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# Argonne Aational Laboratory UNCLASSIFIED QUARTERLY PROGRESS REPORT ON PHYSICAL SCIENCES

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November, December 1961, January 1962

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#### ARGONNE NATIONAL LABORATORY 9700 South Cass Avenue Argonne, Illinois

#### UNCLASSIFIED QUARTERLY PROGRESS REPORT ON PHYSICAL SCIENCES

#### November, December 1961, January 1962

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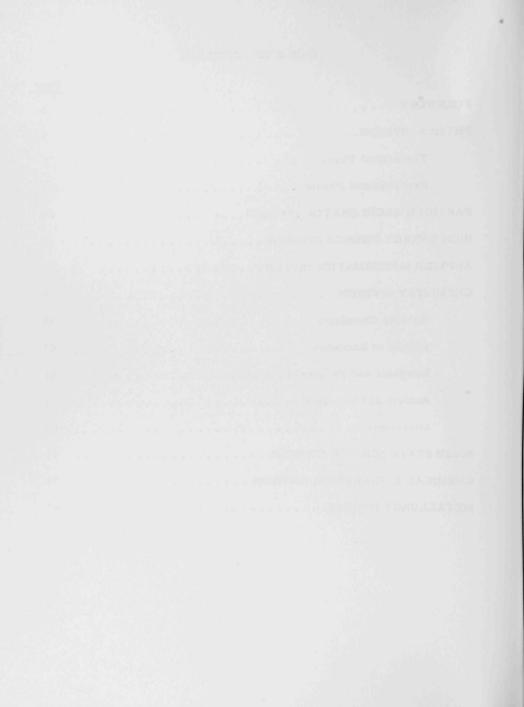
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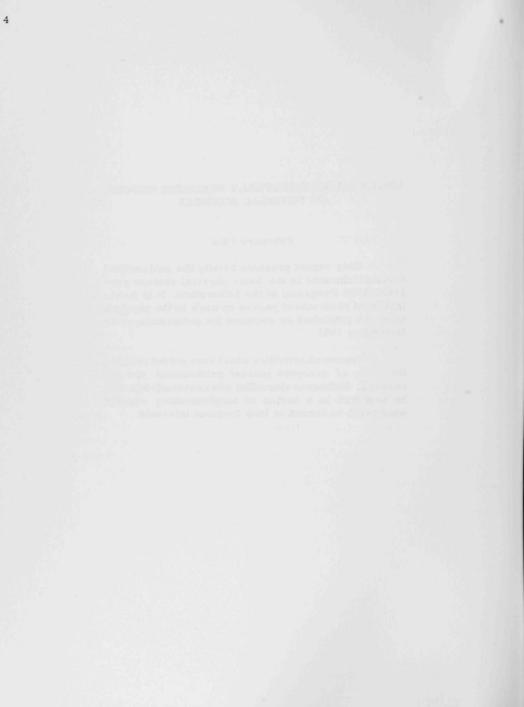


#### UNCLASSIFIED QUARTERLY PROGRESS REPORT ON PHYSICAL SCIENCES

#### February 1962

This report presents briefly the unclassified accomplishments in the basic physical science program (5000 Program) of the Laboratory. It is a collection of abstracts of papers on work in the physical sciences published or accepted for publication since November 1961.

Research activities which have not yet reached the state of accepted journal publications are not covered. Neither is classified work covered; this will be reported in a series of supplementary reports which will be issued at less frequent intervals.



#### PHYSICS DIVISION

#### Theoretical Physics

#### TIME REVERSAL AND SUPERSELECTION Hans Ekstein Nuovo Cimento, in press

The physical requirements on the time reversal operator are reformulated in terms of observables and proper states. These requirements entail superselection rules which are consistent with experiment.

## THE PION-PION EFFECT ON LOW-ENERGY PION-NUCLEON SCATTERING

M. Marinaro\* and Katsumi Tanaka

Nuovo Cimento, in press

The pion-pion resonance contribution to low-energy pion-nucleon scattering has been obtained in closed form by integrating over the circle that characterizes the  $\pi$ - $\pi$  cut. Its effects on the S-wave amplitude and on the isotopic spin-flip contributions of S- and P-wave amplitudes in  $\pi$ -N scattering were then studied.

The present approach differs from a previous phenomenological method in that one can control and understand the nature of the singularity that is included in the calculation. When the isotopic spin-flip S-wave amplitude in  $\pi$ -N scattering is extrapolated from physical to unphysical values of the square of the total energy, a smooth energy dependence is found in the unphysical region. The  $\pi$ - $\pi$  contributions to S<sub>1/2</sub> and P<sub>1/2</sub> states of  $\pi$ -N are shown to be related by a mass reversal

### TOTAL CROSS SECTIONS AT HIGH ENERGIES Kichiro Hiida, Michitoshi Soga and Katsumi Tanaka Phys. Rev. Letters, in press

Total cross sections which are well known experimentally are nearly constant and seem to satisfy the following inequalities from several Bev to the highest energy available at the present moment ( $\gtrsim 20$  Bev).

$\sigma(\pi, p) > \sigma(\pi, p)$	(1)
$\sigma(K^-,p) > \sigma(K^+,p)$	(2)
$\sigma(\bar{p}, p) > \sigma(p, p)$	(3)

(1)

Pomeranchuk and other authors have proved that the total cross section for a particle on a target must be identical with that for its antiparticle on the same target at sufficiently high energy under some conditions.

It is the purpose of this paper to explain inequalities (1) to (3) and to predict other relations among total cross sections at high energies under a hypothesis on generalized isospin independence. The three inequalities and other relations are explained on the basis of four facts: (a) the isospin of the  $\Lambda$  particle is zero; (b) all hyperons have strangeness of the same sign; (c) the strangeness of all hyperons is negative; and (d) the pion and kaon have baryon number zero. Inequality (1) is explained by (a), inequality (2) by (a) and (c), and inequality (3) by (a), (b), and (d). If hyperons had positive strangeness, then the direction of inequality (2) would have been reversed. If the hyperons did not all have the same sign, then there would be no basis for inequality (3).

# ELASTIC NUCLEON-NUCLEON SCATTERING AT HIGH ENERGIES AND SMALL ANGLES

Kichiro Hiida

Bull. Am. Phys. Soc. 7 40 (January 1962) Abstract Phys. Rev. Letters, in press

The proton-proton elastic-scattering cross section for an incident energy in the range 12-27 Bev, and for scattering angles  $\theta \lesssim 60$  milliradians has been measured at CERN with counters. This work suggests a mechanism to explain the characteristic features of the experimental cross section. This mechanism is the diffraction scattering of a virtual boson (pion or kaon) by the two nucleons, i.e., the two-boson exchange (diffraction scattering) process. By using the optical theorem, it is shown that in our process there is the same kind of enhancement factor as in the mechanisms giving rise to the quasi-elastic peaks in high-energy nucleon-nucleon and pion-nucleon scatterings.

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QUASI-ELASTIC PEAKS IN HIGH-ENERGY NUCLEON-NUCLEON AND PION-NUCLEON SCATTERING

S. D. Drell\* and Kichiro Hiida

Bull. Am. Phys. Soc. 6 434 (November 1961)

Abstract

A bump in the energy spectrum of inelastically scattered protons emerging from proton-nucleus collisions for incident energies in the range 9-25 Bev and for scattering angles of 20-60 milliradians has been reported by Cocconi <u>et al</u>. at CERN. Their recent experiment on C and CH<sub>2</sub> shows a possible structure in the inelastic peak in the form of camel humps. Our purpose is to suggest a mechanism giving rise to the bump. This mechanism is the diffraction scattering of a pion in the cloud of the target nucleon. The main results of calculations for the conditions of observation at CERN will be presented. Further, we should like to suggest that there should be a quasi-elastic diffraction peak in the process  $\pi + N \rightarrow \pi + \pi + N$ . The results of calculations are compared with an experiment at CERN.

#### NUCLEAR MODELS AND SURFACES

D. R. Inglis

Revs. Mod. Phys., in press

Nuclear models such as the shell model and the distorted-shell model, or collective model, have been very successful in correlating nuclear data and have much in common in the way they describe clustering of nucleons in angular position. In heavier nuclei this clustering tendency manifests itself as partial formation of alpha-particle-like clusters in the nuclear surface. For very light nuclei, which are almost all surface, the tendency is stronger and there is a distinct break between Li<sup>7</sup> and Li<sup>6</sup>. The former is still well approximated by the shell model, but Li<sup>6</sup> is not, resembling instead an extreme cluster model consisting of an alpha and a deuteron, according to recent experimental evidence. The formation of a nuclear shell may thus be considered a collective phenomenon, and the critical nucleon number for the p-shell is 3. NUCLEAR MODELS, THRESHOLD STATES AND REARRANGEMENT ENERGY

D. R. Inglis

Nuclear Phys., in press

When a parameter such as the nuclear radius is varied to raise the energy of a nuclear state towards the top of a potential barrier, the rate of rise is decelerated by the penetration of the barrier and the consequent spreading out of the wave function. This enhances the probability that states will be found in the energy intervals where this penetration becomes large. In the simplest treatment of a potential well for a neutron, the height of the barrier has been taken to be B, indicated by the neutron threshold. The plot of the neutron energy, as a function of nuclear radius, curves over to become asymptotic to the threshold over only a small range of radius. The enhancement of the likelihood of a state near threshold is thus rather small. Empirically there seems to be a small enhancement of about this magnitude, although there are too few cases to be sure. It is instructive to consider in two dimensions the potential and wave function of a system of two interacting nucleons moving in a one-dimensional box. Here the deuteron channel is illustrative of a cluster channel, where a similar enhancement would be expected were it not for the Coulomb potential which suppresses the effect for charged-particle thresholds.

The separation energy of a nucleon leaving a nucleus is determined not only by the breaking-off of its interactions with the other nucleons but also by the rearrangement energy  $\triangle$ . This is the energy decrease resulting from the strengthened interactions of the remaining nucleons when they rearrange their mutual separations and symmetries to take advantage of the absence of the removed nucleon. For finite nuclei this is expected to be rather different from the rearrangement energy calculated for infinite nuclear matter. In the determination of the penetration of a nucleon wave function into the classically forbidden region outside the nucleus, the height of the barrier is given by the breaking of the interactions but without benefit of rearrangement since the wave function exists also inside the nucleus. The shell-model potential which confines wave functions thus has a barrier height  $B + \Delta$ , higher by the rearrangement energy  $\Delta$  than the separationenergy barrier B. The usual harmonic oscillator wave functions are a better approximation to wave functions thus confined than would be expected without recognition of this role of rearrangement energy.

In cases in which the last nucleon is very slightly bound so that its amplitude inside the nucleus may be small (as in Be<sup>9</sup>) and particularly when the residual nucleus consists of closed shells relatively little influenced by the last nucleon (as for the proton in F<sup>17</sup>) the rearrangement energy is expected to be exceptionally small. That these wave functions are not narrowly confined is thus consistent with the confining role of  $\Delta$  in normally bound states. The rearrangement barrier seems to have been observed in a highenergy (p,2p) reaction. The plausible assumption that the rearrangement energy  $\Delta$  is roughly proportional to the probability of the bound nucleon being inside the nuclear potential well influences in a peculiar way the likelihood of finding a state near threshold. There is a sort of regenerative effect. As the level is raised towards or slightly beyond threshold, the increased penetration of the rearrangement barrier  $B + \Delta$  decreases the amplitude of the internal part of the wave function. This in turn decreases  $\Delta$  and lowers the barrier  $B + \Delta$ , thus further increasing the penetration. If the intrinsic rearrangement energy is rather small, the result is to increase the already somewhat enhanced likelihood of finding a state near threshold.

## TIME-REVERSAL INVARIANCE AND FLUX QUANTIZATION

Murray Peshkin

Bull. Am. Phys. Soc. 7 117 (February 1962) Abstract

The quantization of trapped flux threading a thick superconducting ring has been explained under the following assumptions: (1) Electrons deep in the superconductor are free, at least in the sense of Bloch waves. (2) The magnetic interaction may be replaced by an external (Hartree) field. (3) All other interactions are invariant under time reversal. (4) An interaction of the BCS type connects degenerate pairs of states related to each other by time reversal, and produces the Meissner effect. A two-fold degeneracy of time-reversed states was deduced from assumptions (1), (2), and (3) when the trapped flux is lhc/e with integral l. Inclusion of half-integral  $\ell$  required the additional assumption of cylindrical symmetry to guarantee quantization of the angular momentum of each superconducting electron. The present work shows that cylindrical symmetry is completely irrelevant. Time-reversal symmetry of the entire system, including the flux, leads to the desired degeneracy for half-integral as well as for integral  $\ell$ . The present proof therefor applies to a superconducting loop of any shape. The effective substitution of 2e for e results from the two-fold degeneracy induced by invariance under time reversal.

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## STATISTICAL MECHANICS OF EQUALLY LIKELY QUANTUM SYSTEMS

Norbert Rosenzweig Bull. Am. Phys. Soc. 7 91 (January 1962)

Abstract

Statistical properties of complex atoms and nuclei were previously explained in terms of Wigner's Gaussian ensemble  $E_G$  in the space of real symmetric matrices of dimensionality N. A new but closely related ensemble  $E_R$  in the same space but with the restriction Spur  $H^2 = R^2$  (R is a positive constant) is considered. This allows one to satisfy Dyson's requirement that all systems (matrices) are equally likely. The mathematical idealization of an arbitrary change in the law of force of a system consists of an orthogonal transformation U on the vector H in the  $\frac{1}{2}N(N+1)$  dimensional vector space with scalar product (G, H)  $\equiv$  Spur GH.  $E_R$  is determined uniquely by the statement that  $E_R$  shall be invariant under a change of representation of states.) As in previous work, the statistical properties of the energy states are determined by the invariant group of orthogonal matrices in N dimensions. EG and ER have identical joint distributions of eigenvalues (relative to the mean spacing) as  $N \rightarrow \infty$ .

#### ISOBARIC-SPIN SPLITTING OF SINGLE-PARTICLE RESONANCES J. B. French\* and M. H. Macfarlane Nuclear Phys. 26 168-176 (July 1961)

When a single proton is added to, or a single neutron removed from, a definite shell-model orbit in a target nucleus, the total strength can in general be divided into two parts, each part being characterized by a definite value of the isobaric spin T. This separation is pertinent even when the target isobaric spin is a redundant quantum number determined simply by the neutron excess, and probably in many cases when the isobaric spin is not conserved in the individual states which contribute to the strength. General expressions are given for the total strengths and for the strengths of the T-components. The practical problem of observing this effect as a T-splitting of giant resonances is discussed briefly.

# PROPERTIES OF NUCLEI WITH NEUTRONS AND PROTONS IN THE $\mathrm{lf}_{7/2}$ Shell

R. D. Lawson

Phys. Rev. 124 1500-1505 (December 1, 1961)

Abstract in ANL-6445, p. 6

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\*University of Rochester

SYMMETRY THEORY OF THE AHARONOV-BOHM EFFECT: QUANTUM MECHANICS IN A MULTIPLY CONNECTED REGION

L. J. Tassie and Murray Peshkin Ann. Phys. 16 177-184 (1961)

Abstract in ANL-6445, p. 6

NEUTRON SCATTERING BY THE COMPLEX HARMONIC OSCILLATOR POTENTIAL

J. Sokoloff

Phys. Rev. 124 826-829 (November 1, 1961)

Abstract in ANL-6445, p. 7

#### GROUP THEORY AND ITS APPLICATION TO PHYSICAL PROBLEMS Morton Hamermesh

Reading, Mass.: Addison-Wesley Publishing Company, 1961. p. 507

The purpose of this book is to introduce physicists to the use of group theoretical methods in research. The book begins by covering the elements of group theory. The point symmetry groups of crystals are derived from elementary geometrical considerations, and magnetic symmetry groups (color groups) are also discussed. The theory of group representations is presented in detail, followed by a derivation of the irreducible representations of the point symmetry groups. Theorems about real representations and simply reducible groups are derived. Physical applications are given to crystal fields, perturbation theory and selection rules. A complete treatment of the permutation groups is given. The elements of the theory of Lie groups and Lie algebras are described. The rotation group in 2 and 3 dimensions is discussed and applied to the double-valued representations of the crystal point groups. A complete discussion is given of linear groups in n-dimensional space. This includes the unitary group, the orthogonal group, and the symplectic group. The irreducible representations of all of these groups are constructed. The results are applied to the theory of atomic and nuclear spectra, and includes a discussion of supermultiplets and seniority.

The final chapter on projective representations gives an introduction to more recent developments in the theory of the Galilean group and the Lorentz group. A discussion of "little groups" provides an introduction to the theory of crystal space groups.

### Experimental Physics

## EXPERIMENTAL ANALOG STUDY OF CONTAINMENT OF DENSE PLASMAS IN RESONANT-CAVITY FIELDS A. J. Hatch and J. W. Butler\*

J. Electronics and Control, in press

An analog experiment has been devised to study the conditions for the equilibrium of dense plasma cores contained by rf cavity fields. Plasma cores are simulated by copper spheres, spheroids, and other configurations. Frequency shifts that result from finite perturbations in (1) size, (2) position, and (3) configuration are measured. The measurements are interpreted by use of the Wien-Ehrenfest adiabatic theorem to yield information on equilibrium of the core. Measurements indicate that cores in a spherical cavity are in stable equilibrium against all three types of perturbation only in the magnetic quadrupole mode and in higher order magnetic multipole modes of the cavity fields.

### INTERFERENCE EFFECTS OF RADIOFREQUENCY FIELDS IN RESONANCE RADIATION

M. N. Hack

Nuovo Cimento 22 (1) 168-177 (October 1, 1961)

Abstract in ANL-6445, p. 7

# HIGH-FREQUENCY DIELECTRIC CONSTANT OF HIGH-FREQUENCY PLASMOIDS

A. J. Hatch

Bull. Am. Phys. Soc. 7 133 (February 1962) Abstract

The high-frequency dielectric constant K of a high-frequency lowpressure plasmoid has been determined by two different experimental methods that yield widely divergent values. Typical results are presented. One value, K  $\approx$  +4, is determined by a method of circuit substitution. The other value, K  $\approx$  -9, is determined from the ratio of the external field to the internal field as measured by an rf field probe. These values are reconcilable from considerations of simple classical dispersion theory and the geometrical relation between the plasmoid and the exciting electrodes. The results are consistent with the mechanism in which the plasmoid is considered as a quasi-dielectric medium with an excess of positive space charge about which an electron bunch executes forced bound oscillations. The distinction between these oscillations and the Langmuir type of plasma oscillations is discussed.

\*Applied Mathematics Division

#### CONFERENCE SUMMARY

#### D. R. Inglis

Proc. Rutherford Jubilee Intern. Conf., Manchester, England, 1961, Ed. J. B. Birks. London: Heywood and Co., Ltd., 1961. pp. 837-845

The author has summarized very briefly the main contributions to the conference and attempted to relate them to each other.

