⁻⁴	0.10	-
	5x10 ⁻⁴	0.60	0.08
Acetic Acid	1x10 ⁻⁴	0.02	-
	4x10 ⁻⁴	0.10	-
	1x10 ⁻³	0.17	0.02
Aerosol AY	1x10 ⁻⁶	0.08	
	2x10 ⁻⁶	0.17	
	2x10 ⁻⁵	0.77	-
	6x10 ⁻⁵		0.25
	2x10 ⁻⁴		1.40
Sodium benzoate	2x10 ⁻⁵	0.37	0.09
	2x10 ⁻⁴		0.15
Benzene	1x10 ⁻⁶	-	
	2x10 ⁻⁶	0.05	
	2x10 ⁻⁵	0.37	-
	1x10 ⁻⁴	1.33	0.30
	1x10 ⁻³		0.80
Pentane	2x10 ⁻⁴	0.43	0.69
Gelatin	2 ppm	0.11	0.09
	10 ppm	0.49	0.15
Sodium formate	1x10 ⁻³	0.10	
Propionic acid	1x10 ⁻⁴	0.93	
Quinoline	2x10 ⁻⁵	0.51	

and better reproducible, with the new method than with the old. Thus, the former titration was found to be reproducible to 0.02 ml of 0.0044 N ceric sulfate, and the latter to 0.05 ml of 0.014 N permanganate so that the precision of the former titration corresponds to 0.007 mg of oxygen per liter, and that of the latter to 0.057 mg. Blanks with pure water were in the range 0.00-0.02 ml of ceric reagent, and 0.10-0.20 ml of permanganate. Thus, while the blanks with the former were in agreement within the precision of the titration, the poor reproducibility of the blanks with permanganate led to an approximately two-fold increase in error over that due to the titration alone. In sum, then, the oxygen consumption values in the ferrous iron - hydrogen peroxide test are significant to about 0.01 mg of oxygen per liter, while the values in the permanganate test are significant to only about 0.10 mg per liter.

Examination of Table I shows that nearly all the compounds studied gave higher oxygen consumption values with the ferrous iron - hydrogen peroxide test than with the permanganate test. Keeping in mind the above limits of error, significant values are, in general, obtained with the former test at concentrations lower by an order of magnitude than with the latter. Both tests vary considerably in sensitivity toward different compounds; however, this variation is more extreme with permanganate than with ferrous iron and hydrogen peroxide. The results obtained with the above representative group of organic compounds indicate that any compound containing a C-H linkage in a position not adjacent to a C=O bond should give a positive test with the new method at concentrations of the order of 0.1 ppm, while with a few particularly stable compounds, such as acetone and acetic acid, the limit of detection is of the order of 10 ppm.

Effect of Chloride

It has been established previously⁵ that chloride ion suppresses the induced oxidation of ferrous iron under conditions such as those studied above. This suppression involves, first, reaction of a hydroxyl radical with a chloride ion, forming a chlorine atom; the chlorine atom then reacts with ferrous iron in preference to reacting with organic compounds. Since chloride ion is a common constituent of water from various sources, a procedure has been developed by means of which the suppressing action of chloride can be eliminated. In this procedure, the chloride ion is tied up as soluble, undissociated mercuric chloride, which does not interfere with any stage of the determination.

Reagents. Mercuric nitrate, 0.01 M, in 0.2 N sulfuric acid, prepared in purified water. Sodium nitroprusside, 10%, in water.

Procedure. First, the chloride content of a 100-ml aliquot is determined by titration with mercuric nitrate;⁶ 0.3 ml of nitroprusside reagent is added; then mercuric nitrate is added from a 10-ml buret until a turbidity is noticeable.

To another 100-ml aliquot is then added the same amount of mercuric nitrate as used above; addition of ferrous iron and hydrogen peroxide, and titra-

⁶E. Votoček, Chem.-Ztg. 42, 257 (1918)

tion with ceric sulfate, are then carried out as described above. It should not be necessary to run a blank determination on the mercuric nitrate, but if desired, this may be carried out with a solution 10^{-3} M in potassium chloride.

Results in the Presence of Chloride

It was first shown that the titration of ferrous iron with ceric sulfate gives accurate results in the presence of mercuric nitrate (5×10^{-4} M), and also in a solution of potassium chloride (1×10^{-3} M) which has been titrated with mercuric nitrate in the presence of nitroprusside, as above. An attempt was made to carry out the ferrous iron - hydrogen peroxide reaction in the same solution in which the titration of chloride has been performed; however, as shown in the accompanying Table II, poor results were obtained, due to the presence of the nitroprusside. The suppressing effect of chlorides upon the reaction in the presence of gelatin, ethanol, sodium benzoate, or acetone, and the elimination of this suppressing effect by the addition of the correct amount of mercuric nitrate (in the absence of nitroprusside) are also shown in Table II.

II. <u>Results Obtained by the Ferrous Iron - Hydrogen Peroxide</u> <u>Method in the Presence of Chloride</u>				
Organic Compound	KCl ($\underline{M} \times 10^3$)	Hg(NO ₃) ₂ ($\underline{M} \times 10^3$)	Nitro- prusside	Apparent Oxygen Consumption (mg/liter)
None	1	-	-	-0.01
	-	0.5	-	0.01
	1	0.5	-	-0.01
	-	-	Present	-0.05
	1	0.5	Present	-0.03
Gelatin (10 ppm)	-	-	-	0.50
	1	-	-	0.13
	1	0.5	-	0.49
	-	-	Present	0.15
	1	0.5	Present	0.14
Ethanol (2×10^{-5} M)	-	-	-	0.22
	0.1	-	-	0.16
	1	-	-	0.09
	1	0.5	-	0.35
Sodium Benzoate (2×10^{-5} M)	-	-	-	0.35
	1	-	-	0.20
	1	0.5	-	0.41
Acetone (5×10^{-4} M)	-	-	-	0.56
	1	-	-	0.11
	1	0.5	-	0.59

As seen in Table II, the oxygen consumption (as calculated from the titration data) in the presence of mercuric chloride is not less than, and is in some cases greater than, in its absence. Apparently, the mercuric chloride can play a part in the chain reaction.

Acknowledgement

The author is indebted to Professor I.M. Kolthoff for suggesting the present application of the ferrous iron - hydrogen peroxide reaction.

NUCLEAR RECOIL FOLLOWING NEUTRINO EMISSION FROM Be⁷

R. Davis, Jr.

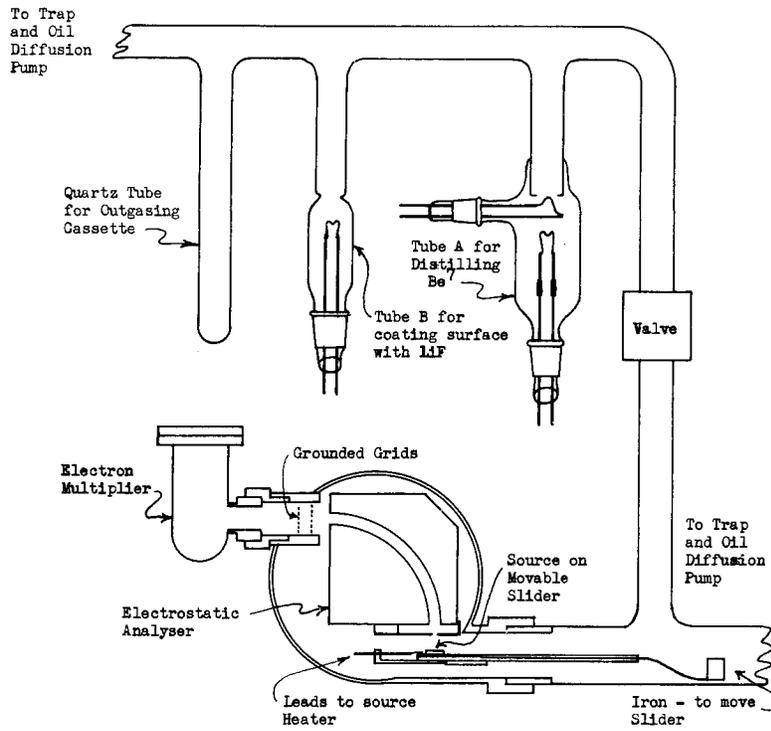
Abstract

The energy spectrum of recoil ions following electron capture and neutrino emission in Be⁷ is being studied. The measurements have been improved by use of an electrostatic analyzer and electron multiplier detector and by maintaining at elevated temperatures the surface from which the recoils originate. Data are presented which show a peak in the energy distribution, consistent with a line spectrum of the energy expected if a single neutrino is emitted modified by energy losses experienced by the ions in leaving the surface.