ENERGY DEPENDENCE OF THE  $B^{10}(d,p) B^{11}$  ANGULAR DISTRIBUTION Benjamin Zeidman, J. L. Yntema and G. R. Satchler\*

Proc. Rutherford Jubilee Intern. Conf., Manchester, England, 1961, Ed. J. B. Birks. London: Heywood and Co., Ltd., 1961. pp. 515-516

Abstract in ANL-6445, p. 8

# ANGULAR CORRELATIONS IN INELASTIC SCATTERING OF PROTONS FROM ${\rm Mg}^{24}$

T. H. Braid, J. L. Yntema and Benjamin Zeidman

Proc. Rutherford Jubilee Intern. Conf., Manchester, England, 1961, Ed. J. B. Birks. London: Heywood and Co., Ltd., 1961. pp. 519-520

Abstract in ANL-6445, p. 9

#### THE $(d, He^3)$ REACTION NEAR Z = 28

J. L. Yntema, T. H. Braid, Benjamin Zeidman and H. W. Broek Proc. Rutherford Jubilee Intern. Conf., Manchester, England, 1961, Ed. J. B. Birks. London: Heywood and Co., Ltd., 1961. pp. 521-522

Abstract in ANL-6445, p. 9

#### THE $(\alpha, t)$ REACTION ON NUCLEI

#### J. L. Yntema

Proc. Rutherford Jubilee Intern. Conf., Manchester, England, 1961, Ed. J. B. Birks. London: Heywood and Co., Ltd., 1961. pp. 513-514

Abstract in ANL-6445, p. 9

# ELASTIC AND INELASTIC SCATTERING OF 43-MEV ALPHA PARTICLES IN THE NI REGION

H. W. Broek, T. H. Braid, J. L. Yntema and Benjamin Zeidman Proc. Rutherford Jubilee Intern. Conf., Manchester, England, 1961, Ed. J. B. Birks. London: Heywood and Co., Ltd., 1961. pp. 517-518

Abstract in ANL-6445, p. 10

<sup>\*</sup>Oak Ridge National Laboratory

STUDIES OF (d,t) REACTIONS ON THE ISOTOPES OF NICKEL

M. H. Macfarlane, B. J. Raz, J. L. Yntema and Benjamin Zeidman Proc. Rutherford Jubilee Intern. Conf., Manchester, England, 1961, Ed. J. B. Birks. London: Heywood and Co., Ltd., 1961. pp. 511-512

Abstract in ANL-6445, p. 10

#### GLASS SCINTILLATORS FOR NEUTRON DETECTION

L. M. Bollinger and G. E. Thomas

Proc. Symp. on Neutron Time-of-Flight Methods, Saclay, July 24-26, 1961, Ed. J. Spaepen. Brussels: Euratom, 1961. pp. 431-436

Abstract in ANL-6445, p. 14

A  $\gamma\text{-}\mathsf{RAY}$  SPECTROMETER FOR STUDIES OF RESONANT-CAPTURE  $\gamma\text{-}\mathsf{RAY}$  SPECTRA

L. M. Bollinger, R. T. Carpenter, R. E. Cote and H. E. Jackson Proc. Symp. on Neutron Time-of-Flight Methods, Saclay, July 24-26, 1961, Ed. J. Spaepen. Brussels: Euratom, 1961. p. 431

Abstract in ANL-6445, p. 15

SPIN ASSIGNMENT OF RESONANCES FROM CAPTURE GAMMA-RAY SPECTRA

L. M. Bollinger and R. E. Cote

Proc. Symp. on Neutron Time-of-Flight Methods, Saclay, July 24-26, 1961, Ed. J. Spaepen. Brussels: Euratom, 1961. pp. 199-201

Abstract in ANL-6445, p. 12

## LESSONS LEARNED FROM A CHOPPER ACCIDENT

G. E. Thomas, R. E. Cote and L. M. Bollinger

Proc. Symp. on Neutron Time-of-Flight Methods, Saclay, July 24-26, 1961, Ed. J. Spaepen. Brussels: Euratom, 1961. pp. 297-300

Abstract in ANL-6445, p. 13

#### ISOTOPIC IDENTIFICATION OF RESONANCES FROM CAPTURE GAMMA-RAY SPECTRA

H. E. Jackson and L. M. Bollinger

Proc. Symp. on Neutron Time-of-Flight Methods, Saclay, July 24-26, 1961, Ed. J. Spaepen. Brussels: Euratom, 1961. pp. 191-197

Abstract in ANL-6445, p. 13

#### ANALYSIS OF RESONANT-CAPTURE $\gamma$ -RAY SPECTRA

R. T. Carpenter, J. P. Marion and L. M. Bollinger
Proc. Symp. on Neutron Time-of-Flight Methods, Saclay, July 24-26, 1961, Ed. J. Spaepen. Brussels: Euratom, 1961. pp. 563-564
Bull. Am. Phys. Soc. <u>6</u> 418 (November 1961)

Abstract in ANL-6445, p. 14

Geometrical considerations in the measurement of the ratio  $\rm L/r$  in the scattering of polarized nucleons

J. E. Monahan and A. J. Elwyn

Nuclear Instr. & Methods, in press ANL-6420 (September 1961)

This report describes a FORTRAN II program which is used to evaluate the effect of a spatially extended analyzer and detector on the measurement of the left-right asymmetry in the scattering of polarized particles. In particular, the initial scatterer is assumed to be a point source and the analyzer (second scatterer) and detector are treated as planes whose dimensions are adjustable as input data in the program. The calculation also allows for any given angular distribution of particle flux from the source if this distribution can be represented as a finite power series in the cosine of the angle of emission. A similar representation is used to describe the scattering properties of the analyzer. The integrals over the finite dimensions of the analyzer and detector are evaluated by a standard Newton-Cotes quadrature approximation for multidimensional integration. A discussion of this approximation as well as a listing of the FORTRAN program are included as appendices to this report. A COMPUTER PROGRAM FOR ANALYSIS OF COMPLEX CONTINUOUS BETA-RAY SPECTRA

S. B. Burson and R. G. Helmer

Bull. Am. Phys. Soc. <u>6</u> 451 (November 1961) Abstract

In collaboration with Mr. W. J. Cody and M. J. A. Gregory (Argonne Applied Mathematics Division), a two-stage computer program (IBM-704) has been developed for the analysis of complex beta-ray spectra. Only the second stage is described. The first stage accomplishes standard data reduction.

A spectrum comprising as many as 13 components can be analyzed. Each component is presumed to consist of a linear combination of allowed and unique first-forbidden transitions and is represented by three parameters: the slope m of its Fermi plot (related to relative intensity), the endpoint energy  $\epsilon_0$ , and the shape-partition factor  $\alpha$ . Before the calculation, initial estimates must be made for all parameters of the components assumed to be present. Any of the parameters may be held fixed. Pairs of end points may be related when such energy differences are known. The computation is an iterated least-squares fit to any selected portion or portions of the data. The free, or unfixed, parameters are varied simultaneously in order to minimize the function  $X^2 = \Sigma_i w_i [N_i - \bar{N}_i(p_j)]^2$ , where  $N_i$  and  $N_i(p_j)$  are the experimental and calculated counting rates, and  $w_i$  is the weight factor. Criteria for convergence, available options, and some of the known limitations are discussed.

# ANALYSIS OF GAMMA-RAY SPECTRA OBTAINED WITH A NaI CRYSTAL WITH AN ANTICOINCIDENT ANNULUS

J. E. Monahan, Sol Raboy and C. C. Trail

Proc. Total Absorption Gamma-Ray Spectrometry Symp., Gatlinburg, Tenn., May 10-11, 1960. TID-7594, pp. 168-187

A computer program was developed to analyze complex gamma-ray spectra obtained with a scintillation spectrometer with an anticoincident annulus of NaI. The photopeaks are fitted with a least-squares calculation which assumed that the peaks are Gaussian. The contributions from Compton processes and pair production are removed by subtracting the isolated spectrum of each gamma ray, determined separately. The method permits the determination of the width, peak height, and channel position of each photopeak in the spectrum. A "chi-squared" test of the fit to the photopeaks is made. The uncertainties associated with the parameters include statistical uncertainties as well as any uncertainties from the non-Gaussian character of the photopeak. By this procedure the resolution function of the spectrometer and the energies of unknown gamma rays can be obtained in terms of standard lines in the spectrum. Relative intensities of the gamma rays may be obtained by dividing the product of the height and width (the relative area of the photopeak) by the photoefficiency obtained from a Monte Carlo calculation.

POLARIZATION OF NEUTRONS IN SCATTERING FROM LIGHT NUCLEI AND IN THE  $Li^7(p,n)$  Be<sup>7</sup> REACTION

A. J. Elwyn and R. O. Lane

Nuclear Phys., in press

The left-right asymmetries of polarized neutrons scattered from Li<sup>6</sup>, Li<sup>7</sup>, Be<sup>9</sup>, B, C<sup>12</sup>, O<sup>16</sup>, and Mg were measured at scattering angles of 45° and 90° for neutron energies from 0.1 to 2.4 Mev. Polarized neutrons were obtained from the Li<sup>7</sup>(p,n) Be<sup>7</sup> reaction at an emission angle of 51° (lab.). In energy intervals near certain resonances, Li<sup>7</sup>, O<sup>16</sup>, and Mg scatterers were used as analyzers to determine the polarization in the reaction. A clearly-defined peak in the polarization is observed near  $E_{\rm p} \approx 2.2$  Mev. Its width is about 0.15 Mev. These results are compared with earlier measurements and with previous calculations based on level parameters in Be<sup>8</sup>. These results for the  $Li^{7}(p,n)Be^{7}$  reaction were combined with previous measurements at higher energies to obtain the polarization in the scattering from the various light nuclei investigated. Of particular interest are (1) the large polarization observed in scattering from Mg, (2) the persistence of the polarization at an almost constant value of 0.35 in the scattering from Li<sup>7</sup> (at 45°) at neutron energies up to 2.4 Mey. and (3) the observation that the polarizations in the nuclei with spin ( $\text{Li}^6$ , Be, and B) are usually smaller than those for the zero-spin nuclei in the vicinity of resonances for the nuclei involved. The results for some of the nuclei are compared with calculations based on analyses in terms of level parameters.

#### NEUTRON POLARIZATIONS IN SCATTERING FROM Li<sup>6</sup>, Li<sup>7</sup> AND Mg R. O. Lane, A. J. Elwyn and Alexander Langsdorf, Jr. Bull. Am. Phys. Soc. 6 430 (November 1961) Abstract

The azimuthal asymmetry in the scattering of partially polarized neutrons from the Li<sup>7</sup>(p,n) Be<sup>7</sup> reaction (at 51° emission angle relative to the incident proton direction) has been measured at energies from 0.2 to 2.0 Mev for Li<sup>6</sup> and Li<sup>7</sup>, and from 0.2 to 0.7 Mev for Mg. Asymmetries were determined at five different angles of scatter simultaneously by measurement of counting rates both with and without the precession of the neutron spin through 180° by the transverse field of an electromagnet. A striking feature of the results is the nearly identical polarizations in Li<sup>6</sup> and Li<sup>7</sup> from 0.5 to 2.0 Mey, where both are approximately of the form  $P(\theta) = A \sin 2\theta$ . From the known neutron source polarization, it follows that A is negative and as large as -0.4 at the higher energies. The angular distribution of the polarization  $P(\theta)$  and that of the unpolarized differential cross section  $\sigma(\theta)$  for natural Mg are presented along with their values predicted from a fit to the total cross section of Mg<sup>24</sup>. The large polarizations (up to 95%) observed in this energy range make Mg attractive as an analyzer in spite of the complications due to the isotopes Mg<sup>25</sup> and Mg<sup>26</sup> in the natural element.

### CAPTURE OF ALPHA PARTICLES BY Mg24

J. A. Weinman, L. L. Lee, Jr., Luise Meyer-Schützmeister and S. S. Malik

Bull. Am. Phys. Soc. 7 72 (January 1962) Abstract

The capture of alpha particles by  $Mg^{24}$  has been observed for alpha energies from 2.80 to 4.40 Mev, corresponding to excitation in Si<sup>28</sup> from 12.39 to 13.80 Mev. Angular distributions of the high-energy gamma rays leading to the ground or first excited state were measured for 8 new resonances. Because of the simplicity of alpha-particle capture by a zerospin nucleus, these angular distributions enable the unique assignment of spins and parities to the prominent resonances, as listed below.

$E_{\alpha}(lab)$	Excitation in Si <sup>28</sup>	Spin and Parity
3.21 Mev	12.74 Mev	2+
3.31	12.83	(0 +  or  4 +)
3.36	12.87	4+
3.42	12.92	4+
3.51	12.99	1-
3.59	13.07	4+
3.66	13.12	2+
3.82	13.26	(4+)
4.36	13.71	2+

## INELASTIC SCATTERING OF α PARTICLES BY Zn<sup>64</sup> AND Zn<sup>68</sup> H. W.Broek, T. H. Braid, J. L. Yntema and Benjamin Zeidman Bull. Am. Phys. Soc. <u>7</u> 82 (January 1962) Abstract

The scattering of 43-Mev  $\alpha$  particles by Zn<sup>64</sup> and Zn<sup>68</sup> has been investigated over the angular range from 18 to 44°. A silicon surface-barrier detector was used. The energy spread was about 0.65%, full width at half-maximum, and was primarily due to the energy spread in the incident beam. In addition to the well-known 2<sup>+</sup> first excited states at about 1 Mev and the 3<sup>-</sup> states at 3.0 Mev in Zn<sup>64</sup> and 2.75 Mev in Zn<sup>68</sup>, groups were observed at 1.8, 2.3, 3.7, 4.1, and 5.0 Mev in Zn<sup>64</sup> and at 1.8, 3.7, 4.3, and 5.3 Mev in Zn<sup>68</sup>. The angular distribution of the groups at 1.8 and 2.3 Mev in Zn<sup>64</sup> and at 1.8, 3.7, and 4.3 Mev in Zn<sup>68</sup> are in phase with the angular distributions of the 3<sup>-</sup> states. The data are compared with previous results for Ni<sup>58</sup> and Ni<sup>60</sup> and with the distorted-wave calculations.

REACTION CROSS SECTIONS FOR Zn<sup>64</sup> (n,2n) Zn<sup>63</sup> AND Zn<sup>64</sup> (n,p) Cu<sup>64</sup> L. A. Ravburn

Bull. Am. Phys. Soc. 6 462 (November 1961) Abstract

Cross sections for these reactions have been measured at several incident neutron energies between 13.5 Mev and 19.5 Mev. An experimental technique was used in which the two 511-kev gamma rays from the annihilation of positrons in the irradiated samples were counted in coincidence by using two NaI scintillation spectrometers. The value of the  $Zn^{64}(n,2n)Zn^{63}$  reaction cross section increased from 75 mb at 13.5 Mev to a maximum of approximately 375 mb at about 18.5 Mev. The value of the  $Zn^{64}(n,p)Cu^{64}$  reaction cross section decreased from 215 mb at 13.5 Mev to approximately 120 mb at 19.5 Mev. Where these measurements overlap those of other investigators, the values are in agreement.

## CHARGE STATES OF MOLECULAR FRAGMENTS FROM CCl\_3Br FOLLOW-ING NUCLEAR DECAY OF ${\rm Br}^{80\,\rm m}$ and ${\rm Br}^{82}$

Sol Wexler

J. Chem. Phys., in press

The patterns of positively-charged fragments from dissociation of molecules following nuclear decay of bound radioactive atoms are characteristic of the mode of nuclear decay. After negative beta emission the mass pattern of the ions is composed almost entirely of singly-charged species, and the modes of molecular disruption appear to be insensitive to the nuclear charge of the radioactive atom, and hence to the size of its surrounding electron cloud. On the other hand, nuclear isomeric transition accompanied by internal conversion leads to mass patterns dominated by multiply-charged atomic species. The data indicate that extensive electron transfer occurs in the molecule prior to rupture. The molecules are apparently shattered as a result of multicenter Coulombic repulsion of separated positive charges.

ISOTOPIC IDENTIFICATION OF NEUTRON RESONANCES OF Cd, Sb, Os AND Pt FROM CAPTURE GAMMA-RAY SPECTRA

H. E. Jackson and L. M. Bollinger

Phys. Rev. 124 1142-1152 (November 15, 1961)

Abstract in ANL-6445, p. 11

 $Hf^{177}\left(n,\gamma\right)Hf^{178}$  AND THE ASSOCIATED ENERGY LEVELS IN  $Hf^{178}$ 

R. K. Smither

Bull. Am. Phys. Soc. <u>7</u> 11 (January 1962)

The capture gamma-ray spectrum of  $Hf^{177}(n,\gamma)Hf^{178}$  was investigated with the Argonne 7.7-m-bent-crystal spectrometer. The observed spectrum consisted of 204 gamma rays with energies below 2 Mev. These precision energy measurements were combined with a series of coincidence experiments to modify and extend the level scheme of Hf<sup>178</sup>. The extended scheme consists of 14 levels of excitation (above the  $0^+$  ground state) at energies (in kev) of 93.14 (2+), 306.50 (4+), 631.92 ((6+)), 1059.27 ((6+)), 1069.38 ((2+)), 1163.86 (2+), 1195.94 (0+, 4+), 1268.99 (2+), 1420.27 (1, 2+), 1430.88 (3, 4+), 1472.95 (2+, 4+), 1485.27 ((2+)), 1513.16 ((2+)), (1575.31) ((2)), (1654.72) ((2)), (1669.59) ((2)), 1752.28 (3, 4<sup>+</sup>), and 1776.24 ((4)). The double parentheses indicate uncertainty in the spin assignments. For levels above 1060 key, the probable error in the energy relative to the ground state is about 0.3 kev. while the error associated with the energy spacings between these levels above 1060 kev is about 0.05 kev. Many of the low-energy gamma-ray transitions between the upper levels are observed. Their role in the determinations of the spins and parities of the upper levels is discussed.

THE DECAY OF 74W<sup>188</sup>(65 d) AND 75Re<sup>188</sup>(18 hr) S. B. Burson, D. Zei and Teymoor Gedayloo Bull. Am. Phys. Soc. <u>7</u> 35 (January 1962)

Abstract

Abstract

Tungsten oxide enriched in W<sup>186</sup> was irradiated for about 15 days in the MTR reactor, Arco, Idaho. Successive neutron capture produced the 65-day W<sup>188</sup>. After chemical purification, the beta-ray spectrum was studied by the use of magnetic spectrometers and absorption techniques. The sources used in accumulating the spectrometer data were in equilibrium with the 18-hr daughter, Re<sup>188</sup>. The beta-ray spectra are being analyzed by use of a computer program compiled for this purpose. All quoted experimental results are preliminary. The spectrum of Re<sup>188</sup> between 0.4 and 2.15 Mev is in accord with previously published measurements. The unusual character of the spectrum (slightly concave toward the energy axis) is confirmed. The spectrum of W<sup>188</sup> is resolved into two components with end-point energies of  $431 \pm 5$  and  $342 \pm 5$  kev. The former is concluded to be the ground-state transition. Scintillation measurements on W<sup>188</sup> were facilitated by chemical separation from the Re daughter. Scintillation peaks corresponding to gamma transitions in Re<sup>188</sup> have been observed with energies of about 57, 145, 222, 265, and 290 kev. Several of these peaks clearly are complex. The coincidence data and a tentative decay scheme are discussed.