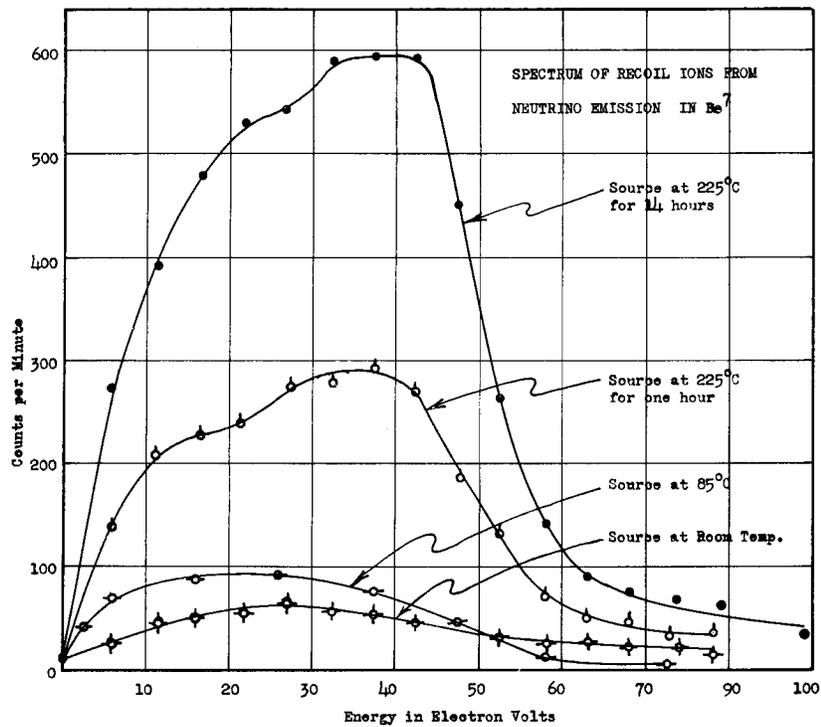
Experiments to measure the nuclear recoil following the neutrino emission in the K-capture isotope Be⁷ were described in the previous progress report. These experiments were directed particularly toward methods of preparing the surface, determining the weight of the surface layer, and measuring the yield of recoil ions from the layer. Lately, the method of measuring the recoil spectrum has been greatly improved. Results of the first set of measurements with the new apparatus will be given in this report, along with a short description of the essential details of apparatus itself.

The Vacuum System and Preparation of the Source

The vacuum system used in the experiment was divided into two separately pumped sections which were interconnected by a valve. The general arrangement of the system is shown schematically in the accompanying Figure 1. The apparatus was arranged in this way so that the source could be prepared in one side of the system by a distillation and then transferred to the opposite side through the vacuum valve. In this way, the transfer could be accomplished in vacuo, and the measuring equipment could be kept free from possible contamination that may result from the distillation of Be⁷. The source was prepared on the surface of a cassette (a platinum foil spot welded to a nickel ring) which could be readily moved to any point in the glass vacuum system with a



1. Apparatus for Studying Neutrino Recoils.



2. Recoil Ion Spectra.

magnet. The source, once prepared, was placed on a slider mounted on the electrostatic analyzer, and moved into position under the plates of the analyzer.

The Be^7 was obtained by proton bombardment of C.P. lithium metal with the University of Pittsburgh cyclotron. The Be^7 was separated chemically from the lithium target by a procedure capable of removing the contaminants usually present in metallic lithium. The efficiency of the procedure for removing these contaminants was tested by qualitative spectroscopic analyses at several points in the procedure. At the end of the chemical separation, carrier-free Be^7 was obtained in a dilute hydrochloric acid solution. This solution, having a volume of about 1 ml, was evaporated a drop at a time on the lower tungsten ribbon from distillation tube A. The operation was accomplished outside of the vacuum system, and the tungsten ribbon was reinstalled in the vacuum system containing the dried deposit. The ribbon was then heated in vacuum to 1400°C , at which temperature the visible contaminants remaining as a residue from the evaporation of the HCl solution in air distilled off. At this point, the ribbon appeared quite clean. The additional operations in the preparation of the recoil source were as follows:

1. The cassette was outgassed in the quartz tube at 900°C for 15 hours.
2. A thin layer of lithium fluoride was then distilled onto its surface in tube B, while care was taken not to let the pressure exceed 3×10^{-6} mm Hg.
3. The Be^7 was then distilled from the lower tungsten ribbon of tube A onto the upper ribbon at about 1600°C , while the upper ribbon was in a position directly above the lower ribbon (see Figure 1). Precautions were taken to outgas the upper ribbon thoroughly at 2000°C prior to the distillation.
4. Finally, the Be^7 was distilled from the upper tungsten ribbon onto the lithium fluoride surface on the cassette. The cassette was placed above this ribbon just before the final distillation. During these distillations, pressures rose to 5×10^{-6} mm Hg, but immediately after the distillations, the pressure dropped to its normal operating level of 4×10^{-7} mm Hg.

The source thus prepared was moved through the valve to the electrostatic analyzer for the measurements.

The Electrostatic Analyzer

The electrostatic analyzer used for measuring the recoil spectrum is shown also in Figure 1. The analyzer had concentric cylindrical plates with a mean radius of 10 cm and a spacing of 1 cm between the plates. Slits were located at the entrance and the exit of the analyzer to increase its resolution and to insure symmetrical fields at the entrance. However, in these experiments the source was too weak to measure at high resolution, so it was necessary to remove these slits. A pair of grounded grids was introduced in place of the upper slit to shield the analyzer from the 2000 v on the first dynode of the electron multiplier. Without the slits a monoenergetic ion of 50-v energy would give a peak having a half-width of about 5 v. A center-tapped resistor was connected between the plates of the analyzer so that a

voltage applied to the plates was equally divided above and below ground. The center-tap of the resistor and the metal backing of the recoil source itself were grounded to the brass vacuum chamber containing the analyzer. The energy of singly ionized atoms passing through the analyzer is given by the expression:

$$E = \frac{|\nu_2 - \nu_1|}{2 \log(r_2/r_1)} = 5.246 |\nu_2 - \nu_1| ,$$

where r_1 and r_2 are the radii of the cylindrical plates, and $|\nu_2 - \nu_1|$ is the voltage drop across the plates. However, it must be pointed out that ions leaving the LiF surface and passing the brass plates of the analyzer are subject to a field arising from the contact difference in potential between these dissimilar materials. The magnitude of this contact difference in potential was not measured in the present experiments, but would be expected to have a retarding effect on the ions of several volts.

The electron multiplier used was developed by R.P. Stone¹ of the R.C.A. Laboratory, Princeton, N.J., and was loaned for this work through the courtesy of I. Wolff of the R.C.A. Laboratory. In these experiments, it was necessary to accelerate the ions into the first dynode of the tube to produce a pulse large enough to operate the counting circuit. For this reason, the first dynode was operated 2000 v negative. The multiplier and analyzer were tested prior to the experiments with ions (from thermal ion sources) accelerated to definite energies from 5 to 80 v. The efficiency of the multiplier for these particles was not determined.