LOW-LYING LEVELS IN Hg<sup>200</sup>

R. T. Carpenter, R. K. Smither and R. E. Segel Bull. Am. Phys. Soc. <u>7</u> 11 (January 1962) Abstract

Gamma-gamma coincidences have been taken on various  $Hg^{199} + n$  resonances. Particular attention was paid to two-step cascades proceeding through levels in  $Hg^{200}$  at about 1 Mev excitation, which is the region of the second excited state. A prominent 6.98-0.68-0.37 Mev cascade emanating from the 175-ev (J=1) resonance was identified. This establishes the existence of a level at 1.05 Mev. No crossover has been detected from this level. The position of the state has been determined with sufficient precision to assure that it is distinct from the 0.95 Mev state seen following the  $\beta$ -decay of  $Tl^{200}$ . Observation of a 6.77-0.89-0.37 Mev cascade from the 34-ev (J=1) resonance identifies a new level at 1.27 Mev. Thus, three levels are now established between the first excited state at 0.37 Mev and the large number of closely spaced levels which start at about 1.6 Mev.

#### THE El GAMMA-RAY STRENGTH FUNCTION FOR $144 \le A \le 202$ R. T. Carpenter and L. M. Bollinger Bull. Am. Phys. Soc. 7 10 (January 1962) Abstract

The systematics of the radiative de-excitation of compound nuclear states formed by neutron capture is being studied. Because the partial radiation widths measured in resonances are members of the extremely broad Porter-Thomas distribution, and because off-resonance values may be strongly influenced by interference effects, it is necessary to consider values of the partial widths measured in the peaks of the neutron resonances and averaged over many resonances. The quantity  $\langle \Gamma_{\gamma i} / E_{\gamma i} \rangle / D$ , analogous to the neutron (scattering) strength function, may then be obtained as a quantity characteristic of the particular radiative transition considered. Values of this "gamma-ray strength function" have been obtained for 26 El transitions in 13 nuclides between Nd<sup>144</sup> and Hg<sup>202</sup>. The results are in good agreement with the predictions from the Weisskopf estimate. Within statistical error, the value is independent of any of the final states so far considered.

TOTAL NEUTRON CROSS SECTION OF Th<sup>229</sup>

R. E. Cote, Herbert Diamond\* and J. E. Gindler\* Bull. Am. Phys. Soc. 6 417 (November 1961) Abstract

The Argonne fast chopper has been used to measure the total neutron cross section of Th<sup>229</sup>. Because of the small size of the sample (about 2.4 mg), less than 1% of the normally available beam intensity could be used, a condition that limited the flight path to 25 m and hence the resolution to  $0.09 \ \mu sec/m$ . Furthermore, the results of the measurements are confined to the immediate vicinity of the neutron resonances because of this small available sample of Th<sup>229</sup>. Resonances were observed at 0.608, 1.254, 1.40, 1.71, 1.93, 2.66, 3.15, 4.10, 5.49, 6.89, 9.15, 10.4, 12.5, and 15.2 ev. The discussion of these results includes a comparison between this total crosssectional measurement and a measurement of the fission cross section which shows resonances at 0.240, 0.563, and 0.727 ev.

PRECISION MEASUREMENTS OF THE NEUTRON TOTAL CROSS SECTION OF  $U^{235}$ 

A. Saplakoglu

Nuclear Sci. and Eng. 11 312-317 (November 1961)

A careful measurement has been made of the total cross section of  $U^{235}$  as a function of neutron energy for neutrons within the energy range 0.004 to 0.4 ev. The cross section at an energy of 0.0253 ev has been found to be 694  $\pm$  1.5 barns.

TEMPERATURE SHIFT IN THE MÖSSBAUER SPECTRUM OF METALLIC IRON

R. S. Preston, Juergen Heberle, T. R. Hart and S. S. Hanna Bull. Am. Phys. Soc. <u>7</u> 39 (January 1962) Abstract

The temperature shift in the Mössbauer spectrum of Fe<sup>57</sup> in metallic iron has been measured from 4°K to 1300°K. The shift is attributed chiefly to the change in  $\langle v^2 \rangle$  of the atoms (second-order Doppler shift), but in part it is due also to the temperature dependence of the isomer shift. Below 700°K the observed temperature shift is nonlinear and consistent with a Debye temperature of 450° although there is evidence that this effective Debye temperature is not strictly constant. From 700°K to 1043°K (the Curie point) the curve is linear with a slope  $(\partial \nu/\partial T)/\nu = 1.48 \times 10^{-15}$ deg<sup>-1</sup>, which may be compared with the value  $3R/2Mc^2 = 2.44 \times 10^{-15}$  deg<sup>-1</sup>. The curve is discontinuous at the Curie point, but is again linear (probably with the same slope) above this. A second, and larger, discontinuity is observed at 1190°K, the temperature of transition to the  $\gamma$  phase of iron.

#### MÖSSBAUER EFFECT IN Gd<sup>155</sup>

Carolyn Littlejohn Herzenberg, Luise Meyer-Schützmeister,

L. L. Lee, Jr., and S. S. Hanna

Bull. Am. Phys. Soc. 7 39 (January 1962) Abstract

Recoilless resonant absorption has been observed for the second excited state of  $Gd^{155}$  at 87 kev. A source of 1.7-yr  $Eu^{155}$  was prepared in the Argonne research reactor by neutron irradiation of  $Sm^{154}$  in the form of  $Sm_2O_3$  (99.2%  $Sm^{154}$ ). The absorber was gadolinium metal, which is ferromagnetic below room temperature. The source and absorber were cooled to 4°K in separate helium cryostats so that the source could be moved relative to the absorber to obtain a velocity spectrum. The spectrum showed an absorption dip, the drop in intensity being about 3% and the width about 8 mm/sec. Structure observed in the dip was not well resolved. The expected natural line width is 0.6 mm/sec. Absorbers of  $Gd_2O_3$  and two Gd-Al alloys (1% and 5% Gd) were also investigated, but the absorption spectrum was not simplified or better resolved in these samples. A rough analysis indicates that the internal magnetic field at the nucleus is less than  $10^6$  oe.

### MÖSSBAUER EFFECT FOR Fe<sup>57</sup> IN BERYLLIUM

J. P. Schiffer, Juergen Heberle and P. N. Parks Bull. Am. Phys. Soc. 6 442 (November 1961)

Abstract

In order to study the behavior of impurities in a lattice, a  $Co^{57}$  source was electroplated onto a Be disk. The activity was diffused into the Be by heating. The resonant absorption of 14-kev gamma rays from this source was studied as a function of velocity. The gamma-ray line was unsplit but broadened to about 0.33 mm/sec. The Mössbauer f for the source is  $0.60 \pm 0.04$  at 80°K. The temperature shift between 80° and 290°K was found to be  $0.113 \pm 0.005$  mm/sec or  $5.5 \times 10^{-8}$  ev. Using the Debye model as a simple approximation, one can calculate an effective Debye temperature for the Fe atoms in Be from these data in two ways. From the f value one obtains  $150 \pm 10^{\circ}$ K for  $\theta_{\rm D}$  and from the temperature shift one gets  $440 \pm 40^{\circ}$ K. An absorber was prepared by plating enriched Fe<sup>57</sup> onto a Be disk and heating it; the absorption line was broadened asymmetrically, probably because of the higher concentration of Fe atoms. DISSOCIATION OF MOLECULES BY NUCLEAR DECAY OF CON-STITUENT ATOMS

Sol Wexler

Proc. IAEA Symp. on Chemical Effects of Nuclear Transformations, Prague, October 23-28, 1960. Vienna: Intern. Atomic Energy Agency, 1961, pp. 115-145

The patterns of positively-charged fragments, resulting directly from molecular dissociation due to beta-decay of tritium and of Br<sup>82</sup>, and isomeric transition of Br<sup>80m</sup> in various isolated molecules, have been measured by mass-spectrometric techniques. In the beta transformation of organically-bound tritium to He<sup>3</sup>, the carbon-helium bond almost always ruptures, with the positive charge from the increase in nuclear charge going with the organic fragment. The organic fragment may dissociate further by C-C bond rupture and loss of neutral H and H, as shown by the large number of ions from C2H5T, p- and s-C3H7T, and o-, m-, p- and  $\alpha$ -monotritiated toluenes. The similarity of the fragmentation patterns of the two isometric propanes and especially of the four isometric toluenes suggests that the influence of the location of the radioactive atom in the molecule on the dissociation following beta-decay is often obscured by secondary processes in the excited daughter before break-up. Principal differences in the propane spectra are consistent with greater stability of the secondary propyl structure relative to that of the primary isomer. Empirical estimates of the distributions of excitation energies made available to the daughter molecular ions  $(C_2H_5He^3)^+$  and  $(C_3H_7He^3)^+$  by the betatransformation agree reasonably with expectations from the theoretical model based on perturbation of the electrostatic environment of the electronic cloud by the sudden change in nuclear charge. In the decay of TH and T<sub>2</sub>, the respective  $(HHe^3)^+$  and  $(THe^3)^+$  daughters usually remain bound, but stability against dissociation depends slightly on the mass of the bonding partner. The behaviors of 1,2-C2H4BrBr<sup>82</sup> and CCl3Br<sup>82</sup> are in most respects similar to those of tritiated organic molecules.

Nuclear internal conversion and subsequent Auger transitions in the isomeric transition of Br<sup>80</sup> in CH<sub>3</sub>Br produces a charged distribution ranging from Br<sup>1+</sup> to Br<sup>13+</sup> and peaked at Br<sup>7+</sup>. The presence of singly, doubly, and triply charged carbon-containing fragments indicates that the CH<sub>3</sub>Br<sup>80</sup> daughter dissociates by Coulomb repulsion. The charge spectrum of Br from CCl<sub>3</sub>Br<sup>80</sup> is also peaked; patterns of carbon and chlorine ions are observed. For BrBr<sup>80</sup>, the spectrum of charged bromines is peaked at Br<sup>5+</sup>

CHARGE STATES OF MOLECULAR FRAGMENTS FOLLOWING NUCLEAR DECAY

Sol Wexler

Papers Presented at Mass Spectrometry Conf., Chicago, June 4-9, 1961. ASTM Committee E-14, p. 106. Abstract

A comparison of the positive ionic fragments from dissociation of trichlorobrommethane by  $\beta^-$ ,  $\gamma$  decay of 35.9-hr Br<sup>82</sup> and from isomeric transition of 4.4-hr Br<sup>80m</sup> was made by mass spectrometric techniques. Virtually all the products following beta decay are singly charged, while distributions of multiply-charged atomic species dominate the fragmentation pattern after the isomeric transition. The results indicate that negative beta decay affects the molecule rather mildly, while the effect is violent following isomeric transition with internal conversion. In the latter mode of nuclear decay the molecule apparently explodes as a result of multi-center Coulombic repulsion.

#### THE HEAT OF FORMATION OF THE CN RADICAL

Joseph Berkowitz

J. Chem. Phys., in press

The vapor in equilibrium with graphite and nitrogen in the temperature range 2200°-2500°K has been analyzed with a mass spectrometer. The partial pressure of CN radicals measured in this way has been used to calculate  $\Delta H_{f}^{\circ}(CN) = 109 \text{ kcal/mole}$ , equivalent to  $D_{0}(CN) = 7.5 \pm 0.1_{5} \text{ ev}$ . The results of a variety of experiments are compared with this one, and in some cases, reinterpreted. The appearance potential of CN<sup>+</sup> from CN is found to be 14.2  $\pm$  0.3 ev. Other possible azocarbon species up to C<sub>6</sub>N<sub>6</sub> have been investigated and found to be much less abundant than CN.

## DOUBLE-OVEN EXPERIMENTS WITH LITHIUM HALIDES

Joseph Berkowitz, H. A. Tasman and W. A. Chupka Abstracts of Scientific Papers Presented at the 18th Intern. Congr. of Pure and Applied Chemistry, Montreal, August 1961. Toronto: Univ. Toronto Press, 1961. p. 109

In virtually all of the applications of the mass spectrometer for the determination of high-temperature properties, one or more of the following assumptions have been made: (1) a measured ion peak corresponds to a specific molecular progenitor; (2) the cross section for ionization of a molecule by electrons is the sum of the cross sections of its component atoms (additivity rule); (3) when a Knudsen cell is combined with a mass spectrometer, the partial pressure of a given molecular species within the cell is related to its ion intensity by the relation

 $P_i = k_i I_i T , \qquad (1)$ 

where  $k_i$  is a constant depending upon the species involved and the geometric arrangement of the ion source, but independent of the pressure and temperature of the Knudsen cell. These assumptions have been tested for each of the lithium halides, by use of a specially designed double oven. Milne earlier suggested such a system for the measurement of relative ionization cross sections, but the assumptions inherent in his method are very difficult to achieve experimentally. Gorochov has proposed a double-oven scheme for unraveling fragmentation patterns when several species are present. In the "constant-source" double chamber that has been constructed, Gorochov's equations are directly applicable, but the form of the relations describing the relative cross-section ratio is altered from Milne's scheme.

The fragmentation ratios of monomer and dimer obtained for lithium halides are as follows:

	$M^{+}/MX^{+}$	$M^{+}/M_{2}X^{+}$	$MX^{+}/M_{2}X^{+}$
LiF	(4.5)	0.138	0.001
LiCl	0.30	0.125	0.03
LiBr	0.46	0.13	0.066
LiI	0.16	0.21	0.06

Using these fragmentation patterns, one may evaluate the ratio of total ionization cross sections of dimer to monomer. For all of the lithium halides except LiF, this ratio lies between 1 and 2. The collection efficiency of the mass spectrometer is most likely responsible for the discrepancy in LiF.

The double-oven arrangement has also been employed to determine dimerization energies of the lithium halides, using both second and third law methods. REACTION OF GRAPHITE WITH HYDROGEN. HEAT OF FORMATION OF THE METHYLENE RADICAL

W. A. Chupka, D. J. Meschi and Joseph Berkowitz Abstracts of Scientific Papers Presented at the 18th Intern. Congr. of Pure and Applied Chemistry, Montreal, August 1961. Toronto: Univ. Toronto Press, 1961. p. 115

The reaction of graphite with hydrogen in a Knudsen cell at pressures in the range 0.1-1.0 mm and temperatures up to  $2600^{\circ}$ K has been investigated with a mass spectrometer. The most abundant species in the vapor were carbon and hydrogen atoms and molecules and  $C_2H_2$ . Small amounts of  $C_2H$ , CH, CH<sub>2</sub>, and CH<sub>3</sub> were detected. The partial pressures of these species were estimated from the intensities of the parent ions produced by electrons of low voltage. The partial pressures of CH and CH<sub>3</sub> agreed fairly well with those calculated from available thermochemical data. The measured partial pressure was used to calculate a heat of formation of 80 kcal/mole for CH<sub>2</sub>.

Attempts to approach equilibrium from another direction (by pyrolysis of various compounds) were unsuccessful in that the concentrations of CH, CH<sub>2</sub>, and CH<sub>3</sub> were always much too high for equilibrium with graphite and hydrogen. However, the disproportionation reaction  $2CH_2 \rightarrow CH + CH_3$ appeared to reach equilibrium and yielded a value of 86.0 kcal/mole for the heat of formation of CH<sub>2</sub> by both second and third law methods.

ENERGY DISTRIBUTION AND FRAGMENTATION PROCESSES RESULTING FROM ELECTRON IMPACT ON PROPANE AND n-BUTANE

W. A. Chupka and Manfred Kaminsky

J. Chem. Phys. 35 1991-1998 (December 1961)

Abstract in ANL-6349, p. 20

#### WEATHER MODIFICATION M. B. Rodin\* and D. C. Hess ANL-6444 (December 1961)

It is suggested that applying heat directly to a rain cloud, or to a moist air mass with rain potential, may alter the natural precipitation in a given geographical region. The immediate effect of the heat is to increase the buoyancy of the cloud or air parcel. The result, which depends on a number of interrelated factors may be either (a) to cause precipitation where it would not naturally occur, or (b) to suppress precipitation where it would naturally occur. Several possible applications are suggested. Since the heat supplied is supplemented by the latent heat resulting from condensation in the moist air mass, the results may more than justify the cost. However, substantial amounts of heat are involved. The heat can be supplied from fossil fuels, nuclear reactors, or a combination of both; but the logistics favor the use of large nuclear reactors wherever safety criteria can be met. Not only the efficiency and economics of the process, but also its feasibility, can be finally decided only on the basis of information that is not now available.

#### PARTICLE ACCELERATOR DIVISION

# ON THE FEASIBILITY OF ACCELERATING POLARIZED PROTONS WITH THE ARGONNE ZGS

David Cohen

Rev. Sci. Instr., in press

A computing program was developed for simultaneously tracing trajectories and classical, relativistic spin precessions around the Zero Gradient Synchrotron (ZGS). Depolarizing resonances, previously predicted, were found and their properties were computed; there were 36 significant resonances, 12 of which were serious. A method is proposed for avoiding these 12 resonances by using two or four pulsed quadrupole magnets around the ZGS ring. These would rapidly shift  $\mu_z$  at appropriate energies during the acceleration cycle. With this method, a proton beam, injected into the ZGS with P = 1, would have P > 0.7 at the end of the acceleration cycle.



#### HIGH ENERGY PHYSICS DIVISION

#### OBSERVATION OF $\mu^{-}$ CAPTURE IN LIQUID HYDROGEN R. H. Hildebrand

Phys. Rev. Letters 8 34-37 (January 1, 1962)

Preliminary observations in a hydrogen bubble chamber of the capture process

 $\mu + p - n + \nu$ 

and a rough evaluation of the absolute capture rate are reported. A  $99\frac{1}{2}\%$  pure muon beam from the Chicago cyclotron is brought to rest in an 8-liter hydrogen bubble chamber. The incoming particles are identified as muons by their residual range vs curvature in the 20-kilogauss field of the chamber. Reaction 1 is identified by the absence of a decay electron and by the appearance of a recoil proton created by the neutron. The following capture rate was obtained: Method 1: Events identified by non-decay of muons and by recoil protons,  $\Lambda = N_{cap}/\tau_{\mu} N_{S}$ ;  $\Lambda = 420 \pm 120 \text{ sec}^{-1}$ . Method 2: Events identified only by nondecay of muons,  $\Lambda \leq N_{nd}/(\tau_{\mu} N_{S})$ ;  $\Lambda \leq 710 \pm 75 \text{ sec}^{-1}$ . This rate is consistent with a V-A capture theory. It excludes a V + A interaction.

PRELIMINARY EVALUATION OF A CERENKOV IMAGE-AMPLIFYING DETECTOR

William Kernan, Arthur Roberts, T. A. Romanowski, R. A. Schluter, S. D. Warshaw, D. O. Caldwell\* and D. A. Hill\*

Proc. Intern. Conf. on Instrumentation for High-Energy Physics, Berkeley, California, September 12-14, 1960. New York: Interscience Publ., 1961. pp. 93-97

One of the authors has previously proposed a new type of Cerenkov detector in which the cone of light produced by a fast particle in a radiator is focused by a lens and forms a circular image on the photocathode of the first of a cascade chain of image-intensifier tubes. An analysis of the properties of such a detector has been made. In this paper a progress report is presented on an evaluation of the optical properties of a complete detector system, which has been set up as a joint effort of Argonne and MIT groups at the Brookhaven National Laboratory, and will shortly be tested with particles from the Cosmotron.

(1)

DESIGN AND CONSTRUCTION OF A SYSTEM OF PULSED MAGNETS R. L. Kuskowski, T. B. Novey and S. D. Warshaw

Proc. Intern. Conf. on Instrumentation for High-Energy Physics, Berkeley, California, September 12-14, 1960. New York: Interscience Publ., 1961. pp. 9-11

A plan to measure the magnetic moment of the  $\Lambda^{\circ}$  hyperon by measuring the moment of the transversely polarized particle has resulted in the system of pulsed magnets described. The desire to obtain as large as possible an integrated field over the path of the rapidly decaying hyperon led the authors to construct a small solenoid about 7 cm long and with an inner diameter of about 2 cm, capable of supporting fields in excess of 200 kilogauss. Because of the economics of high-energy accelerator operation, it was decided to make the operation of this coil over extended periods as reliable as possible and with a good probability that it would last for more than 10,000 pulses. In practice the coil is to be replaced with an identical coil after 5,000 operations. Part of the same experiment requires a cloud chamber, and for reasons of convenience the magnet for this - although operated at a 20-kilogauss level or less - was made of a pair of simple rectangular iron-free coils, also pulsed, but with a much longer pulse duration than the solenoid. Both pulsed systems are based on a capacitive discharge, with several ignitrons in a parallel-anode firing configuration used as the switch. The small solenoid (called the P magnet because it is used to precess the magnetic moment) is installed between these coils and, therefore, at the time it is pulsed, it is itself in a rather strong field gradient.

#### EXPERIMENTAL PROOF OF THE SPIN DEPENDENCE OF THE MUON CAPTURE INTERACTION AND EVIDENCE FOR ITS (F-GT) CHARACTER

G. Culligan,\* J. F. Lathrop,\* V. L. Telegdi,\* R. Winston\* and

R. A. Lundy

Phys. Rev. Letters 7 458-464 (December 15, 1961)

The authors have measured the time dependence of the rates at which neutral products (neutrons or/and nuclear gamma rays) are emitted in the capture of muons by  ${}_{9}F^{19}$  in order to determine the spin dependence. The time dependence  $N_n(t)$  and  $N_{\gamma}(t)$  was measured for  ${}_{9}F^{19}$ , using a LiF target (Li has a negligible capture rate). The neutral capture products were detected with a liquid scintillator; a pulse-shape discriminator circuit at this counter's output enabled one to select either  $\gamma$ - or n-induced pulses. From the data collected the authors have concluded that, in general 1)  $\mu^-$  capture is spin dependent (A'  $\neq$  0); and, for  ${}_{9}F^{19}$  in particular 2) this spin dependence is such that  $\Lambda_- > \Lambda_+$  (A' > 0); 3) its magnitude is close to the maximum possible one, i.e., to that predicted for an (F + xGT) interaction with x $\simeq$ -1; 4) both the absolute rates and their spin dependence agree with the prediction of a universal (V - A) interaction, and exclude a (V + A) interaction; 5) there is a fast  $F_+ - F_-$  conversion process, of the predicted rate.

#### A MULTICHANNEL FOCUSSING CERENKOV COUNTER

R. A. Schluter

Proc. Intern. Conf. on Instrumentation for High-Energy Physics, Berkeley, California, September 12-14, 1960. New York: Interscience Publ., 1961. pp. 91-92

Of the information presented at the image surface of a focusing Cerenkov counter, only the signal of a particle of one chosen velocity is usually used. By use of the glass or quartz fiber bundle described, it is proposed to convey the light efficiently from various corresponding photomultipliers. Several modes are therefore made possible, among which are: (a) response to several chosen velocities simultaneously, (b) simultaneous recording of particles of a different mass, as for monitoring purposes, and (c) summing of light at radii off the chosen radius to obtain an anticoincidence signal for delta rays.



#### APPLIED MATHEMATICS DIVISION

THE SOLUTION OF MANY REGION REACTOR KINETICS PROBLEMS ON AN ANALOG COMPUTER

C. N. Kelber,\* L. C. Just and N. F. Morehouse, Jr. Nuclear Sci. and Eng. <u>11</u> 285-289 (November 1961)

Abstract in ANL-6445, p. 23

NaI AND CsI EFFICIENCIES AND PHOTOFRACTIONS FOR GAMMA-RAY DETECTION

W. F. Miller and W. J. Snow

Nucleonics 19 (11) 174-175 (November 1961)

Abstract in ANL-6349, p. 31.

A TECHNIQUE FOR THE NUMERICAL SOLUTION OF CERTAIN INTEGRAL EQUATIONS OF THE FIRST KIND

D. L. Phillips

J. Assoc. Computing Mach. 9 (1) 84-97 (January 1962)

The method described here should work reasonably well on problems where the unknown function f is assumed to be a relatively smooth function. The truncation error should be as small as, or smaller than, the errors in g. The most difficult task is to choose  $\gamma$ . When the errors in g are relatively small,  $\gamma$  should probably be chosen such that e is approximately the same magnitude as these errors. When the errors in g are relatively large,  $\gamma$  should probably be chosen such that e is somewhat smaller than these errors. In any case several values of  $\gamma$  should be tried, and the best value should be the one that appears to take out the oscillation without appreciably smoothing the function f.

#### BASIC LOGIC "NOR" MODIFIED 749 FOR 10-MC, TWO-PHASE CLOCK F. O. Salter

Electronic Design (January 4, 1962)

In our computer work we needed a two-phase, 10-mc clock that would be stable with both time and normal temperature changes; and we wanted to use our standard logic element for as much of the clock as possible. The circuit we designed used a basic NOR circuit combined with two delay lines.

\*Reactor Engineering Division

PARTIAL WAVE THEORY OF POSITRON-HYDROGEN ATOM COLLISIONS Kenneth Smith

Proc. Phys. Soc. 78 (4) 549-553 (October 1, 1961)

Abstract in ANL-6445, p. 23

#### THE EFFECT OF VIRTUAL EXCITATION OF THE 2s STATE ON THE ELASTIC SCATTERING OF ELECTRONS BY ATOMIC HYDROGEN Kenneth Smith, R. P. McEachran\* and P. A. Fraser\* Phys. Rev., in press

The elastic scattering of electrons by hydrogen atoms for electron energies below the first threshold of excitation of the atom (10.2 ev) is investigated numerically, making full allowance for exchange and for the virtual excitation of the 2s state. Singlet and triplet phases for the s-, p-, and d-partial waves have been obtained. While the calculation is essentially preliminary to a more extensive eigenfunction expansion calculation for this problem, which would allow for non-spherical distortion of the atom, the results do show that significant changes from the first exchange approximation may be expected as one includes more states in the expansion. In particular, just below the n=2 excitation threshold the singlet s-phase and the triplet p-phases begin to increase sharply, and what may be a Wigner cusp shows in the total cross section.

Predicted angular distributions are compared with the recent measurements of Gilbody, Stebbings, and Fite. The phase shifts are compared with those of the exchange approximation, and also with those of Geltman, who performed a variational calculation allowing for the virtual excitation of the 2s and 3s states.

### ELEMENTARY DIVISORS AND SOME PROPERTIES OF THE LYAPUNOV MAPPING X—AX + XA\*

Wallace Givens ANL-6456 (November 1961)

In his monograph "The General Problem of Stability of Motion," Lyapunov established a connection between the location of the eigenvalues of a general n by n real matrix and the signature of a quadratic form. There does not appear to be available in the literature a full discussion which relies wholly on algebraic techniques and does not employ the connection with the solution of a system of linear differential equations. The Lyapunov result and some of the recent extensions of it by Taussky are explored here with simple algebraic methods.

The matrix correspondence which is the subject of this paper arises if one differentiates the hermitian (or, in the real case, the quadratic) form uGu\*, where  $G = G^* =$  the conjugate transpose of G, and u is a row vector, and makes use of the differential equation, du/dt = u A, for A, an n by n matrix, to get d(uGu\*)/dt = u(AG + GA\*)u\* = uHu\*. The mapping of the hermitian matrices G-H = AG + GA\* is referred to as the Lyapunov mapping determined by A, and the central result is that if H is negative definite for some positive definite G, then every eigenvalue of A has negative real part (A is stable); and, conversely, if A is stable, the correspondence is one-to-one and for H negative definite G is positive definite.

For the complex field there is little gain in replacing G by a matrix X which is not assumed to be hermitian since this merely extends the real linear mapping of a real  $n^2$  dimensional vector space (of matrices G) to a complex space of the same dimension. This is not true if A is real and G is symmetric, for then a linear of a real vector space of  $\frac{1}{2}$  n(n + 1) dimensions is being extended to one of  $n^2$  dimensions which, however decomposes into the direct sum of mappings of symmetric matrices and of skew symmetric ones. The primary emphasis in this paper is on establishing easy and convenient techniques for a further study of the Lyapunov mapping.

#### COST FUNCTION STUDIES FOR POWER REACTORS

#### J. M. Heestand and L. T. Wos

ANL-6442 (November 1961)

A function to evaluate the cost of electricity produced by a nuclear power reactor is developed. The basic equation, revenue = capital charges + profit + operating expenses, is expanded in terms of various cost parameters to enable analysis of multiregion nuclear reactors with uranium and/or plutonium for fuel. A corresponding IBM 704 computer program, which will compute either the price of electricity or the value of plutonium, is presented in detail in the appendices. TRANSPORT SOLUTIONS TO THE ONE-DIMENSIONAL CRITICAL PROBLEM

G. J. Mitsis ANL-6459 (December 1961)

The new method of Case for treating the one-velocity transport equation is applied to a uniform, one-dimensional multiplying medium. The method leads to exact expressions for the neutron distribution and criticality conditions. These expressions depend on expansion coefficients which are shown to satisfy a Fredholm integral equation. The results of diffusion theory with the exact Milne problem extrapolation distance are shown to correspond to the zeroth-order approximation of the Neumann series solution to the Fredholm equation.

### GAMMA I. A GENERAL THEOREM-PROVING PROGRAM FOR THE IBM 704

J. A. Robinson

ANL-6447 (November 1961)

GAMMA I is a FORTRAN-compiled program for the IBM 704 Electronic Data-Processing Machine. It embodies a certain general, uniform procedure H of mathematical logic for seeking out a proof of any theorem within any mathematical theory which is given in formal axiomatic form.

The procedure H is theoretically complete. Using it, one will always discover a proof for a theorem if there is one to be discovered. However, as a practical instrument, the procedure H has severe limitations; in most cases of strong mathematical interest it calls for the execution of more steps than can be carried out in any reasonable time by the fastest machines ever likely to be available. The actual capability of GAMMA I is therefore no greater than these practical limitations inherent in the procedure H will allow. Nevertheless, GAMMA I is remarkably effective in a wide class of cases, including, for example, the modern algebraic theory of lattice structures. Both a detailed description of GAMMA I itself and an extended discussion of the underlying method, and of the necessary background of mathematical logic are provided.

#### CHEMISTRY DIVISION

#### Nuclear Chemistry

### A NEW APPROXIMATION FOR PAIRING FORCES IN NUCLEI

#### R. R. Chasman

Phys. Rev. Letters 7 418-419 (December 1, 1961)

A pairing force interaction accounts for several features of nuclear structure. Numerical calculations have been made for this type of interaction on nuclei having a closed neutron or proton shell, using the quasiparticle approximation. Recently an exact calculation done on an electronic computer showed that the quasi-particle approximation was not very accurate but that one could obtain accurate solutions by projecting out that part of the quasi-particle solution corresponding to the correct number of particles. This note develops a simple method for solving the pairing force problem, which is somewhat better than the quasi-particle approach in its first approximation and can be improved by an iteration technique to any desired accuracy.

### THEORETICAL REACTION CROSS SECTIONS FOR ALPHA PARTICLES WITH AN OPTICAL MODEL

J. R. Huizenga and G. Igo Nuclear Phys., in press

The transmission coefficients  $\underline{T}_{\underline{\ell}}$  and total reaction cross sections  $\underline{\sigma}_{\underline{R}}$  for alpha particles in the energy range 0-46 Mev interacting with twenty target nuclei with atomic numbers ranging from 10 to 92 are calculated with a previously-determined complex nuclear potential. The dependence of the  $\underline{T}_{\underline{\ell}}$  values and hence  $\underline{\sigma}_{\underline{R}}$  on the Woods-Saxon parameters is investigated as a function of projectile energy. The optical model reaction cross sections are compared to those derived from (1) a square well potential and (2) a model which approximates the real optical model potential barrier by a parabola and makes use of the Hill-Wheeler penetration formula for a parabolic potential.

### CORRELATION OF FISSION-FRAGMENT KINETIC-ENERGY FINE STRUCTURE WITH SEMI-EMPIRICAL MASS SURFACE

Robert Vandenbosch and T. D. Thomas\*

Bull. Am. Phys. Soc. 7 37 (January 1962)

Abstract

Recently, fine structure has been observed in the kinetic energy spectra of fission fragments from the thermal-neutron-induced fission of U<sup>235</sup>. This structure is most pronounced for high total kinetic energies, corresponding to final fragments at low excitation energies. Thus, the structure may reflect an inhibition due to limitations on the available energy, as has also been noted by Milton and Fraser. Using tables of empirical masses we have calculated the available excitation energy for various mass divisions in the fission of U<sup>235</sup> with thermal neutrons. There is a striking correlation between the calculated excitation energies (for even mass products) and the structure reported by Gibson et al. A simple model illustrates the effect that the mass surface has on the yield of fission fragments. We assume that the yield,  $Y = \sigma_{12}(E_k) \rho_1(E_1) \rho_2(E_2)$ , where  $\sigma_{12}$  is the inverse cross section for fission fragments of energy E<sub>L</sub> to coalesce and  $\rho_1$  and  $\rho_2$  are the state densities of the two fission fragments. The results of this simple calculation are in remarkable agreement with the experimental data.

\*Princeton University

ANGULAR DISTRIBUTION OF FISSION FRAGMENTS FROM HELIUM-ION-INDUCED FISSION OF Bi, Pb, Tl AND Au

Ramesh Chaudhry, Robert Vandenbosch and J. R. Huizenga Bull. Am. Phys. Soc. <u>6</u> 419 (November 1961) Abstract

The  $W(174.5^{\circ})/W(90^{\circ})$  ratios for 42.8-Mev helium-ion-induced fission of bismuth, lead,  $Pb^{206}$ , thallium and gold are 2.26  $\pm$  0.07.  $2.47 \pm 0.08$ ,  $2.46 \pm 0.08$ ,  $2.53 \pm 0.08$ , and  $2.62 \pm 0.08$ , respectively. The energy dependence of K<sub>0</sub> deduced from the experimental anisotropy measurements is similar to the predicted energy dependence from statistical theory if the nuclear temperature at the saddle point is proportional to the square root of the excitation energy. These results indicate that the effective moment of inertia at the saddle point is independent of excitation energy in contrast with the heavy element (uranium region) results. With the assumption that the effective moment of inertia at the saddle point which is deduced for each target at the highest energy is the rigid-body value, the stretching at the saddle point is calculated for each compound nucleus for various simple geometric configurations. For example, if the saddle point is represented by two tangent prolate spheroids, the ratios of the major to minor axes (C/A) for the fissioning nuclei At<sup>213</sup>, Po<sup>210</sup>, Bi<sup>209</sup> and Tl<sup>201</sup> are 1.30, 1.52, 1.67 and 1.82, respectively. Furthermore, if the symmetric scission point is assumed to have the same configuration, the value of (C/A) at the time of scission which is derived from kinetic energy measurements is 2.24 for all nuclei, consistent with the empirical relation,  $E_{\rm K} = 0.121 \ Z^2/A^{1/3}$ .

#### HELIUM-ION-INDUCED FISSION OF Bi, Pb, T1 AND Au

J. R. Huizenga, Ramesh Chaudhry and Robert Vandenbosch Bull. Am. Phys. Soc. 6 418 (November 1961) Abstract

The fission cross sections for helium-ion-induced fission of bismuth, Pb<sup>206</sup>, thallium and gold have been measured with solid-state detectors as a function of bombarding energy. The fission cross sections of the above targets with 42.8-Mev helium ions are 7.3, 1.8, 0.65, and 0.28 mb, respectively, and the cross sections decrease rapidly with reduced energy projectiles. The competition between fission and neutron emission as a function of excitation energy is compared with theoretical predictions of  $\Gamma_f/\Gamma_n$ . From such comparisons fission thresholds for At<sup>213</sup>, Po<sup>210</sup>, Bi<sup>209</sup> and Tl<sup>201</sup> are derived as  $15.8 \pm 2.0$ ,  $18.6 \pm 2.0$ ,  $20.6 \pm 2.0$  and  $19.9 \pm 2.0$  Mev, respectively. The saddle point mass surface of these nuclei relative to a reference mass surface lies on a smooth curve with the heavy-element data indicating that the shell structure is completely destroyed during the distortion from the equilibrium to the saddle deformation. An empirical equation for fission thresholds is deduced which is thought to be valid for nuclei with  $Z^2/A \geq 32.5$ .

HALF-LIFE OF NICKEL-63

D. L. Horrocks and A. L. Harkness\* Phys. Rev., in press

The half-life of  $Ni^{63}$  was calculated to be 91.6  $\pm$  2.9 years from specific activity measurements. Liquid scintillation counting techniques were used to measure disintegration rate.

NEUTRON DIFFRACTION STUDIES OF  $CaC_2$ ,  $YC_2$ ,  $LaC_2$ ,  $CeC_2$ ,  $TbC_2$ ,  $YbC_2$ ,  $LuC_2$ , AND  $UC_2$ 

Masao Atoji

J. Chem. Phys. 35 1950-1960 (December 1961)

The complete-matrix least-squares analysis of the neutron diffraction intensities of CaC<sub>2</sub>, YC<sub>2</sub>, LaC<sub>2</sub>, CeC<sub>2</sub>, TbC<sub>2</sub>, YbC<sub>2</sub>, LuC<sub>2</sub> and UC<sub>2</sub> yielded the C--C distances in the C<sub>2</sub> groups, 1.191  $\pm$  0.009, 1.275  $\pm$  0.002, 1.303  $\pm$  0.012, 1.283  $\pm$  0.004, 1.293  $\pm$  0.009, 1.287  $\pm$  0.010, 1.276  $\pm$  0.012, and 1.340  $\pm$  0.007 A, respectively. The statistical averages of the neutron scattering amplitudes obtained from the dicarbide data and those reported previously are 0.488  $\pm$  0.007, 0.796  $\pm$  0.009, 0.832  $\pm$  0.014, 0.482  $\pm$  0.006, 0.756  $\pm$  0.020, 1.262  $\pm$  0.012, 0.73  $\pm$  0.02, and 0.851  $\pm$  0.022, all in 10<sup>-12</sup> cm with positive sign, for Ca, Y, La, Ce, Tb, Yb, Lu, and U, respectively.