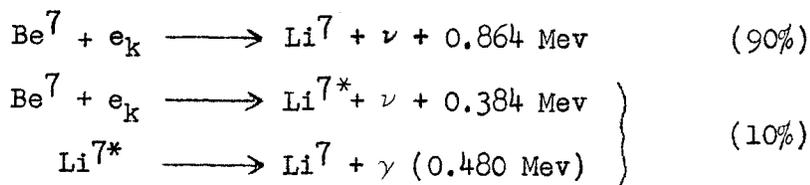
Results and Discussion

As mentioned, the source was not sufficiently intense to make measurements with the slits in place. Removing these caused some delay; consequently, a freshly distilled source was not measured. After several hours, the measurements at room temperature shown in the accompanying Figure 2 were obtained. It is known from the earlier experiments that the yield of ions from the surface decays with time, which may be ascribed to the surface being covered by adsorbed or condensed gases in the vacuum system, or recrystallization of the surface deposit. Measurements were continued by increasing the temperature of the surface. Results are shown for 85 and 225°C, taken successively; an additional curve obtained after the source had remained at 225°C for 14 hr is included. It is seen clearly that the yield of ions increases many fold with increasing temperature, and standing at elevated temperatures further increases the yield. This result is interpreted as due to thermal cleansing of the surface by distillation of adsorbed contaminants. One would expect an accompanying change in the shape of the spectrum in the direction of an increased number of high energy ions. This was observed on increasing the temperature from 85 to 225°, but the change in shape was not markedly augmented after the 14-hr heating, although the yield of ions increased by a factor of two. All the curves shown exhibit a sharp drop at the low end of the spectrum,

¹R.P. Stone, Rev. Sci. Inst. 20, 935 (1949)

less than 5-10 v, but this may be caused by a reduction in the sensitivity of the apparatus for these low energy ions. This point will be examined further in future experiments.

The decay scheme of Be^7 may be represented as follows:



If the K-capture decay is accompanied by the emission of a single neutrino, 90% of all Li^7 nuclei should recoil with an energy of 57.3 ev. Multiple neutrino emission, on the other hand, should lead to a broad spectrum of recoil energies with a maximum recoil energy of 57.3 ev. The results presented are not clean enough to distinguish clearly between these two possibilities. However, the high energy side of the spectra, particularly the ones at 225° , is quite steep. This is most reasonably understood as a monoenergetic peak with broadening at the low energy side introduced through collisions of the recoiling ions with surface contaminations. The exact end point cannot be obtained from these data since the contact potential fields mentioned previously were not measured. Also, the observed recoil energy must be corrected for the energy of binding the atom to the surface. It must be further emphasized that these curves were obtained at low resolution.

In future experiments, the resolution of the instrument will be increased, and the contact potentials will be measured.

HALF-LIFE OF I^{129}

S. Katcoff, O.A. Schaeffer, J. Hastings

The half-life of I^{129} is being investigated by measurements of the absolute disintegration rates and isotopic constitutions of iodine samples of known mass extracted from reactor-irradiated uranium metal. The metal used had cooled for two years. The uranium was dissolved in HCl, and a small amount of normal iodine was added as carrier. After oxidation with hydrogen peroxide, the elementary iodine was removed by counter-current extraction into CCl_4 . It was purified by several cycles of reduction to iodide, extraction into water, oxidation to iodine and re-extraction into CCl_4 . The purification cycles were continued until PdI_2 samples showed constant specific activity when measured in a "Nucleometer."

For the measurements of the absolute disintegration rates and isotopic ratios, methyl iodide samples were prepared by reaction of the radioactive iodine with methanol and red phosphorus at 110° in a sealed tube. By means of a break-off seal, the methyl iodide vapor was transferred to a calibrated vacuum system in which metal valves were used to avoid stopcock grease. For each run, a few aliquots were removed for counting, for iodine analysis, and for isotope ratio determination.

The counters were 2 cm in diameter and 30 cm long, and had 2-mil tungsten center wires and gold or silver cathodes.¹ They were filled with the CH₃I at a partial pressure of around 10 microns, and with methane at 76 cm. The counting was done in the proportional region on both voltage and gain plateaus. Preliminary experiments showed that the counting efficiency for Co⁶⁰ gamma rays decreased when the partial pressure of CH₃I was larger than about 40 microns. In the first run, two gold cathode counters and one silver counter were used. In the latter, 8% of the counting rate remained after the counter had been pumped out and filled with pure methane, but 26% and 100% of the counting rate remained with gold cathode counters. In the second run, a single silver cathode counter was used which had previously been exposed to inactive CH₃I. In this case, a maximum of 2% of the counting rate remained after pumping out.

The iodine analyses were done as follows: An aliquot of the CH₃I was condensed into a small bulb containing about 20 mg sodium metal; this bulb was heated to 210° to form NaI, which was then added to a solution containing 10 µg/ml of Pd⁺⁺. The resulting solution was placed in a Cary spectrophotometer, and the height of the absorption peak at 3700 Å was measured. The reference cell contained the identical amount of Pd⁺⁺ as the cell containing the iodide sample. This is a modification of the method of R.B. Krauss.²

The isotopic abundances were determined by comparing the I⁺ peaks at masses 127 and 129 in a 60° Nier-type mass spectrometer.

Tentative results are given in the accompanying table. The analyses for total iodine are accurate to about ±10 µg. In run I, 26%, 8%, and 100% of the counting rate remained after pumping out the counters for samples 1, 2, and 3, respectively. In run II, nearly all of the activity could be pumped out. However, this memory effect cannot account for the large discrepancy between the two runs, because a sample on the wall of a counter will count with a lower efficiency than the same sample in the gas, which would lead to a longer apparent half-life in the case of wall adsorption.

Tentative Results						
Run	Sample	Abundance of I ¹²⁹	Observed Counting Rate	Disintegration Rate Corr. to Total Sample	Total Weight of Iodine	T _{1/2} (years)
I	1	9.02%	660 c/m	263 d/s	242 µg	8.6 x 10 ⁶
	2		312	105	106	9.5 x 10 ⁶
	3		127	49	38	7.4 x 10 ⁶
II	1	7.98%	641	218	376	14.3 x 10 ⁶
	2		173	59	119	16.8 x 10 ⁶

¹W. Bernstein and R. Ballentine, Rev. Sci. Inst. 21, 158 (1950)

²F.D. Snell and C.T. Snell, Colorimetric Methods of Analysis, Vol. I. D. Van Nostrand Co., New York, 1936. p.564

When solid samples of PdI_2 (1 mg/cm^2) were counted in a "Nucleometer," the assumption of 50% geometry and 20% backscattering correction led to half-life values of 39×10^6 and 30×10^6 years for runs I and II, respectively. The reason for the disagreement in results between the two sets of gaseous samples is being investigated. Parker and coworkers³ have reported a half-life of 20-40 million years from measurements of solid samples.

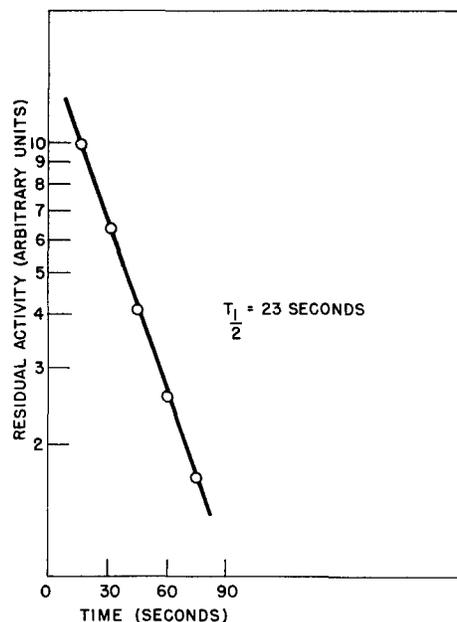
³G.W. Parker, G.E. Creek, T.M. Herbert, P.M. Lantz, and W.J. Martin, ORNL 286

THE GENETIC RELATIONSHIP IN Ag^{110}

J.A. Miskel

Recent studies¹ of the radiations emitted by Ag^{110} have indicated that the 270-d activity is due to a level isomeric with the 24-sec ground state. This genetic relationship has been confirmed by the separation of a short-lived activity from a sample of Ag^{110} obtained from Oak Ridge.

The separation was effected by collection of activity on copper electrodes immersed in an ether solution of silver tetraphenylporphin.* Two copper electrodes separated by about 3 mm were immersed in the solution, and a potential difference of 600 v was applied. After about 3 min, one of the electrodes was removed, washed with ether, and then counted with an end-window G-M tube. The G-M tube was connected to an Autoscaler and a Brush recording oscillograph. The sample was followed to constant background (3-4 min after separation). The accompanying figure shows a plot vs. t of the logarithm of the total number of counts above the constant background observed between $t=t$ and $t=\infty$ (3 min). The background, which accounted for about 80% of the total counting rate at $t=0$, was due principally to the 270-d activity.