The paramagnetic scattering analyses revealed that all metal atoms in these dicarbides are in their trivalent Hund ground state, except Ca (divalent), Yb (possible valency of 2.8), and U (possibly tetravalent). The scattering data also deduced the screening constants for the 4f electrons in Ce, Tb, and Yb as 39, 43, and 43, respectively, which are compared with those obtained by other methods. The bond numbers for the rare-earth dicarbides are briefly discussed.

NEUTRON DIFFRACTION STUDIES OF La<sub>2</sub>C<sub>3</sub>, Ce<sub>2</sub>C<sub>3</sub>, Pr<sub>2</sub>C<sub>3</sub> AND Tb<sub>2</sub>C<sub>3</sub> Masao Atoji and D. E. Williams J. Chem. Phys. <u>35</u> 1960-1966 (December 1961)

Abstract in ANL-6445, p. 26

\*Special Materials Division

# ISOMERIC CROSS-SECTION RATIOS FOR SOME $(n, \gamma)$ AND $(\alpha, \kappa n)$ REACTIONS

C. T. Bishop ANL-6405 (August 1961)

Isomeric cross-section ratios for several nuclear reactions in the medium mass region were measured. The cross-section ratios of isomers produced by the thermal neutron irradiation of Se<sup>80</sup>, Rh<sup>103</sup>, Pd<sup>108</sup>, Te<sup>128</sup> and Cs<sup>133</sup> were measured. Isomeric cross-section ratios for the formation of the isomeric pair In<sup>110</sup> and In<sup>110m</sup>, produced in the Ag<sup>107</sup>( $\alpha$ ,n) and the Ag<sup>109</sup>( $\alpha$ ,3n) reactions were also measured at several energies of the incoming projectile. The neutron irradiations were carried out in the Argonne Research Reactor CP-5. Helium ions were accelerated with the Argonne constant frequency 60" Cyclotron to a maximum energy of 43 Mev. The relative amounts of the isomers produced in the reactions were determined by scintillation counting. In the case of the In<sup>110</sup> isomers the efficiencies of the scintillation counter for detecting each isomer were measured, so that absolute cross sections as well as cross-section ratios could be determined for these isomers.

The isomeric cross-section ratios were also calculated theoretically with a statistical model in which angular momentum effects were included. By comparing experimentally-measured cross-section ratios for the formation of isomeric pairs to the calculated ratios, information about the dependence of the nuclear level density on angular momentum was obtained. The results for both the  $(n,\gamma)$  and the  $(\alpha,xn)$  reactions gave an average nuclear spin density parameter  $\sigma$ , of 3 to 5. This parameter is defined in the equation,  $\rho(J) = \rho(0) (2J+1) \exp[-(J+1/2)^2/2\sigma^2]$ , in which  $\rho(J)$  is the density of levels with spin J,  $\rho(0)$  is the density of levels with spin zero, and  $\sigma$  is the nuclear spin density parameter which characterizes the distribution in spin. A more detailed analysis of the isomeric cross-section ratios obtained by the Ag<sup>107</sup>( $\alpha$ ,n) and the Ag<sup>109</sup>( $\alpha$ ,3n) reactions showed that a theoretically-calculated energy dependent value of  $\sigma$ , using a moment of inertia less than the rigid value at low excitation energies, was in agreement with the experimental results.

### FISSION FRAGMENT ANISOTROPY AND PAIRING EFFECTS ON NUCLEAR STRUCTURE

Robert Vandenbosch, H. Warhanek and J. R. Huizenga Phys. Rev. 124 846-853 (November 1, 1961)

Abstract in ANL-6445, p. 28

REACTION CROSS SECTIONS OF  $U^{233}$  AND  $U^{238}$  WITH 18-43 MEV HELIUM IONS

J. R. Huizenga, Robert Vandenbosch and H. Warhanek Phys. Rev. <u>124</u> 1964 (December 15, 1961)

The fission cross sections have been measured for  $U^{233}$  and  $U^{238}$  targets bombarded with 18- to 43-Mev helium ions. These targets were chosen because of their large fission cross sections. In addition, the spallation cross sections are known and represent with 43-Mev helium ions only about 4 and 9% of the reaction cross sections of  $U^{233}$  and  $U^{238}$ , respectively. The fission fragments were detected with solid-state counters in a small evacuated scattering chamber. The fission-fragment counting rates were converted to disintegration rates with previous measurements of the fission-fragment angular distributions. The experimental reaction cross sections are in good agreement with reaction cross sections calculated with an optical model in which the complex nuclear potential derived by Igo for alpha-particle elastic scattering is employed. The dependence of the optical-model cross sections on the various Woods-Saxon parameters is discussed.

FAST-NEUTRON-INDUCED FISSION CROSS SECTIONS OF Pu<sup>241</sup> AND Am<sup>243</sup> D. K. Butler\* and R. K. Sjoblom

Phys. Rev. 124 1129-1131 (November 15, 1961)

Abstract in ANL-6445, p. 28

### THE THERMAL-NEUTRON-FISSION CROSS SECTION OF 10.1-HR Am<sup>244</sup>

S. E. Vandenbosch and James Gray, Jr.

J. Inorg. and Nuclear Chem., in press

The thermal-neutron-fission cross section of the 10.1-hr isomer of  $Am^{244}$  has been determined by counting fissions induced by neutrons in the thermal column of the Argonne reactor, CP-5. A decrease in fissionability with the characteristic 10.1-hr half-life was observed. The fission cross section of 2300  $\pm$  300 barns was obtained by comparing the fission counting rate of  $Am^{244}$  with that of a U<sup>233</sup> standard.

### SPONTANEOUS TERNARY FISSION OF Cf<sup>252</sup>, Cm<sup>244</sup> AND Cm<sup>242</sup>

D. J. Henderson, Herbert Diamond and T. H. Braid\*

Bull. Am. Phys. Soc. <u>6</u> 418 (November 1961)

#### Abstract

The frequency and energy of long-range alpha particles in coincidence with spontaneous fission were measured with surface barrier silicon detectors and CsI crystal detectors. The spectrum of long-range alphas from Cf<sup>252</sup> has a peak at 15.5 Mev. Its full width at half-maximum is 13 Mev. Cf<sup>252</sup> emitted one long-range alpha above 9.8 Mev per 312  $\pm$  17 fissions. Cm<sup>244</sup> emitted one long-range alpha above 11.6 Mev per 273  $\pm$  57 fissions. Cm<sup>242</sup> emitted one long-range alpha above 10.6 Mev per 978  $\pm$  210 fissions.

#### BETA-DECAY OF Es<sup>254</sup>

#### P. P. Day, S. E. Vandenbosch and J. P. Unik Bull. Am. Phys. Soc. <u>6</u> 451 (November 1961) Abstract

The beta-decay of  $Es^{254}$  has been studied using gamma-gamma and beta-gamma scintillation coincidence techniques and a double-lens beta-ray spectrometer. E2 transitions of 103.5 ± 1, 544 ± 5, 583 ± 3, 648 ± 2, and 692 ± 2 kev have been placed in a level scheme of  $Fm^{254}$  with levels at 44 ± 3 (0,2+), 148 ± 3 (0,4+), 692 ± 2 (2,2+), and 734 ± 4 (2,3+) kev. Two beta-spectra of 477 ± 4 (72%) and 1127 ± 2 (28%) kev were observed. The observation of the (2,2+) gamma-vibrational state at 692 kev in  $Fm^{254}$  indicates that there is a sharp decrease in the gamma-vibrational energy for 154 neutrons. Gamma-vibrational bands have previously been observed at 1030 kev in  $Pu^{238}$  (144 neutrons) and  $Cf^{250}$  (152 neutrons). By following the decay of two points on the beta spectrum and the decay of the high-energy gamma rays, a half-life of 39.3 ± 0.2 hr was obtained. During the course of this work transitions of 93 ± 2, 377 ± 3, 386 ± 1, and 427 ± 3 kev were observed from the decay of 20-day  $Es^{253}$ .

#### A NON-INTERCEPTING ACCELERATOR BEAM POSITION SENSOR

K. W. Johnson, T. E. Klippert and W. J. Ramler Nuclear Instr. and Methods, in press

nation intervention, in prose

A non-intercepting beam position sensor consisting of two sets of pick-up coils, resonant tuned, are used with a differential amplifier and an oscilloscope to determine the spatial position of a pulsed beam from an electron linear accelerator. A pulsed beam of 100-ma peak can be positioned to about 0.5 mm. Recent work indicates the feasibility of using this position sensor technique with an external cyclotron beam. The design, method of construction, and performance of the linac sensor is discussed. A brief summary of the cyclotron sensor is given.

\*Physics Division

#### AN ELECTROSTATIC PARALLEL-PLATE ELECTRON ENERGY SELECTOR FOR DETERMINATION OF CRITICAL IONIZATION POTENTIALS

D. A. Hutchison

Proc. Conf. on Mass Spectrometry, September 12, 1961, Oxford, England. London: Pergamon Press, in press

An ion source employing a monoenergetic electron beam is described. The energy selection is provided by a set of plane-parallel plates across which an electric potential, V, is placed. The electron beam, which impinges on a slit in one of the plates, experiences a uniform electrostatic field opposed to the direction of beam motion. When the beam of energy, E, enters at an angle,  $\theta$ , to the slit plane, it returns to the slit plane with a range  $x = (2d E/V) \sin 2\theta$ , where d is the distance between the plane-parallel plates. The ribbon-shaped beam emerges through a second slit at x and is focussed into an ionization chamber by means of a line-focus lens system. The beam is then passed through an analyzer set of plane-parallel plates, where the energy distribution of the beam is determined. The resolving power of the energy selector is found to be near that of the predicted resolving power R =  $E/\Delta E = x/S$ , where S is the slit width. With x = 1.75 inches, S = 0.010 inches, and a beam energy of 10 volts, an energy distribution curve of electron current from the analyzer plates versus energy is found to have a  $0.06_3$  volt width at half-peak value. Employing this beam the  ${}^{2}P_{3/2}$  and  ${}^{2}P_{1/2}$  ground states of Ar<sup>+</sup> are resolved in the appearance potential curve with a separation of 0.18 ev in agreement with the optical value.

#### Effects of Radiation

RADICAL SPECIES DETECTED IN  $\gamma\text{-}IRRADIATED\ \text{K}^{14}\text{NO}_3$  CRYSTALS BY E.P.R.

Joseph Cunningham, J. A. McMillan,\* Bernard Smaller,\* and E. L. Yasaitis\*

Preprints of Papers Read at the 5th Intern. Symp. on Free Radicals, July 6-7, 1961, University Uppsala, Sweden. Stockholm: Almqvist & Wicksell, 1961. Paper No. 13

J. Phys. Chem. Solids, in press

Crystals grown from aqueous solutions of K<sup>14</sup>NO<sub>3</sub> and K<sup>15</sup>NO<sub>3</sub> were irradiated with gamma rays and observed at 77 or 4°K. Spectra were recorded with the crystal c-axis perpendicular or parallel to the axis of rotation, R. R was maintained perpendicular to the magnetic field H. Those triplets here tentatively identified with radicals containing bound nitrogen appeared as doublets in K<sup>15</sup>NO<sub>3</sub> with total hyperfine splitting reduced in the ratio of the nuclear magnetic moments of N<sup>14</sup> and N<sup>15</sup>. Triplet I was observed after irradiation at 4 or 77°K to ca  $10^{19}$  ev g<sup>-1</sup>. It was tentatively identified with  $(NO_2^-)^-$  radicals. Triplet II was observed only after irradiation exceeding  $3 \times 10^{20}$  ev g<sup>-1</sup>. It was identified with NO<sub>2</sub> radicals. Triplet III was observed with high intensity at 4°K in crystals irradiated at 4°K. Both the instability and small A (hyperfine splitting) of triplet III suggest its identification with NO32 radicals. Triplet IV is attributed to NO radicals because its parameters are very similar to those reported for NO in KCl/NO3 crystals. Singlet I was observed only at 4°K. It appeared in crystals irradiated at 77° and was not observed in crystals irradiated at 4°K until these crystals were annealed at 77°K. The resemblance of the g (spectroscopic splitting factor) values of singlet I to those reported for O7 indicates that O7 radicals were formed in irradiated KNO3.

RADIATION CHEMISTRY OF WATER WITH PULSED HIGH INTENSITY ELECTRON BEAMS

A. R. Anderson and E. J. Hart

J. Phys. Chem. <u>66</u> 70-75 (January 1962)

Abstract in ANL-6445, p. 31

\*Solid State Science Division

# ABSOLUTE RATE CONSTANT FOR THE REACTION OF HYDROXYL RADICALS WITH BENZENE IN WATER

L. M. Dorfman, R. E. Bühler and I. A. Taub

J. Chem. Phys., in press Letter

The absolute rate constant for the reaction of hydroxyl radicals with benzene has been determined in the benzene-water system. By synchronized flash absorption spectroscopy of pulsed-irradiated aqueous benzene solutions, a transient spectrum having a broad uv absorption with a strong maximum at 313 m $\mu$  has been observed. Observations indicate that the hydroxyl radical is the precursor of this transient radical. By fast photoelectric recording of the transient absorption at 313 m $\mu$ , after a 0.4  $\mu$ sec pulse of 15-Mev electrons at an average current of 60 ma, the rate of formation of the radical has been directly observed in the fast reaction

 $OH + C_6H_6 = Radical$  .

Data were obtained at benzene concentrations of  $1 \times 10^{-4}$  and  $2 \times 10^{-4}$  M, and at an initial  $(OH)_0 < 5 \times 10^{-6}$  M. Under these conditions the reaction is pseudo first order, and the rate curve fits a first-order rate law. The rate constant obtained for  $OH + C_6H_6$  is  $k_1 = 4.3 \pm 0.9 \times 10^9$  M<sup>-1</sup> sec<sup>-1</sup> at 23°C. The magnitude of the observed rate constant raises a question about whether Reaction 1 is a hydrogen abstraction involving rupture of a C-H bond with a bond energy of 102 kcal/mole. The high value of  $k_1$  indicates addition to the ring forming the hydroxycyclohexadienyl radical is more likely:

 $OH + C_6H_6 = HOC_6H_6$ 

Further evidence for ring addition has been obtained by measuring the rate constant for the reaction of OH with  $C_6D_6$ . If hydrogen abstraction is involved, a substantial deuterium isotope effect in rupture of the C-D bond may be expected. However, no isotope effect was found, and it can be concluded that Reaction 1 consists of OH-addition to form the hydroxycyclohexadienyl radical, to which the transient spectrum is to be assigned. This conclusion is also supported by spectrographic evidence soon to be published.

(1)

PULSE RADIOLYSIS STUDIES: TRANSIENT ULTRAVIOLET ABSORPTION SPECTRA IN AQUEOUS SOLUTIONS OF BENZENE

L. M. Dorfman and R. E. Bühler

Abstracts of Scientific Papers Presented at the 18th Intern. Congr. of Pure and Applied Chemistry, Montreal, August 1961. Toronto: Univ. Toronto Press, 1961. pp. 49-50

Pulse radiolysis studies of solutions of a number of aromatic compounds have been carried out with a 6-joule, 5-microsecond pulse of 15-Mev electrons from a linear accelerator. The absorption spectra of transients have been observed by synchronized flash absorption spectroscopy. Rate curves have been obtained by measurement of the decay of the absorption using photomultiplier techniques.

With solutions of benzene in water the major transient absorption is a band with a strong maximum at 3120 A. Experiments indicate that this transient is formed by interaction of hydroxyl radicals with benzene. The transient disappears in a second-order process with an apparent rate constant of  $1.5 \times 10^5 \epsilon$  liter mole<sup>-1</sup> sec<sup>-1</sup>, where  $\epsilon$  is the molar extinction coefficient of the transient. It is consistent with our observations, along with prior radiation chemical studies, to assign this absorption spectrum to the phenyl radical.

When chlorobenzene, bromobenzene, or iodobenzene is the solute in water, a similar spectrum is obtained, shifted in each case to slightly longer wavelengths. These spectra are tentatively assigned to the halogenated phenyl radicals.

At the time of writing of this abstract, detailed studies of the products are in progress in an attempt to determine  $\in$  from material balance and optical absorption determinations.

PHOTOCHEMICAL PRIMARY PROCESS IN BIACETYL VAPOR AT 4358 A

W. A. Noyes, Jr., W. A. Mulac and M. S. Matheson

J. Chem. Phys., in press

At 4358 A at room temperature the quantum yield for the primary dissociation of biacetyl increases with intensity. It is thus implied that the primary process is second order in some active species. By use of the rotating sector it is shown that the species responsible for this effect has a mean life close to that ascribed to an excited triplet state for biacetyl. At higher temperatures this intensity effect disappears and one of the products strongly inhibits both the phosphorescence and the primary dissociation. At these temperatures the data may best be treated by assuming that the triplet state of biacetyl undergoes a unimolecular dissociation with an activation energy of about 15 kcal.

### LA PHOTOLYSE PAR ECLAIR DE QUELQUES SOLUTIONS AQUEUSES

Abstract

M. S. Matheson

J. Chim. Phys. <u>58</u> 381-382 (1961)

The principle of flash photolysis is very simple. A sample of gas or liquid in a cell is illuminated with a short flash of great intensity. This flash produces unstable species in sufficient concentration that their absorption spectra can be observed. The whole spectrum is either recorded at a given time with another weaker flash, or the absorption for a single wavelength is traced as a function of time by means of a lamp of constant intensity. For spectroscopy one tries to obtain the shortest flash possible in order to study the fastest reaction. The spectroscopic lamp used as a source of illumination to register absorption spectra must emit a continuous spectrum. Further, it is necessary to know with precision the period of time that passes between the flash of the photolysis lamp and that of the spectroscopic lamp.

For kinetic studies one replaces the spectrograph with a monochromator, the spectrographic plate by a photomultiplier cell and the flash of the spectroscopic light by a light of constant intensity. The photolysis lamp produces a disturbance in the circuits for the kinetic measurements due on the one hand to the scattered light arising from the photolysis lamp and on the other hand to diverse electric effects. It is necessary to be sure that the response of the system is proportional to the intensity of the light that traverses the reaction cell. It is also necessary to be sure that the concentration of the unstable species is uniform in the part of the cell traversed by the analysing light. The application of flash photolysis to the study of potassium iodide and potassium bromate in aqueous solution is described.