Decay curve for short-lived Ag^{110} activity between $t=t$ and $t=\infty$ vs. t .

¹K. Siegbahn, Phys. Rev. 77, 233 (1950); M. Goldhaber and A. Sunyar, private communication

*We are indebted to Professor G.D. Dorough of Washington University for supplying the tetraphenylporphin used in the preparation of the silver compound.

Repeated experiments gave half-lives between 21 and 30 sec. A typical curve is shown in the figure. The time between the removal of the electrode from the active solution and the start of counting was about 12 sec.

Separation occurred at both the anode and cathode with about equal efficiency, although the background was generally lower on the anode. Separation was also obtained when a copper electrode was immersed in the solution with no potential applied, but the separation was not as clean. No separation was observed when an uncharged platinum electrode was introduced.

The complexity of the Ag^{110} decay makes a determination of the separation factor difficult. A direct comparison of the ratio of the counting rates (observed with a 3.5 mg/cm^2 counter window) of the separated 24-sec activity and the 270-d activity in solution gave an efficiency of about 25%, using Siegbahn's estimate of 3% for the intensity of the 24-sec branch.

It is probable that the silver tetraphenylporphin can be used for preparing high-specific-activity samples of 270-d silver by a Szilard-Chalmers process.

REACTOR SCIENCE AND ENGINEERING DEPARTMENT

Theoretical Group

The study of the systematics of even-even alpha emitters which was discussed in the last progress report has been completed; a full scale report has been prepared, an abstract of which follows:

Empirical relationships are found, of the form:

$$\log \lambda = a + b/v, \quad Z \text{ constant,}$$

for values of $Z = 84, 86, 88, 90, 92,$ and 94 . The Geiger-Nuttall rule applies, in this form, to the even-even isotopes of a given element, with the exception of some isotopes of polonium and emanation. The exceptional properties of the latter isotopes are probably explainable in terms of shells in nuclear structure. Relationships of the form

$$\log \lambda = A + B/v, \quad (A-2Z \text{ constant})$$

are found for members of different radioactive series, and are related to the disintegration schemes of the thorium and uranium families. Further empirical relationships are found between alpha disintegration energy and the neutron excess, and between the disintegration constant and the neutron excess.

Values of the radii and "internal potentials" are calculated from the rigorous form of the Gamow-Condon-Gurney theory. The radii of the "normal" even-even alpha emitters can be represented by:

$$r_0 = 1.57 A^{1/3} \times 10^{-13} \text{ cm,}$$

while the "internal potential," U , can be represented by:

$$E-U = 0.52 \text{ Mev,}$$

where E is the total alpha disintegration energy.

The empirical relations $\log \lambda = a + b/v, Z \text{ constant}$ are compared with theory. The values of the half-lives of Th^{224} , Ra^{220} , and Em^{216} are predicted.

(I. Kaplan)

Electron Capture in K^{40}

A 17.8-mg sample of KNO_3 enriched to 7.13% in K^{40} , obtained from Oak Ridge, is being used to study the electron capture process in K^{40} . An X-ray spectrometer* detects the soft X-rays resulting from the electron capture.

*W. Bernstein, H.G. Brewer, Jr., and W. Rubinson, Nucleonics 6, 39 (1950).

The problem of reducing the background due to the presence of the beta particles from K^{40} (60 times as many betas as X-rays) has disclosed some interesting characteristics of this type of spectrometer. Since the betas lose only part of their energy in the counter, and the specific ionization for high energy electrons varies only slowly with energy, the betas give a broad peak on a pulse height vs. energy curve at some pulse height region determined by the type of gas and the pressure in the counter. By a suitable choice of the gas and the pressure, the background peak of the betas can be shifted out of the region of interest of the X-ray peak. The optimum filling for the K^{40} case (argon X-rays) from the preliminary experiments is krypton with 10% methane at slightly less than atmospheric pressure. The resolution of the instrument under these conditions is 20-25%.

The data show consistently the presence of argon X-rays from the K^{40} sample, as two previous investigations seem to indicate.**

Final results on this work will be reported in the near future.

(L.B. Borst, J.J. Floyd, V.L. Sailor)

Radioisotope Development

The Hot Laboratory Operations Group has had under investigation for some time the problem of making short-lived iodine isotopes available for medical and biological use at the Laboratory. This work was concentrated rather early into developing a "milking" generator for I^{132} . The basic requirements were: a safe, easily handled, transportable container for the Te^{132} and the other active and inactive fission product telluriums; and a liquid system from which iodine can be recovered from selenium and tellurium and their compounds. The design of the "milking" generator is substantially complete. Testing of $LiCl$ and other chloride admixtures have shown these to be satisfactory for iodine recovery, with little or no tellurium carry-over. The iodine recovery is lower than might be expected (~25%) but further study has shown this to be characteristic of the degree of oxidation resulting from dissolution of the uranium. A sample of uranium foil has been sent to Oak Ridge for irradiation.

(L.G. Stang, Jr., W.F. Charlesworth, W.D. Tucker)

Waste Concentration

During the last quarter, the Waste Concentration Group has been involved in the following tasks:

1. Experimental process development (pilot plant)
2. Process design and evaluation
3. Compressive distillation project (semi-works)

**F.C. Thompson and S. Rowlands, *Nature* 152, 103 (1943); E. Bleuler and M. Gabriel, *Helv. Phys. Acta.* 20, 67 (1947).

The development of the filtration and the total condensation process for the reduction of large volumes of slightly contaminated wastes is described in reports BNL I-10, BNL 49(T-16), and BNL 59(C-12). These processes involve evaporative concentration with a high degree of de-entrainment. Studies to date have been made on the effects of the major variables. The results, as recorded in the above reports, indicate that a decontamination factor of 10^6 from feed to product can be achieved with a concentration factor of 100 from feed to concentrate.

Preliminary designs of the full-scale low level waste concentrating plant were made, based on both the filtration and the total condensation processes. This information and sufficient additional information to completely outline the scope of the final detail design were incorporated in a brochure entitled "Technical Information on Waste Concentrating Plant," B. Manowitz, April 12, 1950.

In conjunction with the preliminary design studies, an economic evaluation of the waste concentration project was made and reported in BNL 59(C-12), and in a report entitled "Economics of Liquid Waste Disposal," B. Manowitz. The above studies indicate 1) that a considerable risk was involved in extrapolating from pilot plant data to full plant scale, and that a semi-works program was in order; 2) that compressive distillation showed economic advantages over standard evaporative methods for conditions at this site.

(B. Manowitz, R.H. Bretton)

Meteorology

General

Members of the Meteorology Group have devoted the past three months to the revision of both facilities and procedures in order to make the most effective use of available data in the meteorological control program. The largest number of changes have involved the relocation and recalibration of tower and oil-fog instruments, but the calculation of a new set of radiation dose-rate templates is the most significant accomplishment from the point of view of reactor operations.

Instrumentation

The 410' tower has been completely equipped with Aerovanes, and the 160' tower with Gurley instruments. This insures uniform measurements through the height traversed by each tower. Calibration of the wind instruments is now being accomplished in situ with a synchronous motor geared to simulate a series of wind speeds from 2.4 to 38 m/sec.

The Leeds and Northrup temperature instrumentation has been found to be excellent for our purposes. However, the double-cylinder aluminum housings for the thermohms were extremely difficult to disassemble; they have been replaced by a new design. Calibration of the thermohms has also been substantially improved. A water bath technique is now used, and it is possible to attain sufficiently stable water temperatures to make the difference in

lag between the thermohms and mercurial thermometers of no consequence.

Continuous recordings of vertical, as well as horizontal, wind gustiness at the 355' level on Ace tower have been obtained from a Laboratory-designed bivane since February, 1950. Prior to installation, this equipment was tested at the low speed wind tunnel of the College of Engineering, New York University. The natural period of the vane, in both the vertical and the horizontal, is 40 sec at a wind speed of 1 ft/sec. The bivane, although experimental, has proved to be very durable; it is believed that few alterations will be necessary.