# A CALORIMETRIC DETERMINATION OF THE OXIDATION YIELD OF THE FRICKE DOSIMETER AT HIGH DOSE RATES OF ELECTRONS

A. R. Anderson

J. Phys. Chem. <u>66</u> 180-182 (January 1962) Note

A calorimetric method has been used to measure the oxidation yield of aqueous ferrous sulfate (0.001 <u>M</u> FeSO<sub>4</sub>, 0.001 <u>M</u> NaCl, 0.8 <u>N</u> H<sub>2</sub>SO<sub>4</sub>, aerated) at high dose rates of ~15 Mev electrons from the Argonne electron linear accelerator. The calorimeter was used adiabatically and was designed so that calorimetric and chemical measurements could be made successively and repeatedly without disturbing the geometry of the system. At dose rates  $> 10^{22}$  ev ml<sup>-1</sup> sec<sup>-1</sup> the yield of ferric ions decreases rapidly to a value of ~11.5 ions per 100 ev at a dose rate of ~10<sup>23</sup> ev ml<sup>-1</sup> sec<sup>-1</sup>. At the lowest dose rate employed, 6 x 10<sup>21</sup> ev ml<sup>-1</sup> sec<sup>-1</sup>, the determined G(Fe<sup>3+</sup>) equals 15.2, which approaches the value for  $\gamma$  radiation at much lower dose rates and adds confidence to the calorimetric techniques used in the present work.

# CHEMICAL EFFECTS PRODUCED BY THE NEUTRON IRRADIATION OF PHOSPHORUS COMPOUNDS

T. R. Sato and H. H. Strain

Proc. IAEA Symp. on Chemical Effects of Nuclear Transformations, Prague, October 23-28, 1960. Vienna: Intern. Atomic Energy Agency, 1961. pp. 503-519

Abstract in ANL-6349, p. 40

ZINC BROMIDE WINDOWS FOR NEUTRON AND GAMMA RAY SHIELDING C. H. Youngquist and L. M. Rentschler\*

Trans. Am. Nuclear Soc. <u>4</u> (2) 242-243 (November 1961) Proc. 9th Conf. on Hot Laboratories and Equipment, November 7-9, 1961. Chicago: Am. Nuclear Soc., 1961. pp. 363-375

A new hot laboratory will have a cave with twelve separate working cells, and shielding for three levels of activity. This cave complex will have a total of 40 zinc bromide viewing windows of three different types. The first is a 48-in. thick window composed entirely of zinc bromide solution between glass tank covers. The second, also a 48-in. thick window, has a portion of the zinc bromide replaced by a 6-in. slab of 3.3 density non-browning glass, which acts as a shield to minimize radiation decomposition of the zinc bromide solution. The third window is 28-in. thick and is entirely zinc bromide solution between glass tank covers.

Inorganic and Physical Chemistry

DIRECT FIELD EFFECTS IN ELECTRON PARAMAGNETIC RESONANCE HYPERFINE SPECTRA

J. A. Weil and J. H. Anderson\*\*

J. Chem. Phys. 35 1410-1417 (October 1961)

Abstract in ANL-6349, p. 41

\*Polymer Corp., Reading, Pennsylvania

**\*\*University of Pittsburgh** 

### NUCLEAR MAGNETIC RESONANCE EFFECTS IN AQUEOUS SOLUTIONS OF 1-1 ELECTROLYTES

#### J. C. Hindman

J. Chem. Phys., in press

Experimental data on the effect of varying concentrations of salts of univalent diamagnetic ions on the proton resonance of water are given. A reference scale for the division of the infinite dilution shifts for the salts into contributions for the separate ions is discussed. Factors entering into the separate ion contributions are considered, and a model is developed from which an attempt has been made to evaluate in a quantitative manner the magnitude of these factors. "Effective" hydration numbers are calculated from this model, which treats an ion-water complex as a molecular species. These hydration numbers for cations are very similar to estimates of "primary" hydration obtained from other sources. A decrease in effective hydration number with increasing cation radius is found. It is suggested from the data that of the halide ions, only the fluoride ion forms a hydrate in the chemical sense, the larger halide ions acting primarily to break down the water structure, the effect increasing with increasing anionic radius. These structural effects are expressed in terms of equivalent numbers of hydrogen-bonds made or broken. A structuremaking effect is suggested for the lithium ion. Factors to be considered in the extension of the equations to the interpretation of concentration effects are discussed and evidence presented for different kinds of environmental changes occurring in solutions of different salts.

#### VAPORIZATION OF OXIDES

R. J. Ackermann and R. J. Thorn <u>Progress in Ceramic Science</u>, ed. J. E. Burke. New York: <u>Pergamon Press</u>, 1961. pp. 39-88

Abstract in ANL-6245, p. 30

#### NONAQUEOUS CHEMISTRY

J. J. Katz and Irving Sheft

Chem. Eng. <u>68</u> 223-231 (November 13, 1961)

The following important nonaqueous systems are discussed: 1) liquid anhydrous hydrogen fluoride, 2) liquid sulfur dioxide, 3) liquid ammonia and 4) fused salts.

## ROLE OF GASEOUS SPECIES AND DEFECT STRUCTURES IN DETERMINING PHASE EQUILIBRIA

R. J. Ackermann, R. J. Thorn and G. H. Winslow Abstracts of Scientific Papers Presented at the 18th Intern. Congr. of Pure and Applied Chemistry, Montreal, August 1961. Toronto: Univ. Toronto Press, 1961. p. 125

The role of gaseous species and of defect structures in determining pressure-composition equilibria in three representative systems is discussed. In the case of the aluminum-oxygen system, there are no significant mutual solubilities, so that the phase behavior is determined by the stabilities of the gaseous aluminum, oxygen, Al<sub>2</sub>O, and AlO, the free energies of which have been determined. In the case of the iron-oxygen system, there are principally only gaseous elements but several defect structures. An attempt to analyze the properties of the wüstite phase by the statisticalthermodynamic theory of non-stoichiometric compounds yields an interaction energy between cation vacancies of 6.2 kcal/mole, but shows the phase to be either "non-ideal" or composed of at least two kinds of imperfections. In the case of the zirconium-oxygen system, the decrease in volatility between an oxygen-zirconium ratio of 2.00 and 1.96 can be explained by assuming that oxygen-ion vacancies are created in the dioxide lattice. Employing the measured thermodynamic properties of gaseous monoxide and dioxide and the measured total volatility at a composition of 1.96, one finds that the intrinsic disorder in the stoichiometric dioxide at 2470°C is  $2 \times 10^{-3}$ . These data permit the calculation of the theoretically-expected partial pressures of the various gases and of the free energy of formation of solid ZrO

#### ABSORPTION SPECTRA OF THE II; III, IV, AND V OXIDATION STATES OF VANADIUM IN LiCI-KCI EUTECTIC. OCTAHEDRAL-TETRAHEDRAL TRANSFORMATIONS OF V(II) AND V(III)

D. M. Gruen and R. L. McBeth

J. Phys. Chem. 66 57-65 (January 1962)

The II, III, IV, and V oxidation states of vanadium have been characterized spectrophotometrically in LiCl-KCl eutectic in the range 300-2500 m $\mu$  and as a function of temperature from 400-1000°C. The spectra can be interpreted as arising from electronic transitions within the unfilled 3d shells of the ions. Ligand field considerations show that the low temperature (~400°C) spectra of V(II) and V(III) can be understood in terms of octahedral VCl<sub>6</sub><sup>-4</sup> and VCl<sub>6</sub><sup>-3</sup> complexes. At temperatures higher than 400°C, the spectra of V(II) and V(III) undergo changes which can be interpreted in terms of octahedral-tetrahedral transformations involving the equilibria VCl<sub>6</sub><sup>-4</sup> = VCl<sub>4</sub><sup>-2</sup> + 2Cl<sup>-</sup> and VCl<sub>6</sub><sup>-3</sup> = VCl<sub>4</sub><sup>-4</sup> + 2Cl<sup>-</sup>. The V(IV) spectrum is not strongly affected by temperature. The V(V) spectrum is characterized by a single charge transfer band.

OCTAHEDRAL-TETRAHEDRAL TRANSITION IN SOLUTION FOR  $M_n(II)$ , Fe(II), Fe(III), Co(II), Ni(II) AND Cu(II) CHLORIDES AND DIFFERENCE IN DISSOCIATION OF THE TWO CONFIGURATIONS

L. I. Katzin

Abstracts of Scientific Papers Presented at the 18th Intern. Congr. of Pure and Applied Chemistry, Montreal, August 1961. Toronto: Univ. Toronto Press, 1961. p. 60

In a high-dielectric-constant, low-base-strength medium, such as dimethylformamide, production of the tetrahedral-configuration chloride complexes of first transition elements is promoted. The effect is due to an apparently greater dissociation (weaker complexing) of the octahedral complex configuration, as indicated by the over-all equilibrium expression

 $2^{\text{oct}}(\text{MCl}_2\text{X}_4) = \frac{\text{oct}}{(\text{MCl}_3\text{X}_5)^+} + \frac{\text{tet}}{(\text{MCl}_3\text{X}_5)^-} + 2\text{X}$ 

with X in our experiments being water. The change has been followed by the absorption spectra, for the chlorides of Mn(II), Fe(II), Fe(III), Co(II), Ni(II), and Cu(II). Some relations to current ligand field theories will be discussed.

# THE NICKEL CHLORIDE-CESIUM CHLORIDE PHASE DIAGRAM. TETRAHEDRAL NiCl\_4 = ION IN THE NEW COMPOUND $Cs_3NiCl_5$

Eric Iberson, Rudolf Gut and D. M. Gruen

J. Phys. Chem. 66 65-69 (January 1962)

The phase diagram of the nickel chloride-cesium chloride binary system has been investigated by differential thermal analysis. The system exhibits two congruently melting compounds,  $CsNiCl_3$  (mp 758°) and  $Cs_3NiCl_5$  (mp 547°), as well as three eutectic points at 522, 541 and 747°. These correspond to the compositions 19, 27 and 55 mole % NiCl<sub>2</sub>. The blue compound  $Cs_3NiCl_5$  is isomorphous with  $Cs_3CoCl_5$ . In these 3:1 compounds the transition metal ion is surrounded by four chloride ions in a tetrahedral arrangement. At 417°,  $CsNiCl_5$  decomposes in the solid state to CsCl and yellow  $CsNiCl_3$  in which nickel is octahedrally coordinated. Qualitative considerations show that octahedral crystal field stabilization energies play an important role in determining phase stability in the  $CsCl-NiCl_2$  system as well as in the other known  $CsCl-MCl_2$  systems. The stereochemistry of the chlorine coordination polyhedra in complex chlorides of the transition elements is discussed in the light of crystal field theory and Jahn-Teller distortions.

### ROTATIONAL ANALYSIS OF Cu<sup>65</sup>Cl<sup>35</sup> BANDS

R. K. Asundi, \* P. R. Rao\* and J. K. Brody Nature 192 444-445 (November 4, 1961)

Letter

Very high dispersion and resolution are needed to resolve the rotational structure of the bands of cuprous chloride. The spectrum of  $Cu^{65}Cl^{35}$  has been excited in an electrodeless discharge tube by a 2,450 mc/sec microwave oscillator. All the known band systems of cuprous chloride were obtained with high intensity. The rotational analysis indicates that the upper states of the five systems are either  ${}^{1}\pi$ ,  ${}^{1}\Sigma$  etc. (as shown below) or states which behave like these.

 $B - X(^{1}\pi - ^{1}\Sigma)$   $C - X(^{1}\Sigma - ^{1}\Sigma)$   $D - X(^{1}\pi - ^{1}\Sigma)$   $E - X(^{1}\Sigma - ^{1}\Sigma)$   $F - X(^{1}\pi - ^{1}\Sigma)$ 

The  $\Lambda$ -type doubling in the F state is negligible, whereas that in the D and B states is large. This is apparently due to the circumstance that whereas there is no perturbing state near the F level, the levels D and B have each a perturbing state nearby. The rotational constants calculated from the data obtained in this experiment agree well with the results recently given by Lagerquist.

\*Atomic Energy Establishment, Trombay, Bombay

### HEATS OF FORMATION OF BROMINE FLUORIDES

Lawrence Stein

J. Phys. Chem., in press

Heats of reaction of  $F_2$  with  $Br_2$  were measured with an adiabatic calorimeter in the vicinity of 25° and 105°C. When excess  $F_2$  was used,  $BrF_3$  and  $BrF_5$  were formed in the 25° region, and  $BrF_5$  alone was formed in the 105° region. The standard heats of formation of  $BrF_3$  and  $BrF_5$  at 25°, with reactants and products in the gaseous state, were found to be -64.8  $\pm$  0.2 and -106.2  $\pm$  0.3 kcal/mole, respectively. From the present measurements and equilibrium data in the literature, the standard heat of formation of BrF was found to be -17.7  $\pm$  0.5 kcal/mole.

#### VAPOR PRESSURES OF SCANDIUM, YTTRIUM AND LANTHANUM

R. J. Ackermann and E. G. Rauh

J. Chem. Phys., in press

The vapor pressures of scandium, yttrium, and lanthanum were measured by the effusion method employing a vacuum balance and the respective heats of vaporization by both the vacuum balance and the mass spectrometer. The data are represented by the equations,

> Scandium: log p (atm) =  $(6.08 \pm 0.09) - (21940 \pm 150)/T$ Yttrium: log p (atm) =  $(5.59 \pm 0.07) - (19950 \pm 90)/T$ Lanthanum: log p (atm) =  $(5.44 \pm 0.07) - (17020 \pm 90)/T$

The errors quoted are standard deviations. The heats of vaporization at temperature are 77.9  $\pm$  0.4, 91.3  $\pm$  0.4, and 100.4  $\pm$  0.7 kcal mole<sup>-1</sup> for scandium, yttrium, and lanthanum, respectively, and the corresponding entropy changes are 24.9  $\pm$  0.3, 25.6  $\pm$  0.3, and 27.8  $\pm$  0.4 eu.

# THE HEAT CAPACITIES AND THERMODYNAMIC FUNCTIONS OF ${\rm YH}_2$ AND ${\rm YD}_2$ FROM 5 TO 350°K AND THE HYDROGEN VIBRATION FREQUENCIES

H. E. Flotow, D. W. Osborne and Klaus Otto

J. Chem. Phys., in press

The heat capacities of pure YH<sub>2</sub> and YD<sub>2</sub> were measured by an adiabatic method from 5 to 350°K. The compounds were found by x-ray analyses to consist of a single phase, with the yttrium atoms in face-centered cubic positions. Below 16°K the heat capacities of the two compounds are equal within experimental error, between 16 and 90°K the heat capacity of the hydride is about 0.02 cal deg<sup>-1</sup> mole<sup>-1</sup> greater than that of the deuteride, and at higher temperatures that of the deuteride becomes appreciably greater. The difference in the heat capacities above 100°K is ascribed to a single optical vibration of the hydrogen atoms, whose frequency is shifted upon isotopic substitution. The difference in the heat capacities of YH<sub>2</sub> and YD<sub>2</sub> in the temperature range 100 to 350°K is fitted to  $\pm 0.02$  cal deg<sup>-1</sup> mole<sup>-1</sup> with Einstein heat capacity functions and a frequency of 1030  $\pm$  30 cm<sup>-1</sup> for YH<sub>2</sub> and 1030/ $\sqrt{2}$  for YD<sub>2</sub>. These results are compared with those obtained by inelastic neutron scattering experiments.

The values obtained for the heat capacities, entropy, enthalpy and Gibbs free energy function for YH<sub>2</sub> at 298.15°K are  $8.243 \pm 0.016$  cal deg<sup>-1</sup>mole<sup>-1</sup>, 9.175  $\pm$  0.018 cal deg<sup>-1</sup>mole<sup>-1</sup>, 1403  $\pm$ 3 cal mole<sup>-1</sup> and -4.470  $\pm$  0.009 cal deg<sup>-1</sup>mole<sup>-1</sup>, respectively. The corresponding values for YD<sub>2</sub> are 10.773  $\pm$  0.022, 10.294  $\pm$  0.021, 1659  $\pm$  3 and -4.729  $\pm$  0.095. The enthalpy of formation of YH<sub>2</sub> minus the enthalpy of formation of YD<sub>2</sub> is calculated to be 0.78  $\pm$  0.08 kcal mole<sup>-1</sup> at 0°K and 0.55  $\pm$  0.08 kcal mole<sup>-1</sup> at 298.15°K.

THE PREPARATION AND PROPERTIES OF TcF<sub>6</sub> Henry Selig, C. L. Chernick and J. G. Malm J. Inorg. & Nuclear Chem. <u>19</u>(3/4) 377 (October 1961)

Letter

Abstract in ANL-6349, p. 42

#### GASEOUS OXIDES OF RHENIUM

M. H. Studier

J. Phys. Chem. 66 189 (January 1962)

Several gaseous rhenium oxides have been detected with a Bendix time-of-flight mass spectrometer. During a study of surface ionization, neutral species were volatilized from rhenium surfaces on which samples in nitric acid had been evaporated. Ions produced by electron bombardment of the gaseous species were identified by their masses and corresponded to the empirical formulas: a) Monomers: Re+, ReO+, ReO+, ReO3, ReO4 and b) Dimers: Re2, Re2O4, Re2O2, Re2O3, Re2O4, Re2O5, Re<sub>2</sub>O<sub>5</sub><sup>++</sup>, Re<sub>2</sub>O<sub>6</sub><sup>+</sup>, Re<sub>2</sub>O<sub>7</sub><sup>+</sup>, Re<sub>2</sub>O<sub>7</sub><sup>++</sup>. Gaseous oxides were still observed after they had been evaporated from the filament and the source had cooled to room temperature. As the source was gradually warmed, the intensity of the oxide ion beams increased and the oxides were observed to fractionate with respect to each other. Since Re207 has the highest mass of any oxide observed, it must be a primary gaseous product. All the lower dimeric oxides are primarily fragmentation products of the ionizing electron beam. Relatively high electron energies are required to produce the lower mass dimeric ions. In addition, at a given electron energy the dimeric forms were found to remain in constant ratio to each other with large variations in time, temperature and vapor pressure. The highest mass monomeric oxide, ReO4 is also a primary gaseous product, for it was frequently observed in the absence of oxides of greater mass. Although both  $\text{ReO}_3^+$  and  $\text{ReO}_2^+$  are formed in abundance by fragmentation of higher oxides, marked fractionation of  $\text{ReO}_2^+$ ,  $\text{ReO}_3^+$  and  $\text{ReO}_4^+$  with respect to each other and to the dimeric forms suggests that both ReO2 and  $ReO_3$  have an independent gaseous existence.  $ReO^+$  and  $Re^+$  were observed as fragmentation products only.

Note

THE VAPOR PRESSURES AND OTHER PROPERTIES OF ReF6 AND ReF7

J. G. Malm and Henry Selig

J. Inorg. & Nuclear Chem. 20 (3/4) 189-197 (December 1961)

Abstract in ANL-6349, p. 44

THE PREPARATION AND SOME PROPERTIES OF PLATINUM HEXAFLUORIDE

Bernard Weinstock, J. G. Malm and E. E. Weaver

J. Am. Chem. Soc. 83 4310-4317 (November 5, 1961)

Abstract in ANL-6445, p. 36

THE CHEMISTRY OF URANIUM IN SURFACE IONIZATION SOURCES

M. H. Studier, E. N. Sloth and L. P. Moore

J. Phys. Chem. 66 133-134 (January 1962)

A Bendix time-of-flight mass spectrometer was modified to permit the measurement of ions emitted from the surface of electrically heated filaments. The uranium system has been studied and it was demonstrated that by control of the oxidizing and reducing agents on a heated filament and in the surrounding atmosphere, the emission of any one of the following ions can be favored.