The cascade impactor, described in BNL 48, has been calibrated for use with the oil-fog smoke. Four jets are used, ranging from 6.444 to 0.841 mm². Sonic velocity is reached in the final stage. A number of samples of oil-fog smoke have been taken, and methods of analysis have been investigated with the assistance of the Biology Department and the Photography and Graphic Arts Group.

(D.A. Mazarella)

Analysis

The most important improvement in the meteorological control scheme has been the revision and extension of the mathematical basis of the dose-rate templates described in BNL 48. These templates, which are used to convert meteorological data to ground-level radiation dose-rate values, are necessarily based on not only the oil-fog tests, but also on a number of assumptions that cannot be verified prior to reactor operations. It has been possible, however, to revise and extend the mathematical treatment, and to refine some of the approximations so that the accuracy is believed to be significantly improved.

The initial rise of the effluent plume above the stack, hitherto neglected, has been taken into account by means of an "effective stack height" parameter for both inversion and lapse conditions. This rise of the plume has been investigated experimentally in a number of wind-tunnel tests, but no full-scale tests are reported in the available literature. There is general agreement, however, that the principal parameter of consequence is the ratio of stack exit velocity to horizontal wind speed. The buoyancy is of less significance, except under nearly calm conditions.

In the new dose-rate templates, a more exact model of turbulent diffusion has been used to calculate the dose-rate under lapse conditions when vertical diffusion occurs, and the beta contribution has been properly accounted for. The diffusion equation for a continuous point source developed by O.G. Sutton, is the model from which the ground-level dose-rate has been calculated. The oil-fog tests have shown that this equation can be adapted for use in the Laboratory reactor control scheme. It is not certain, however, that the method of adaptation used would be suitable for other localities.

(P.H. Lowry)

Forecasting

The forecast program has also undergone a significant change in the sense that the emphasis has been placed on complete stability of the system, rather than development. This has provided an opportunity for intensive practice in the day-to-day situations that will confront the forecasters when the reactor reaches full power. Both scientists and technicians have participated in the practice sessions routinely, and all are now well versed in the technique.

For the first time data are available that give a direct indication of the accuracy of forecasts in terms of reactor operations. Between January and June, 1950, the practice operational forecasts calling for restriction of operations 24 hours in advance were accurate in 75% of the cases, whereas the micrometeorological forecasts made in the preceding six months were correct in only 60% of all cases.

(M.E. Smith)

Cooperative Projects

Cooperative research programs with the National Advisory Committee for Aeronautics and with New York University have been approved and are now in operation. The NACA project is concerned with the correlation of meteorological measurements of turbulence with those obtained from aircraft in flight; the New York University program is concerned with the comparison of wind tunnel tests and natural atmospheric dispersion.

Geology

Work has continued on driven wells to determine the geologic environment as it affects and controls the movement of the ground water in this area. Until the genesis of the formations is better known, the limited data available from the present net of observation wells cannot provide a satisfactorily definitive picture of the movement of the ground water. The mechanical analysis of the cores from one of the deep wells is nearly finished. The data obtained will shed some light on the origin of the Cretaceous formations. Samples furnished to Harvard University for the study of the plant spores will provide additional data. The study of microfossils of the Gardiners clay is completed; a report on it is being written.

(W. de Laguna, L. Hasl, L. Weiss)

BIOLOGY DEPARTMENT

Biological Effects of Radiation

Cooperative Experiments

Tradescantia, exposed for long periods of time in the gamma field, produces interesting morphological deviations from the normal type. J. Gunkel of Rutgers University, in cooperation with A.H. Sparrow of the Biology Department, is studying the mechanisms of the developmental abnormalities in irradiated Tradescantia by a comparison of normal and abnormal material.

W.R. Singleton is also growing material for cooperative projects with several groups of investigators. It appears that continuous radiation of the growing plant may be more effective in producing interesting mutations. It is also possible that some selective action will take place, because, at their most sensitive stage, the germ cells appear to be more sensitive than the somatic cells, as evidenced by the almost normal growth of the plant as a whole at comparable exposures. The accompanying table lists the various projects under way.

The projects listed in the table are primarily pilot experiments, and are being carried out on an entirely informal basis.

Trillium

Because of the variability in the chromosomal properties of Trillium erectum obtained from commercial sources, it has been decided to start growing this plant on the Laboratory site. Some 1,000 plants have been set out in the woods; they should provide, in time, a source of clonal lines for some of the future experiments. The last of the material irradiated this year is being prepared for cytological examination; analyzing of this material is under way. The studies cited are necessary for the analysis of the radiated material; they furnish, for the first time, the range and types of chromosome abnormalities seen in control material, and thus furnish a sound basis for the evaluation of the radiation effect on the chromosomes of Trillium erectum.*

(A.H. Sparrow)

Potatoes

Tubers irradiated by fast neutrons from the Oak Ridge reactor are now growing on the site. It appears at this time that 1200 rep of fast neutrons is the approximate lethal dose to potatoes, for as yet none of the tubers receiving this dose has produced plants showing above ground. As was expected,

*"Spontaneous chromosome fragmentation in Trillium erectum L.," R.C. Sparrow and A.H. Sparrow; "Supernumerary chromosomes in diploid and triploid Trillium erectum L.," A.H. Sparrow and V. Pond. Both submitted for publication in Genetics.

Cooperative Projects with W.R. Singleton Under Way on the Effects of
Continuous Gamma Irradiation on Mutations and Physiology of Growing Plants

Material	Investigator	Desired Change, or Purpose of Experiment
1. <u>Nicotiana rustica</u>	E.G. Beinhart U.S. Regional Lab., Philadelphia, Pa.	Higher nicotine content. Fewer suckers on plants.
2. Pearl millet	Glenn W. Burton Geneticist, Georgia Costal Plain Expt. Station, Tifton, Ga.	Shorter lines of millet similar to reduced corn.
3. <u>Lespedeza dericea</u>	M.M. Meyers Hd. Agronomist, Div. Forage Crops & Dis- eases, Beltsville, Md.	Lower tannin content to make it more palatable to cattle.
4. Barley	D.W. Robertson Hd., Agronomy Dept., Colo. Expt. Sta., Ft. Collins, Colo.	Changes in genes con- trolling chlorophyll production.
5. Cos lettuce Cowpeas	Lyle T. Alexander Principal Soil Sci- entist, U.S.D.A., Beltsville, Md.	Physiological study on the effects of gamma rays.
6. <u>Nicotiana rustica</u>	F.G. Gustafson Hd., Botany Dept., Univ. of Michigan, Ann Arbor, Mich.	Assay vitamin contents of leaves of irradiated plants.
7. Corn	L.J. Stadler Geneticist, U.S.D.A. and Univ. of Missouri	Determine mutation rates induced by gamma rays in a stock of known low mutation rate.

the lethal dose for neutrons was lower than for X-rays or gamma rays. In confirmation of last year's experiments, the percentage seed germination from tubers which had received 300 r of X-radiation was significantly increased. More work on this effect is under way to obtain the dosage dependence of this effect.*

A few high yielding potato plants were obtained last year from tubers irradiated in 1948. These and samples of the control material have been turned over to the Long Island Vegetable Research Farm for further testing. Some seedlings from irradiated stock have been given to F.J. Stevenson of the U.S.D.A. for further study.

(A.H. Sparrow)

Cytochemistry

The Feulgen reaction is being examined critically to ascertain its quantitative validity in cytological material. The adsorption of the dye in the fixed nucleus is being examined in cooperation with S. Freed, K. Sancier, and M. Slavin of the Chemistry Department. Two distinct peaks in the light absorption have been found in the fixed nucleus, that is, a resolution of these maxima has been brought about in the cell that is only suggested in solution. This effect is unique; it has not been reported previously, but gives rise to interesting speculations concerning the state of nucleic acids in the nucleus. Using a microscope spectrograph arrangement, together with combinations of reflecting and quartz optics, ultraviolet adsorption curves of the unstained fixed nuclei have been obtained. While the results are in general agreement with those of Caspersson, the new method should aid greatly in the cytochemical studies of cells.

It has been found that 20,000 r (sufficient to depolymerize nucleohistone in solution) does not give visible evidence of depolymerization of DNA in either the living or the fixed cells from anthers of the Trillium plant. However, faster hydrolysis of the fixed material with N HCl at 60°C resulted from irradiation. There was no effect on the hydrolysis of the material in the irradiated living cell. These differences in properties are not understood, and are being studied further.

(M.J. Moses)

Corn

In last summer's experiment on the genetic effects of continuous gamma irradiation in corn, high mutation rates were found when pollen from one irradiated genetic stock, A B Pl R Pr Su Wx Y Sh (BNL-1), was placed on another genetic stock, A b pl r pr Su/su wx sh (BNL-2), in an unirradiated field. These high rates could have been due to one of the following: 1) An inherent

*"Effects of X-ray, neutron, and chronic gamma irradiation on growth and yield of potatoes," A.H. Sparrow and E. Christensen. Submitted for publication in American Journal of Botany.

high mutation rate in the particular stock used; 2) a higher mutation rate in the microspore as compared to the megaspore stage (most of the spontaneous rates have been worked out on the megaspore); 3) the gamma radiation from the Co⁶⁰ source. Possibly all three factors contributed to the unexpectedly high results. This year, the experiments are designed to determine the contribution of each of the factors to the observed mutation rate; sufficient plants are being exposed so that some two to three million seeds can be examined. As part of the radiation experiments, two control plots are being grown in unirradiated areas. Each is a crossing plot, one using BNL-1 as the seed stock and BNL-2 as the pollinator, the other using the same two stocks to make reciprocal pollinations. This experiment should establish the mutation rate of BNL-1 in both micro- and megaspore.

In another experiment, an attempt is being made to determine genetically whether irradiation produced mutations are gene changes or are due to chromosome deletions. Pollen of a dominant stock C Sh Wx from the gamma field will be placed on a recessive c sh wx; the frequency of loss of c, sh, and wx, both singly and in combination, will be determined. The amount of crossing over between C and Sh is 3.3%, and between C and Wx is 26%. If losses of C are chromosomal losses, then Sh would be affected more than Wx. If the losses of C are due to gene changes, there should be no effect on Wx and Sh crossover frequencies.

One of the interesting lines of corn under study appears to have the properties of an ancestor of the modern corn plant. Attempts to mutate the gene producing the profound change in morphology by radioactive phosphorus or by gamma rays have been unsuccessful.*

Material is also being grown to determine how frequently a gene mutation which shortens the height of the corn plant can be obtained by radiation. Such a mutation has appeared once (spontaneously) in a sweet corn line, and has now been incorporated into six field corn inbreds for making short hybrids (about 6' tall). Preliminary indications show this type of corn to have a higher grain-to-stalk ratio and to be more efficient in the use of fertilizer than normal tall corn. If this change can be induced by gamma radiation, it would greatly speed up the incorporation of the short gene into the numerous hybrids of interest. To test this possibility, an early inbred Minn A 158 is being grown in the gamma field, and the pollen is being transferred to short plants in control plots. As further controls, pollen from short plants is being used on the Minn A 158. The results should give some indication of frequency of this type of mutation with gamma rays (W.R. Singleton).

Work is continuing on the use of triphenyltetrazolium chloride (TPTZ) as a redox dye to indicate the viability of seed. Preliminary results indicate that, in contrast to the successful application of this dye to test heat and cold inactivation of seed, X-ray inactivation cannot be detected by this means. In one experiment, corn seeds were soaked overnight and exposed to 15,000 r. Visual tests were positive for viability, and the inten-

*"Corn grass, a dominant monogenic spontaneous mutant, and its possible significance as an ancestral type of corn," W.R. Singleton. Submitted for publication in Genetics.

sity of staining in the irradiated seeds was as great as given by unirradiated seeds, despite the fact that the irradiation produced a 65% decrease in growth rate. Since TPTZ is a redox dye, it is evident that X-rays damage the growth potential of the seeds without damage to the enzyme systems producing color with the dye. Doses as high as 30,000 r are without effect on the succinic dehydrogenase activity of the seeds (R. Van Reen, M. Koester).

Rats

Indications of a negative potassium balance in rats after X-irradiation led to a study of nitrogen excretion, since this excretion would be expected to increase if the potassium were coming from damaged cells. The initial experiments done on animals fed ad lib after irradiation gave nitrogen retention. Since this retention might be due to some masking of the irradiation effect in the fed animals, the experiments have been repeated in irradiated fasted rats. These animals eliminate between 25 and 55% more nitrogen than do fasted controls. To check whether the water and electrolyte disturbances following irradiation were due to a post irradiation bacteremia, aureomycine has been administered to the experimental animals with their food. It has been found that aureomycine does not affect the diuresis or polydipsia following irradiation, although the control animals who had the aureomycin without irradiation showed an increase in water intake, starting about the third day, which appeared to be correlated with a mild diarrhea.

(A. Edelman)

E. coli

Control experiments have been completed on the effects of X-rays on the growth and mutation frequency produced in E. coli. Growth was apparently normal and complete up to 50,000 r (5,000 r/hr). Although the phosphorus concentration of the media was varied tenfold, no effect of phosphorus was found on the mutation frequency. This experiment provided the required control for the experiments on internal radiation -- in which the variation of total phosphorus greatly changes mutation frequency -- since it alters the concentration of internal radioactive phosphorus. The evidence is now complete that internal radiation from P³² is a more effective agent for producing mutations than external radiation, probably because of a "transmutation effect." A second conclusion from this experiment is that growing bacterial cells are relatively more resistant to radiation than resting cells, while in higher organisms just the reverse appears to be true.

A study of the appearance of mutants emphasizes the importance of phenotypic lag in bacterial genetics. It often took as many as three generations before the total mutation effect was expressed; the initial distribution of mutants was quite different from that obtained later.

Variations in the media have made it possible to get uniform growth over a much wider range of phosphorus concentrations, thus making it possible to grow E. coli in the presence of very intense radiation (100 to 200 rep/min). These techniques make it possible to get a quantitative evaluation of "phosphorus recoil" as a mutagenic agent.

The streptomycin requirements of the mutated organisms have been studied. It has been found that the streptomycin-requiring mutants do not produce any change in the streptomycin titers of the solution, that the growth stimulating function of streptomycin remains after its antibiotic activity has been destroyed.*

(B.A. Rubin)

Fibrinogen

With the help of A.O. Allen of the Chemistry Department, bovine fibrinogen has been irradiated with 2-Mev X-rays obtained from the Chemistry Van de Graaff machine. Preliminary results indicate that doses of 200,000 r produce a marked increase in the viscosity of the irradiated solutions. In the ultracentrifuge, significant amounts of an additional component of a higher sedimentation constant are found, together with marked destruction of the main component. Simultaneous studies of the thrombin-induced clottability of these solutions indicate that clotting activity is not significantly decreased, despite evidence for a marked change in the structure of the native fibrinogen. The character of the clots does change, however; the clots formed from the solutions given the greatest radiation are compact and break up with mechanical agitation, while those formed with the original solutions exhibit normal synergetic properties.

(A.H. Scheraga, L.F. Nims)

Tracer Studies of Biochemical Problems

Phosphorus

The study of the effect of alloxan-induced diabetes on the turnover rates of the acid-soluble P compounds of the liver has continued. The additional data obtained indicate that there is a marked difference in the character of the specific activity-time course of the glucose-1-phosphate from that found in normal animals of the same strain.

A study of the fate of radioactive phosphate injected into the cerebrospinal fluid via the cisterna magna has been initiated. The uptake of the tracer by the inorganic phosphate, phosphocreatine, and adenosine triphosphate of the brain, the time-course of the distribution in the plasma, and the uptake by the muscles in animals injected by this route have been compared with the distribution of intravenously injected material given in the same dose. The time-course of the P³² concentration in the plasma was followed for 4 hr after the injection, after which the muscle and brain were frozen in situ and analyzed. The experiments were carried out on cats.

It was found that there is a very rapid exchange of the tracer between

*"The nature of streptomycin requirement and its effects on the genetics of streptomycin resistance in E. coli," B.A. Rubin. Submitted for publication in Genetics.

the organic P compounds within the brain cells and that present in the cerebrospinal fluid. The evidence is that isotopic equilibrium between these two locations is reached within the period of the observations.