Reducing Agents (e.g. carbon)

### $U^+, UO^+, UO^+_2, UO^+_3$

Oxidizing Agents (e.g. oxygen)

#### KINETICS OF THE V(III)-Np(V) REACTION IN PERCHLORATE SOLUTIONS E. H. Appelman and J. C. Sullivan

J. Phys. Chem., in press

The kinetics of the reaction V(III) + Np(V)  $\rightarrow$  V(IV) + Np(IV) were studied in perchloric acid solutions. The empirical form of the rate law is  $\frac{-d[Np(V)]}{dt} = [Np(V)] [V(III)] \{k_1 + k_2^0[Np(IV)] [V(IV)]^{-1} [H^+]^{-1.5}\}$ . At 25°, in LiClO<sub>4</sub>-HClO<sub>4</sub> solutions 3.0 <u>M</u> in total perchlorate,  $k_1 = 0.30 \text{ M}^{-1} \text{ sec}^{-1}$ , and  $k_2^0 = 0.16 \text{ M}^{0.5} \text{ sec}^{-1}$ . Under these conditions, for the  $k_1$  path  $\Delta H = 14.6 \pm 0.8 \text{ kcal/mole and } \Delta S = -12.3 \pm 2.6 \text{ eu}$ . The second term of the rate law has been interpreted in terms of the rapid equilibrium Np(IV) + V(III)  $\implies$  Np(III) + V(IV) followed by the reaction Np(III) + Np(V)  $\rightarrow$  2Np(IV). A comparison has been made between the mechanisms of this and analogous reactions. THE MICROSCALE PREPARATION AND MICROMETALLURGY OF PLUTONIUM METAL

S. M. Fried, E. F. Westrum, Jr., \* H. L. Baumbach, \*\* and P. L. Kirk<sup> $\dagger$ </sup>

The Metal Plutonium, ed. A. S. Coffinberry and W. N. Miner. Chicago: The University of Chicago Press, 1961. pp. 18-25

The investigations summarized in this chapter comprise microchemical and micrometallurgical studies of plutonium made during 1943 and 1944 under the pressure of wartime conditions at the Manhattan Project Metallurgical Laboratory operated by The University of Chicago for the United States War Department. These studies led to the first successful preparation of plutonium metal and provided data essential to the macroscale technology of plutonium production that followed very soon thereafter at Los Alamos. Because microscale metallurgical methods are of continuing applicability in the isolation and investigation of synthetic and other rare elements, a description of these techniques is of importance as a contribution to the subject of laboratory procedures in modern chemical and metallurgical research.

### INFRARED SPECTRA OF HEXAFLUORIDES OF THE SECOND TRANSITION GROUP ELEMENTS

H. H. Claassen

Spectrochim. Acta <u>17</u> 1132 (October 1961) Abstract

The vibrational spectra of the hexafluorides of the third transition group elements, which contain from zero to four non-bonding 5d electrons, have been studied in recent years and found unusually interesting because of a dynamical Jahn-Teller effect that results in a broadening of certain infrared and Raman bands.

Several corresponding (4d) hexafluorides of the second transition group elements have recently been prepared in this laboratory. Infrared spectra of these molecules are reported. Both infrared-active fundamentals have been observed for each of the molecules, and most of the other fundamentals have been determined from combination bands. The broadening of certain combination bands that has been ascribed to a Jahn-Teller coupling in the 5d hexafluorides is even more pronounced in the corresponding 4d hexafluorides.

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#### COORDINATION NUMBERS AND CONFIGURATIONS OF TRANSITION-METAL COMPLEXES IN FUSED SALTS

Rudolf Gut and D. M. Gruen

Abstracts of Scientific Papers presented at the 18th Intern. Congr. of Pure and Applied Chemistry, Montreal, August 1961. Toronto: Univ. Toronto Press, 1961 p. 182

In recent years, absorption spectra of transition-metal ions dissolved in fused salts have provided detailed information concerning coordination numbers and configurations of complex ions in melts. The spectra have been interpreted in two ways: first, by making use of the results of ligand field theory, and second, by direct comparison of melt spectra with spectra of crystals of known structure.

This paper will present results on some bi- and tri-valent metal ions in a variety of chloride melts.

In particular, observations on V(III) dissolved in chloride melts will be reported which show the dependence of coordination number on cation composition, temperature, and chloride-ion activity.

In some alkali-metal chloride melts, V(III) appears to be present as octrahedral  $VCl_6^3$  complexes. Additon of  $AlCl_3$  to such a melt lowers the Cl<sup>-</sup> activity by formation of  $AlCl_4^-$ . The competition for Cl<sup>-</sup> between Al(III) and V(III) results in the breakdown of  $VCl_6^3$  complexes and the formation of tetrahedral  $VCl_4^-$  complexes. In other experiments similar effects have been observed by increasing the temperature or by substituting one alkali-metal ion for another. The results of these studies have been supplemented by spectroscopic measurements on single crystals, and the relationship between the melt and crystal spectra will be discussed.

#### ELECTRON SPIN RESONANCE OF STABLE ORGANIC FREE RADICALS: THE DISSOCIATION OF HEXAPHENYLETHANE

J. A. Weil, C. A. Hutchison, Jr., A. Kowalsky and G. W. Wheland Preprints of Papers Read at the 5th Intern. Symp. on Free Radicals, July 6-7, 1961, Univ. Uppsala, Sweden. Stockholm: Almqvist & Wicksell, 1961. Paper No. 72

A determination of the equilibrium constant  $\underline{K}$  of dissociation of hexaphenylethane (HPE) in benzene into triphenylmethyl (TPM) radicals has been made by means of paramagnetic resonance. Previous measurements of  $\underline{K}$  have been carried out by various other techniques including colorimetric studies and static magnetic susceptibility experiments, but these are subject to various difficulties not inherent in the resonance experiments. The equilibrium constant  $\underline{K}$  was determined for solutions at concentrations 0.0875, 0.127 and 0.131 moles/liter and was found to have the mean value 2.92  $\pm$  0.09 x 10<sup>-4</sup> moles/liter at 23°C. The results of the static susceptibility work give lower values, possibly because the diamagnetism of the TPM radical may be inordinately large.

#### INFRARED SPECTRA OF WATER IN TRIBUTYL PHOSPHATE CONTAINING DISSOLVED SALTS AND THE EFFECTS OF SOLUTES ON THE TRIALKYL PHOSPHATE SPECTRUM

L. I. Katzin

J. Inorg. & Nuclear Chem. 20(3/4) 300-303 (December 1961)

Abstract in ANL-6394, p. 38

#### RAMAN AND INFRARED SPECTRA AND NORMAL COORDINATE TREATMENTS OF THE HYPOPHOSPHITE AND DIDEUTERIOHYPOPHOSPHITE IONS

J. D. Ziomek, \* J. R. Ferraro and D. F. Peppard

J. Mol. Spectroscopy, in press

Raman displacements, relative intensities, depolarization factors and infrared wave numbers have been obtained for the sodium, potassium, and barium salts of hypophosphorous and dideuteriohypophosphorous acids, respectively, at room temperature. A critical examination of the data was made and the most probable values selected. Results of the normal coordinate treatments (FG matrix method) on the basis of the  $C_{2V}$  are given along with a satisfactory assignment of observed Raman and infrared bands. These results were found to be consistent with the isotopic product rule.

### THE ALKALI SALTS OF 2,2-DIPHENYL-1-PICRYLHYDRAZINE

J. A. Weil and G. A. Janusonis

J. Org. Chem., in press

Several mono-alkali salts, as well as a quaternary ammonium salt of 2,2-diphenyl-1-picrylhydrazine have been prepared. They have been characterized by elemental analysis, acid-base titrimetric analysis, and by use of proton high resolution magnetic resonance. The intense optical absorptions of solutions of these salts have been measured.

## MOLECULAR WEIGHT STUDIES OF SEVERAL ORGANOPHOSPHORUS ACIDS

J. R. Ferraro, G. W. Mason and D. F. Peppard

J. Inorg. & Nuclear Chem., in press

Molecular weight studies of several organophosphorus acids of the types  $(GO)_2PO(OH)$ , (GO)G'PO(OH) and  $(GO)PO(OH)_2$  have been made in several solvents, using an isothermal distillation method. In general, the monobasic acids are dimers in solvents such as n-hexane, cyclohexane, benzene and carbon tetrachloride; monomers in methyl alcohol; and intermediate in chloroform and acetone. Mono-(2-ethylhexyl) phosphoric acid is highly polymeric in n-hexane and cyclohexane, the molecular weight being 8-14.5 times the formula weight; hexameric in benzene and carbon tetrachloride; dimeric in acetone; and monomeric in methyl alcohol. The change in state of aggregation, for both the mono- and di-basic acids, as the diluent is varied, parallels the predicted variation in solute-solvent interaction.

# EFFECTS OF ELECTROLYTES ON ROTATORY DISPERSION OF AQUEOUS TARTRATE SOLUTIONS

L. I. Katzin and Elsie Gulyas

J. Phys. Chem., in press

Rotatory dispersion data over the range 6500-2650 Å, for aqueous tartaric acid systems containing HCl and chlorides of sodium, lithium, calcium, praseodymium or thorium, and for alkaline tartrate, are fitted to a two-term Drude equation. The wavelength parameters obtained are found to be in fair agreement with the absorption spectra. The data are compatible with the hypothesis of direct interaction between the cations and the OH groups of the unionized tartaric acid.

#### Analytical Chemistry

# CONTINUOUS SEPARATION OF GASEOUS MIXTURES BY THERMAL GRAVITATIONAL DIFFUSION

H. D. Frame, Jr., J. R. Kuszewski, J. F. Binder and H. H. Strain Anal. Chem. 33 1741-1745 (November 1961)

Abstract in ANL-6445, p. 38

#### SEPARATION OF ALUMINUM, MERCURIC OR FERRIC IONS FROM VARIOUS CATIONS BY ELECTROCHROMATOGRAPHY H. D. Frame, Jr., H. H. Strain and Joseph Sherma\* Anal. Chem. 34 170 (January 1962) Letter

Various complex-forming substances have been tested for the electrochromatographic separation of one or a few ionic species from multicomponent mixtures. Promising agents were tested with mixtures of about 20 cations including radioactive cesium, strontium and yttrium. Aluminum, mercuric and ferric ions are complexed to form anionic species and are separated from the others which remain as cations.

#### ELUTION CAPACITY OF ORGANIC SUBSTANCES IN SOLUTION-ABSORPTION CHROMATOGRAPHY

M. J. Sabacky, L. B. Jones, H. D. Frame, Jr., and H. H. Strain Anal. Chem., in press

The effectiveness of various eluting agents in solution-adsorption chromatography has been investigated. These eluting agents were compared with a single sorbent system (magnesia plus siliceous earth, 1:2), a single sorbed species ( $\beta$ -carotene), and a single noneluting carrier solvent (low-boiling petroleum ether). Each eluting agent was tested at many concentrations and curves for the resulting R values vs concentration are presented. The position of several eluting agents was determined relative to the solvent front and the carotene in the columns.

Correlations of elution capacity, molecular structure, dipole moments, and dielectric constants are consistent with an elution mechanism involving two dynamic equilibria: 1) a competition for the sorbent surface between the eluting agent, the species to be separated, and the solvent; and 2) a competition between dissolved eluting agent and sorbed eluting agent for the species to be separated.

\*LaFayette College, Easton, Pa.

#### THE BASIS OF SELECTIVITY IN CHROMATOGRAPHY, ELECTROCHROMA-TOGRAPHY AND CONTINUOUS ELECTROCHROMATOGRAPHY

H. H. Strain

Anal. Chem. 33 1733-1737 (November 1961)

Abstract in ANL-6445, p. 38

SEPARATION OF THE ALKALI METAL CATIONS FROM MIXTURES OF VARIOUS CATIONS BY ELECTROCHROMATOGRAPHY Joseph Sherma and H. H. Strain Anal. Chem. 34 76-80 (January 1962)

Differential electrical migration in an ammoniacal solution of ammoniatriacetic acid containing cyanide facilitates the separation and estimation of the alkali metal ions from other univalent ions (silver, thallium, and mercurous) and from all multivalent ions as well. Migration from this aqueous solution into and through a nitromethane solution provides for the separation of the alkali metal ions from one another as well as from the mixture. All the separated alkali metal ions may be located and estimated by flame photometry. Sodium, potassium, rubidium, and cesium may be detected and estimated by neutron activation followed by gamma-ray spectrometry.

DETERMINATION OF OXYGEN IN ZINC, CADMIUM AND MAGNESIUM BY INERT GAS FUSION

B. D. Holt and H. T. Goodspeed

Anal. Chem., in press

Abstracts of Scientific Papers presented at the 18th Intern. Congr. of Pure and Applied Chemistry, Montreal, August 1961. Toronto: Press, 1961, p. 227

In the inert gas fusion method reported here the metal (zinc, cadmium, or magnesium) was separated from the oxide by evaporation in a stream of argon at a pressure of 100 mm Hg. Volatilized from an inductively heated graphite crucible, the metal was condensed on a split tantalum cylinder and subsequently removed from the crucible area. The oxide remaining in the crucible was reduced in situ by the inert gas fusion technique. The entire analysis was performed in a single analytical train, and the total time per sample was about one hour for zinc or cadmium and about  $1\frac{1}{2}$  hours for magnesium. Of the three metals tested for oxygen in the microgram range, the best results were obtained on zinc, with 100  $\pm$  2 per cent recovery of oxygen added as the oxide to the metal.

# LIQUID-LIQUID EXTRACTION OF TRIVALENT RARE EARTHS USING ACIDIC PHOSPHONATES AS EXTRACTANTS

D. F. Peppard and G. W. Mason

Rare Earth Research, ed. E. V. Kleber. New York: The Macmillan Co., 1961. pp 37-50

In considering the partition of trivalent rare earth solutes between two mutually equilibrated, sensibly immiscible, liquid phases - usually organic and aqueous phases - as a fractionation technique, the important factors are 1) the degree of fractionation per stage, 2) the constancy or variance of this degree of fractionation from stage to stage, 3) the ease with which multiplication of stages may be achieved, and 4) the range of partitioning Z-values (atomic number or fictitious atomic number above which all members report preferentially to the organic phase and below which all members report preferentially to the aqueous phase).

The degree of fractionation per equilibrium stage for a given pair of rare earth elements may be calculated from the volume ratio R (volume of equilibrated organic phase divided by the volume of equilibrated aqueous phase per stage) and the K values for each of the rare earths (K is the distribution ratio, i.e., the concentration of the given rare earth in the organic phase divided by the concentration of the same rare earth in the aqueous phase).

SYNERGISM IN THE SOLVENT EXTRACTION OF DI-, TRI-, AND TETRAVALENT METAL IONS. I. SYNERGIC EFFECTS OF DIFFERENT PHOSPHATE ESTERS

T. V. Healy

J. Inorg. & Nuclear Chem. 19 (3/4) 314-327 (October 1961)

Abstract in ANL-6349, p. 47

SYNERGISM IN THE SOLVENT EXTRACTION OF DI-, TRI- AND TETRAVALENT METAL IONS. II. SYNERGIC EFFECTS IN SO-CALLED INERT DILUENTS

T. V. Healy

J. Inorg. & Nuclear Chem. 19 (3/4) 328-339 (October 1961)

Abstract in ANL-6349, p. 48

THE ANALYSIS OF URANIUM ALLOYS USING A HOLLOW CATHODE J. A. Goleb and J. K. Brody

Appl. Spectroscopy 15 166-170 (1961)

Abstract in ANL-6298, p. 50

FIBERGLASS REINFORCED PLASTIC GLOVEBOXES FOR PLUTONIUM ANALYTICAL RESEARCH

J. P. Hughes and A. G. Jastrab

Trans. Am. Nuclear Soc. <u>4</u>(2) 216 (November 1961) Proc. 9th Conf. on Hot Laboratories and Equipment, November 7-9, 1961. Chicago: Am. Nuclear Soc., 1961, pp. 78-86

Gloveboxes suitable for analytical work with plutonium and its alloys must be corrosion resistant, easily cleaned, and flexible with regard to operation. No commercially available glovebox met our requirements, so a design was developed for a glovebox made of fiberglassreinforced plastic that would eliminate chemical corrosion, be easy to clean of radioactive contamination, and allow greater use of inside floor space. Boxes constructed during development have been in service two years with no noticeable deterioration.

#### Miscellaneous

### SPECTRA OF ESCHSCHOLTZXANTHIN AND OTHER CAROTENOID PIGMENTS

H. H. Strain, M. R. Thomas and J. J. Katz J. Org. Chem. 26 5061-5064 (December 1961)

Abstract in ANL-6445, p. 40

EVIDENCE FOR EXCHANGEABLE HYDROGEN IN CHLOROPHYLL J. J. Katz, M. R. Thomas, H. L. Crespi and H. H. Strain J. Am. Chem. Soc. 83 4180 (October 20, 1961)

Abstract in ANL-6445, p. 40

THERMAL DENATURATION OF ORDINARY AND FULLY DEUTERIATED DNA IN  $\rm H_2O$  AND  $\rm D_2O$ 

H. L. Crespi and J. J. Katz

J. Mol. Biol., in press

Fully deuteriated deoxyribonucleic acid was isolated from <u>Escherichia coli</u> grown in a fully deuteriated nutrient medium (99.6%  $D_2O$  with fully deuteriated substrates). The melting temperature of this DNA was found to be essentially identical with that of ordinary DNA in both  $H_2O$  and  $D_2O$  solutions.

# FIRST ISOLATION AHD CHARACTERIZATION OF A FULLY DEUTERIATED PROTEIN

D. S. Berns, H. L. Crespi and J. J. Katz

J. Am. Chem. Soc., in press

An algal chromoprotein, phycocyanin, has been isolated from the blue-green alga Plectonema calothricoides cultured in D<sub>2</sub>O for two years. An identical purification procedure was used to isolate phycocyanin from ordinary water-grown P. calothricoides. The deuterium content of the deuteriated protein was ascertained to be 98.4 atom % D,O by direct analysis. An infrared search was made for the characteristic C-H absorption at 2900 to 3000 cm<sup>-1</sup> in the deuteriated protein, but none was found. Absorption in regions characteristic of C-D and N-D bonds was present. The visible and ultraviolet absorption spectrum, ultra-centrifuge pattern, and electrophoretic properties of the deuterio- and hydrogen-protein preparations were investigated. The absorption spectra in the visible region of both protein preparations are quite similar and are definitely of the C-phycocyanin type. Further, the number of chromophores in both the deuterio- and hydrogen-phycocyanin molecules is very likely the same. The deuterio-protein exhibits a lower mobility in cellulose acetate electrophoresis, and a mixture of deuterio- and hydrogen-protein is resolved into two bands on electrophoresis at pH 4.70. To ascertain whether the two proteins are chemically identical and differ only in isotopic composition, an analysis of the number of amino acid residues was made. The number within experimental error was the same except for cystine and proline; however the difference here may be due to difficulties in analysis.