When the tracer is injected intravenously, the amount appearing in the brain is very much less. The specific activity of the phosphocreatine and ATP of the brain of the animals receiving the intracisternal injection was from 10 to almost 100 times as high as in the brains of the animals in which the tracer was injected intravenously. Since it is well known that the blood-brain barrier represented by the capillaries within the central nervous system is impermeable to anions, the present results signify that the rate of secretion of phosphate into the cerebrospinal fluid is low. Consequently, it must be assumed that the rate of formation of the fluid is rather low. This finding is in marked contrast to results obtained elsewhere. The concentration of isotope in plasma and cerebrospinal fluid approached isotopic equilibrium rapidly. In these experiments, a needle was inserted into the cisterna magna and the cerebrospinal fluid allowed to drain from this. The inference is that, under these conditions, the rate of secretion of the fluid is quite high. Hence, it appears that draining off this fluid acts as a stimulus to its secretion, and that normally it is formed and absorbed at a low rate.

The specific activity of the phosphocreatine and ATP of the muscles of the animals injected intravenously was found to be about 2-1/2 times as high as the specific activity of these compounds in the muscles of the animals which received the tracer by intracisternal injection. Taking the ratio of these values as a measure of the relative availability of the tracer to the muscles under the two conditions, the indications are that about 2/5 of the amount injected into the cerebrospinal fluid was absorbed into the general circulation during the 4 hr after the injection.

These results are of value in showing the experimental conditions that must be observed for further tracer experiments on the formation and absorption of the cerebrospinal fluid. It is essential that the experiments be done on animals large enough that the removal of small amounts of cerebrospinal fluid will not reduce the volume thereof remaining to the point where the reduction acts as a stimulus to the secretion.

In the animals injected intravenously, the specific activity of the phosphocreatine and ATP of the brain was generally higher than that of these compounds in the muscles. This observation indicates that the muscles are unique among the active tissues of the body in the extremely slow rate of transport of phosphate across their cell membranes.

(J. Sacks, G.G. Culbreth)

Iron

Following incubation of radioactive iron, as the citrate, with duck blood, hemin of constant specific activity has been obtained. Since some radioactivity attaches to recrystallized hemin prepared from blood immediately after mixing with the radioactive iron, it is still not clear that the incorporation of iron is a cellular process. Other than cyanide, none

of the enzyme inhibitors or substrates tested affect the transfer of added iron from plasma to cells.

The study of the blood volumes in the rat by the tagged cell method has been completed, and the results have been submitted for publication.* The values obtained by this method, 4.98 ml/100 gm body weight, are confirmed by others and by an independent method involving hemoglobin extraction. This is considerably lower than the mean value of 7 obtained by the dye injection method (L.M. Sharpe, J.R. Klein).

The sensitivity of bone marrow to whole-body X-radiation is being tested by injecting Fe^{55} in rats 24 hr after irradiation, and determining the rate at which tagged hemoglobin appears in the red cells. If the test proves successful, studies of the sensitivity of the bone marrow to injected P^{32} and Na^{24} will be made (L.M. Sharpe).

Carbon

Radioactive carbon administered to eviscerated cats as bicarbonate has been found in carbons 3 and 4 of the glycogen of skeletal muscle. The labeling suggests processes in muscle similar to those biochemical processes already demonstrated in liver for the fixation of carbon dioxide in glycogen. Glycogen from the brain and heart of the cats was radioactive, but the quantities and activities did not permit location of the active carbon (J.R. Klein).

In collaboration with D.D. Van Slyke and J.A. Plazin of the Medical Department, the classical Van Slyke method of wet combustion of organic compounds for carbon analysis has been adapted to the determination of C^{14} specific activity. The crucial point in this adaptation was the possibility that the manometric machine in which the evolved CO_2 is measured would become contaminated with C^{14} activity and would thus increase the counting rates of a subsequent less active sample. This has been proved not to occur, even though no decontamination procedure is followed other than the usual water washing of the manometric chamber between combustions. A sample counting 50,000 cpm followed by a C^{12} sample contributed no detectable activity to the C^{12} sample, although an increase of 10 cpm over background would have been noticeable.

Two separate methods of counting the activity have been developed. In the first method, the CO_2 gas is drawn from the manometric chamber through the cup opening into $\text{Ba}(\text{OH})_2\text{-BaCl}_2$, and the precipitated BaCO_3 is filtered on a sintered glass disk and counted in the methane flow counter. The second method employs the gas-phase counting technique developed at the Laboratory by Bernstein and Ballentine; it is calculated to be about 30 times as sensitive as the BaCO_3 counting technique when a sample of CO_2 is available which gives an infinite thickness sample of BaCO_3 on the disks. Publication of this work in the near future is anticipated.

*"The blood and packed cell volume of the adult rat as measured by tagged cells," L.M. Sharpe, G.G. Culbreth, and J.R. Klein. Submitted for publication in Proceedings of the Society for Experimental Biology and Medicine.

Analysis of the tissues of the mice fed C^{14} sucrose is continuing with the assistance of K. Kiyono; about half of the mice have so far been canvassed, but a statement of the results obtained is reserved until the whole group has been completed.

Work was recently begun on the metabolism of uniformly-labeled C^{14} ascorbic acid in mice, in collaboration with M. Gibbs, D.D. Van Slyke, J.A. Plazin, A. Edelman, and R. Healey. A micromodification of the Roe method for ascorbic acid has been developed in connection with the measurement of the small amounts of ascorbic acid expected in eluates of mouse urine chromatograms. About 1 mg (ascorbic acid colorimetric equivalent) of a material giving the ascorbic acid color in the standard Roe method is excreted per 24 hr by the mouse when kept on an ascorbic acid free diet. This material is not found on butanol chromatograms of mouse urine at the locations expected for either ascorbic or dehydroascorbic acid. Added ascorbic acid can be recovered (76%) after butanol chromatography and elution, but added dehydroascorbic (I_2 oxidized ascorbic) has not proven recoverable at the location reported by Partridge by $AgNO_3-NH_3$ spray test and confirmed here by the same test. Radioautographs of C^{14} dehydroascorbic acid (I_2 oxidized C^{14} ascorbic acid) after butanol or phenol chromatography indicate no clear-cut location for a dehydroascorbic acid band. Thus, the question as to whether the chromogenic material in mouse urine is dehydroascorbic acid requires further investigation; however, it is certain that this material is not ascorbic acid.

The ultimate purpose of these researches is to produce a method for determining the specific activity of urinary ascorbic acid following the administration of C^{14} ascorbic acid to the mouse. This would measure the pool of ascorbic acid into which the administered material had fallen, and would allow a calculation of the total amount of ascorbic acid oxidized by the mouse by measurement of total respiratory CO_2 activity.

(R. Steele)

Biosynthesis

The fungus Rhizopus oryzae fixes $C^{14}O_2$ into lactic acid; the labeled carbon appears exclusively in the carboxyl carbon of lactic acid. Similarly, when glucose 3,4- C^{14} was fermented, all of the label was in the expected position and none in the beta carbon of the lactic acid. Previous studies on a homofermentative lactic acid bacterium has demonstrated that during fermentation tagged carbon did appear in the beta carbon of lactic acid. It is now evident that the fungus Rhizopus oryzae does not have the biochemical mechanisms for shifting activity from carbon atoms 3 and 4 of glucose to the beta carbon of lactic acid.*

The study of the photosynthetic reactions of the alga Scenedesmus has shown that sucrose is the only tagged free sugar produced by this organism when incubated in the presence of $C^{14}O_2$ up to 4 min in strong light, 5 min

*"On the mechanism of lactic acid synthesis by the fungus Rhizopus oryzae studied with C^{14} ," R. Gastel and M. Gibbs. Submitted for publication in the American Journal of Botany.

in weak light, and 27 hr in the dark. In strong light, labeled carbon atoms appeared in all positions of alanine and malic acid. In alanine, most of the tagging was present in the carboxyl carbon; the alpha and beta carbons had equal percentages of labeling. Malic acid was tagged similarly. The sugar fractions showed activity in all positions, with the highest activity being present in only the 3 and 4 positions at the end of 1.5 min. At 4 min, the sugars became uniformly labeled, with a significant shift in the distribution of carbon labels in the other compounds examined. In the dark, alanine and malic acid were labeled only in the carboxyl carbons; the sucrose, dextrin, and starch had activity only in positions 3 and 4 of the glucose isolated from these fractions.

In collaboration with A.A. Bothner-By of the Chemistry Department, it was found that during the epimerization of glucose-1-C¹⁴ no rearrangement was involved. That is, when fructose or mannose are formed from glucose in the presence of dilute alkali, the carbon chain does not break; there is only a shift of hydrogen.*

In the course of the last three months, five groups of investigators have received purified tagged carbohydrates for their experimental programs. The tagged materials are also being used by members of our own staff.

(M. Gibbs)

Mineral Metabolism

The uptake of lanthanum¹⁴⁰ by hickory trees grown in gravel culture or soil has been found to be extremely slow. Experiments are under way to find out whether the rate can be increased by water culture, since there may be a loss of the isotope to the gravel surfaces in the hydroponic bed.

The Fe⁵⁹ uptake and its displacement by stable iron is being studied by radioautographic methods on larvae of Drosophila melanogaster, repleta, willistoni, ananassae, junebuis, and virilis. The completion of the problem was delayed until a high specific activity Fe⁵⁹ sample was obtained.

The analytical studies of marine sponges are being continued; spectroscopic analyses are being done with the collaboration of M. Slavin of the Chemistry Department.

A group of early spring queens of Vespula germanica have been caught. Some are being examined for manganese distribution; some have been fed Ba-La¹⁴⁰ and are being studied by counter and autograph for La discrimination. A small series was fed Fe⁵⁹ and autographs were made to decide whether or not there exists intestinal localization of this element, as for Ba or Mn.

A group of Drosophila repleta larvae have been fed Ba-La¹⁴⁰. The uptake and distribution have been followed by radioautographs and with counting. Decay curves of a number of specimens have been made to reveal Ba and

*"The epimerization of glucose-1-C¹⁴," A.A. Bothner-By and M. Gibbs, J.A.C.S. (in press).

LA enrichment. No evidence has appeared for the sort of localization in the intestinal cells which is so striking in Vespidae.

With J. Neess, a post-doctoral AEC Fellow, studies have been continued on the uptake and transfer of phosphorus, iodine, and iron in typical fresh water food chains. A mass of data is being accumulated, mostly still uncollated. It is of great interest that I^{131} uptake by the Cladocera studied shows a pattern wholly different from that described for insects, and that iron, often described as a limiting nutrient for phytoplankton, show absolutely minimal conservation by both Cladocera and two species of aquatic insect larvae.

(V.T. Bowen)

MEDICAL DEPARTMENT

Division of the Hospital

During the reporting period, work in the hospital has progressed very satisfactorily. At the end of this quarter, the adult ward had all available beds occupied. The children's ward was utilizing all the small beds which have been received. Additional small beds are on order; when they are received, the census will be permitted to increase. Approximately one-third of the patients have carcinoma of the thyroid, and two-thirds have diseases other than malignancy. Iodine for treatment and tracers is still limited to I^{131} , and will be until the nuclear reactor becomes operative.

(W.N. Miller, L.E. Farr, J.S. Robertson)

Division of Pathology

Influence of Mechanical Injury, Radiation Injury, and Disease States on Body Protein Stores

Studies of the influence of fractures upon the manufacture of new body protein are now being conducted on dogs. The animals receive N^{15} -labeled glycine, either orally or intravenously, as part of measured nitrogen intake. Determinations are made of the nitrogen balance and of the distribution of N^{15} in the various body tissues. Similar nitrogen studies are being carried out on dogs fed on protein-free diet. Various control observations are being made. N^{15} analyses are made with the Consolidated-Nier isotope-ratio mass spectrometer.

(S.C. Madden, J.A. Fancher, Jr., L.I. Gidez)

Correlation of Histological Structures with Specific Chemical Compounds

This study is being carried out in collaboration with Dr. Jean Oliver and members of the Department of Pathology of Long Island College of Medicine. Certain preliminary phases of the work have been completed, but certain technical problems remain to be solved before more active work on this study can be developed.

(S.C. Madden, J.A. Fancher, Jr.)

Division of Bacteriology and Virology

Biological Effects of Radiation (Immunology)

Preliminary observations have been made on the effect of radiation on viral propagation. The results are interestingly suggestive, but the present 2-curie source has been proved inadequate for this purpose. A larger and

better-designed source, mentioned below, is being prepared to continue these experiments.

Limitations of the present cobalt source for irradiation of mice for immunological studies have also hampered progress on this study. The new source designed by L. Stang (Reactor Science and Engineering Department), will be used in the hot lab. It is believed adequate to complete at least preliminary observations.

(W.M. Hale)

Homologous Tissue Immunity

Several reported methods of immunizing mice against transplantable tumors have been tried. Two were found satisfactory for the purposes of the experiments planned, and are being used.

(W.M. Hale)

Tumor Tropism of Viruses

The two viruses are continuing to be serially passaged; one of them seems to be increasing its virulence for neoplastic tissue, but is not yet very specific neoplastically.

During this quarter, the Swiss mouse colony which was carrying pleuropneumonia, Thieler's virus, and choriomeningitis virus has been wiped out. Replacing this colony is another colony, also Swiss, which is "infection-free." It is now breeding a sufficient number of animals for present experiments.

(W.M. Hale)

Bacterial Metabolism

The transforming substance of the pneumococcus has been subjected to radiation from cobalt sufficient to destroy its specific biological properties. By using this substance, mutants have been obtained, but it has not yet been proven whether these are caused by radiation or are due to spontaneous variation.

(R.M. Drew)

Division of Biochemistry

Combined Determination of Total Carbon and C¹⁴

In collaboration with R. Steele of the Biology Department, the manometric wet carbon combination method of Van Slyke and Folch has been modified so that the total CO₂ obtained is first measured from the pressure that it exerts at 10, 2, or 0.5 ml volume, and is then quantitatively transferred for measurement of radioactivity.

For the activity measurement, two procedures have been applied:

1. After the CO_2 pressure is measured, a vessel containing $\text{Ba}(\text{OH})_2$ solution is connected with the manometric chamber. The connections are evacuated, and the CO_2 is transferred to the vessel, where it is precipitated as BaCO_3 . The precipitation is accelerated by shaking, with a motor, both the manometric chamber and the attached vessel with $\text{Ba}(\text{OH})_2$, so that two successive shakings of 1.5 min each complete the transfer and precipitation. The BaCO_3 is obtained as a uniform precipitate, and is transferred to a disk which is applied to a methane flow counter for the activity measurement.

2. The CO_2 , after the pressure is measured, is transferred for activity measurement to an evacuated gas counter, of the type designed by Ballantine and Bernstein. The CO_2 is condensed in an arm of the counter by cooling with liquid nitrogen. The use of the Ballantine-Bernstein counter with CO_2 in the gas form is particularly advantageous for small amounts of C^{14} ; the amount required for a valid count is estimated to be about 1/30 of that required when the carbon is in the form of BaCO_3 .

In combustions of varying amounts of sucrose containing C^{14} , amounts of carbon varying from 0.1 to 6.0 mg have shown a linear relation, the ratio of counts to carbon being within ± 1.5 per unit of the mean throughout the above range.

Both of the above procedures are relatively rapid. Combustion and transfer to either the barium solution or the gas counter can be completed in about 10 minutes.

(D.D. Van Slyke)

Chemical Anatomy of Body Fluids

A program directed at measuring certain features of water and electrolyte distribution in nephrotic children is now under way. The experiments which have been conducted to date have involved the use of Na^{24} only. The present data indicate a great range of individual differences among the nephrotic children, with respect to the time required for equilibration between blood plasma, ascitic fluid, and edema fluid. The experience gained to date has shown the need of longer periods of observation than were originally planned. The design of experiments has been altered to meet the conditions found. Sodium compartment calculations have shown a larger percentage of body weight than was anticipated. In five nephrotic children, this has ranged from 35 to 47% of the observed body weight; in one convalescent nephrotic child the sodium compartment comprised 23% of observed body weight. Two adults who were non-nephrotic had calculated sodium spaces equivalent to 20 and 27% of their observed body weight. The latter figure was surprisingly high, but thus far no explanation has been found to account for the value. These studies are continuing and are being expanded in the variety of observations being made.

(J.S. Robertson, W.N. Miller, L.E. Farr)