### NUTRITIONAL REQUIREMENTS FOR THE CULTIVATION OF FULLY DEUTERIATED YEASTS <u>TORULOPSIS</u> UTILIS AND SACCHAROMYCES CEREVISIAE

V. S. Mohan, H. L. Crespi and J. J. Katz Nature, in press Letter

Although a medium composed of  $H_2O$ , inorganic salts and glucose supported good growth of <u>Torulopsis utilis</u>, the organism would not grow in the medium if  $D_2O$  were substituted for  $H_2O$ . Amino acids, purine and pyrimidine derivatives, sugar and sugar derivatives and vitamins were added to the medium singly. Only thiamin promoted growth. Of the biologically active compounds related to thiamin, only cocarboxylase or the thiazole moiety of the thiamin molecule was an effective supplement to the deuterium oxide medium; the pyrimidine fraction of thiamin was not. Apparently in deuterium oxide <u>T. utilis</u> loses its ability to synthesize the thiazole portion of thiamin but can still synthesize the pyrimidine part. Successive subcultures failed to select for a thiaminless mutant.

<u>Saccharomyces cerevisiae</u> grows satisfactorily in an  $H_2O$ -medium supplemented with calcium pantothenate and biotin. In a  $D_2O$  medium this yeast develops additional nutritional requirements for thiamin, inositol and pyridoxine.

The substitution of deuterioglucose for ordinary glucose in the  $D_2O$ -medium does not alter the requirements for the nutritional supplements.

### NON-ELECTRICAL LIQUID NITROGEN LEVEL CONTROLLER B. D. Holt

Rev. Sci. Instr., in press Note

Nearly all devices for controlling the level of liquid nitrogen in continuously-cooled laboratory equipment depend, to varying degrees, on electricity, and some depend on electronic equipment. The apparatus described is completely nonelectrical. It maintains the liquid nitrogen level within a range of limits from a few millimeters to a few inches. The sensing elements are three argon-filled brass bellows hermetically sealed to copper tubing probes, the ends of which dip into the liquid nitrogen. These bellows mechanically operate two piston valves which control the application of compressed air to the reservoir of liquid nitrogen. SOLAR-FLARE-INDUCED RADIOACTIVITY IN RECOVERED SATELLITE DISCOVERER XVII

J. E. Keith, \* A. Turkevich, \* and G. W. Reed

Abstracts of Scientific Papers presented at the 18th Intern. Congr. of Pure and Applied Chemistry, Montreal, August 1961. Toronto: Univ. Toronto Press, 1961. p. 145

The radioactivity induced in materials (kindly made available by Lockheed Aircraft Corporation, Missile and Space Division) of the recovered satellite, Discoverer XVII is being examined. This satellite was orbiting the earth in a polar orbit for two days at the time of the solar flare of November 12, 1960. Samples of bismuth, isolated radiochemically from a lead sheet on the satellite (which was shielded from cosmic rays by only a few grams per square centimeter of material), have been found to emit X-rays in the 70-kev region. A part of this radioactivity has been identified by X-ray-gamma coincidence counting and decay characteristics as due to 15-day Bi<sup>205</sup>. The specific activity of the top surface of the lead at the time of recovery of the satellite was a few disintegrations per minute of Bi<sup>205</sup> per gram of lead on the assumption that protons are responsible. A timeintegrated flux of  $4 \ge 10^7$  particles per square centimeter incident on the lead, and having an energy between 20 and 50 Mev, would account for the observed amount of Bi<sup>205</sup>. This calculation is based on the known cross section of (p, xn) reactions on separated lead isotopes. The specific activity, as a function of depth in the lead, drops to half its surface value at a depth of about three grams per square centimeter.

\*University of Chicago

### SOLID STATE SCIENCE DIVISION

CALCULATION OF ELECTRON-COUPLED NUCLEAR SPIN-SPIN INTER-ACTIONS IN MOLECULES BY A VARIATION PROCEDURE

D. E. O'Reilly

J. Chem. Phys. 36 274-280 (January 1962)

Abstract in ANL-6394, p. 45

ANALYTICAL HARTREE-FOCK-SELF CONSISTENT-FIELD WAVE FUNCTIONS FOR SOME  $1s^22s^22p^6$  CONFIGURATIONS

L. M. Sachs

Phys. Rev. 124 1283-1289 (November 15, 1961)

Abstract in ANL-6394, p. 46

THE EFFECT OF BARDEEN-HERRING CORRELATION ON VACANCY DIFFUSION IN ANISOTROPIC CRYSTALS

J. G. Mullen

Phys. Rev. 124 1723 (December 15, 1961)

Abstract in ANL-6394, p. 48

FREE RADICAL SPECIES PRODUCED BY RADIATION IN  $\rm H_2O$  and  $\rm H_2O_2$  AT LOW TEMPERATURES

Bernard Smaller and Juan McMillan

Preprints of Papers Read at the 5<sup>th</sup> Intern. Symp. on Free Radicals, July 6-7, 1961, Univ. Uppsala, Sweden. Stockholm: Almqvist & Wiksell, 1961. Paper No. 65

A study has been made of the free radicals produced at low temperature in single crystals of  $H_2O$  and  $H_2O_2$  by ionizing and ultraviolet radiation. The radicals were detected by the electron-paramagnetic resonance technique using equipment operating at 9.1 kMc/sec and double-field modulation for increased resolution.

Single crystals of ice were irradiated at  $77^{\circ}$ K with total doses of approximately  $10^{21}$  ev/cc. The spectra were obtained with the c axis parallel or perpendicular to the axis of rotation, this latter always perpendicular to the static and parallel to the microwave, magnetic fields. The results indicate a cylindrically symmetric radical having 1) an unpaired electron interacting with a proton at approximately 1 A distance, 2) its symmetry axis pointing toward any of the corners of the hexagon, 3) equal populations in the orientations, which are all perpendicular to the c axis of the parent crystal. The symmetry around the O-H bonding is accounted for by rapid rotation of the radical around the axis.

The single crystals of 90% H<sub>2</sub>O<sub>2</sub> were irradiated with ultraviolet light. The paramagnetic resonance spectrum was complex, containing at least seven separate components. With flash illumination a prominent transient species with g-value about 8.013 appears at 77°K; it rapidly decays with a limiting decay time of 80 minutes. A second species with g-value about 2.007 grows in simultaneously and subsequently slowly disappears with a decay time of several days. These two signals have been tentatively assigned to the HO<sub>2</sub> radical which can migrate through the lattice until trapped by a substitutionally situated O<sub>2</sub> molecule. The potential well curves for the O<sub>2</sub> - HO<sub>2</sub> - HO<sub>2</sub>H system are in qualitative agreement with this interpretation.

## SIGN OF THE Li<sup>8</sup> MAGNETIC MOMENT

Donald Connor

Bull. Am. Phys. Soc. 7 25 (January 1962)

Abstract

The sign of the magnetic dipole moment of  $\text{Li}^8$  has been found experimentally to be positive, in agreement with theoretical expectation. Rates of transition among the Zeeman levels were compared for the two senses of circular polarization of a resonant rf field (1977 kc in 3139 gauss). The short half-life (0.85 sec) of  $\text{Li}^8$  required use of the polarized neutron-activation, beta-emission anisotropy detection method previously applied to the measurement of the  $\text{Li}^8$  nuclear g-factor.

# PARAMAGNETIC RELAXATION IN METAL-AMMONIA SOLUTIONS

D. E. O'Reilly

J. Chem. Phys. 35 1856-1862 (November 1961)

Abstract in ANL-6394, p. 51

EFFECT OF LATTICE DEFECTS ON THE REACTIVITY OF GRAPHITE G. R. Hennig and M. A. Kanter

Proc. Fourth Ann. Intern. Symp. on the Reactivity of Solids, May 30 - June 4, 1960, ed. J. H. DeBoer et al. Amsterdam: Elsevier Publishing Company, 1961. p. 649

Abstract in ANL-6245, p. 46

RADIATION DAMAGE RATES IN NUCLEAR REACTORS. I. THE ELECTRICAL RESISTANCE OF GRAPHITE OVER THE TEMPERATURE RANGE 8-90°C: INITIAL DAMAGE AND ITS TEMPERATURE COEFFICIENT

William Primak and Edward Edwards ANL-6321 (September 1961)

The behavior of  $\frac{1}{8}$ -in. spectroscopic graphite rods is shown to be variable beyond the variation of measurement. Statistical measures are given for the variability before and with irradiation. The linear regression of the reciprocal per cent change in resistance against the reciprocal exposure was determined over the range from about 25 to 90% change of electrical resistance. The linear regression of the above regression coefficients was determined for the range from 8 to 90°C. The number of specimens required to achieve a given accuracy in monitoring is calculated. Within the precision of the data, there is no evidence for departure from isothermal damaging, hence no positive evidence of radiation annealing at these temperatures and extents of damage.

BAND STRUCTURE OF SOLID ARGON

R. S. Knox\* and G. F. Bassani

Phys. Rev. 124 652-657 (November 1, 1961)

Abstract in ANL-6394, p. 52

\* University of Rochester

OPTICAL ABSORPTION OF M CENTERS IN POTASSIUM CHLORIDE

Fumio Okamoto

Phys. Rev. 124 1090-1097 (November 1961)

Abstract in ANL-6394, p. 52

## RECOMBINATION OF ELECTRONS AND DONORS IN n-TYPE GERMANIUM G. Ascarelli\* and S. Rodriguez

Phys. Rev. 124 1321-1328 (December 1, 1961)

Abstract in ANL-6394, p. 54

EFFECTS OF SPIN-ORBIT COUPLING IN Si AND Ge

Liu Liu

ANL-6463 (November 1961)

A treatment of spin-orbit effects in some semi-conductors is given using the effective mass method and orthogonalized-plane-wave type wave functions. In this formalism, the spin-orbit splitting of valence states in the crystal is expressed directly in terms of either experimental or calculated values of the spin-orbit splitting of the atomic core states. The calculation yields values in good agreement with experiments for the splitting at  $\Gamma_{25'}$  for Si and at both  $\Gamma_{25'}$  and  $L_{3'}$  for Ge. A demonstration is given of the enhancement of the spin-orbit splitting of valence states in the crystal over the corresponding atomic value.

The shift in the g-tensor due to spin-orbit interactions is studied in Si and Ge. Because of crystal selection rules, the usual two band approximation to the effective mass sum rule is inadequate for Si and, in particular, the core state must be considered. When all important states are included, the calculations yield values in good agreement with experiment. In the case of Ge, it is found that core states do not contribute appreciably to the g-tensor. However, the calculated value for the shift in the transverse component of the g-tensor has an opposite sign to the measured one.

A certain matrix element of the deformation potential for Si is also evaluated based on the measured shift in the g-value due to strain. The result is compared with other deformation potentials in Si.

<sup>\*</sup> University of Illinois

### PARAMAGNETIC RESONANCE OF SOME SILVER (II) COMPOUNDS J. A. McMillan and Bernard Smaller

J. Chem. Phys. 35 1698-1701 (November 1961)

Abstract in ANL-6349, p. 51

SPECIFIC HEAT OF SAMARIUM METAL BETWEEN  $0.4^\circ\,\text{and}\,\,4^\circ\text{K}$ 

O. V. Lounasmaa

Bull. Am. Phys. Soc. 7 55 (January 1962) Abstract

Besides the usual lattice and electronic terms, proportional to T<sup>3</sup> and T, respectively, the specific heat of rare earth metals has two additional contributions: a magnetic specific heat due to exchange interaction between the electronic spins, and a nuclear specific heat due to splitting of the nuclear energy levels in the strong magnetic field produced by the 4f electrons. Samarium metal is antiferromagnetic below 13.6°K and the magnetic specific heat, according to the spin wave theory, should be proportional to  $T^3$ . The nuclear specific heat has a  $T^{-2}$  temperature dependence in the first approximation. We can thus write  $C_{p} = AT^{3} + BT + CT^{-2}$ , where the first term represents both the lattice and magnetic specific heats. Values of the constants, as determined by the method of least squares from 102 experimental points between  $0.4^{\circ}$  and  $4.0^{\circ}$ K, are (in mJ/mole): A = 0.88 - 1.11; B = 12.1; C = 8.6. The magnetic specific heat appears to depend on the time the sample spent in the vicinity of the antiferromagnetic Curie point when it was cooled down; hence the variations in the value of A. Constants B and C should be accurate to 5% and 2%, respectively. The effective magnetic field at the nucleus, as calculated from the value of constant C, is  $3.3 \times 10^6$  gauss.

PHOTOINDUCED FREE-SPIN SPECIES IN  $\beta$ -CAROTENE AND CHLOROPHYLL

Bernard Smaller

Abstracts of Contributed Papers, Intern. Biophysics Congr., Stockholm, July 31 - August 4, 1961. Stockholm: Tryckeri Aktiebolaget Thule, 1961. p. 10

The technique of electron-paramagnetic resonance has been applied to the detection of free-spin species produced by light irradiation on frozen solutions at 77°K of  $\beta$ -carotene and chlorophyll a and b. The appearance of two species can be attributed to the production of both electron excess and electron deficient (or "hole") centers. The systems may be described in terms of a bi-radical or an extreme form of a triplet state. The kinetics of the growth of the species under constant illumination has been studied in terms of both first and second order processes. The relative stability of the components under annealing has also been studied and correlation with photoconductivity effects been found. The presence of dissolved oxygen in the system is to produce a third free radical species at the expense of the "hole." Using flash illumination and dilute chlorophyll solutions almost all of the chlorophyll can be converted into the free radical form. The possible significance of these studies to photosynthesis is indicated.

## FREE RADICALS IN CELLS INDUCED BY HEAVY IONS

E. L. Powers,\* Bernard Smaller, C. A. Tobias,\*\* J.Lyman\*\* and T. Brustad<sup>†</sup>

Abstracts of Contributed Papers, Intern. Biophysics Congr., Stockholm, July 31 - August 4, 1961. Stockholm: Tryckeri Aktiebolaget Thule, 1961.

In the dry spore of Bacillus megaterium it is possible to recognize long-lived free radicals induced by X-rays, and to measure certain of their biological effects. In the basic studies, radical scavengers such as nitric oxide and hydrogen sulfide are used following irradiation to reduce biological effectiveness of X-rays. Approximately 40 per cent of the total effect of soft X-rays can be ascribed to these free radicals that rapidly become toxic in the presence of oxygen. Parallel studies with an electron paramagnetic resonance spectrometer reveals the presence of two general kinds of radicals. Because of their behavior, these may be considered to be the radicals responsible for the biological effects referred to above. Currently under biological and physical study are the radicals formed in these dry cells by bombardment with 167 Mev neon ions, 40 Mev helium ions, and 110 Mev carbon ions to ascertain the effect of increasing LET on the size and nature of the free radical component responsible for radiation injury. The general result is that as LET increases, the long-lived free radical component decreases.

- \* Biological and Medical Research Division
- \*\* University of California, Berkeley
  - <sup>†</sup> The Norwegian Radium Hospital, Oslo

# FACTORS CONTROLLING RADIATION-INDUCED FREE RADICALS IN A BIOLOGICAL SYSTEM

E. L. Powers,\* Bernard Smaller, C. A. Tobias\*\* and J. Lyman\*\* Preprints of Papers Read at the 5<sup>th</sup> Intern. Symp. on Free Radicals, July 6-7, 1961, Univ. Uppsala, Sweden. Stockholm: Almqvist & Wiksell, 1961. Paper No. 54

A series of physical and chemical studies has yielded evidence that free radicals produced in cells by high energy radiation may be responsible for a portion of the biological effects of irradiation. The basic investigations were accomplished with x rays (approximately 20 kev) with the use of dried spores of the bacterium <u>Bacillus megaterium</u>. The criteria used were biological in nature, i. e., the ability of the irradiated spore to germinate and to give rise to a macroscopically visible colony of cells.

By exposing the anoxically irradiated spore to agents such as nitric oxide and sulfide, we had shown that approximately 50 per cent of the anoxic response to radiation might be ascribed to free radicals that become damaging when combined with oxygen. Furthermore, dried spores exposed to high temperature lose these free radicals before they become toxic. The behavior of these radicals toward heat and towards nitric oxide appears to be about the same, while hydrogen sulfide appears to be slightly more efficient as a radical remover.

Parallel physical studies on radical production in these spores with an electron paramagnetic resonance spectrometer have shown at least two general kinds of radicals produced by these x rays. One of these is indicated by a doublet with approximately 20-gauss spacing and the other by a triplet with approximately 30-gauss spacing.

Currently under way are investigations on the efficiency of 20-kev x rays in producing these free radicals, especially in the low-dose region, and the dependence of this efficiency on linear energy transfer. The comparison being made now is between x rays and certain heavy ions with LET's up to 500 kev/ $\mu$ . These physical yield studies are being correlated with chemical studies in which the biological effectiveness of the radical component is being measured under the same conditions utilized in the physical studies.

<sup>\*</sup> Biological and Medical Research Division

<sup>\*\*</sup> University of California, Berkeley

### CHEMICAL ENGINEERING DIVISION

# FLUORINE BOMB CALORIMETRY. III. THE HEAT OF FORMATION OF BORON TRIFLUORIDE

S. S. Wise, J. L. Margrave,\* H. M. Feder and W. N. Hubbard J. Phys. Chem. <u>65</u> 2157-2159 (December 1961)

The heat of formation of boron trifluoride has been measured by direct combination of the elements in a bomb calorimeter.  $\Delta H_{f}^{\circ}$  at 25° was found to be -270.16  $\pm$  0.24 kcal mole<sup>-1</sup>.

THE HEATS OF FORMATION OF SOME INORGANIC COMPOUNDS BY FLUORINE BOMB CALORIMETRY

S. S. Wise

ANL-6472 (January 1962)

Because of the experimental difficulties involved, the heats of formation of many compounds have never been determined or are in serious doubt, in spite of the extensive use of oxygen bomb calorimetry for many decades. The application of precision bomb calorimetry to many of these materials has now been possible through the development of techniques for the use of high-purity fluorine as the bomb oxidant.

A description is given of methods and materials which have been used for handling fluorine safely in routine calorimetric experiments. The construction of suitable combustion bombs and the availability of inert sample supports is discussed.

Since many materials react spontaneously with fluorine, a method is needed for keeping the sample isolated from fluorine until the reaction is desired. The construction and operation of a two-chambered reaction vessel is given in detail. The vessel consists of a standard nickel combustion bomb surrounded by a nickel tank. A valve, which can be operated remotely, allows the flow of fluorine from the tank into the evacuated bomb where contact with the sample is made. The two-chambered vessel fits into a standard, rotating bomb calorimeter.

Very few heats of formation of elemental fluorides are known with high precision; therefore, a redetermination program has been initiated in this Laboratory so that a firm foundation can be given to fluorine calorimetry. In this work, the standard heat of formation of boron trifluoride was verified as  $-270.1_0 \pm 0.2_4$  kcal mole<sup>-1</sup>. A new value for the heat of formation of silicon tetrafluoride was determined to be  $-386.0_2 \pm 0.2_4$  kcal mole<sup>-1</sup>.

A value of  $-59.5_1 \pm 0.7_2$  kcal mole<sup>-1</sup> has been derived for the heat of formation of boron nitride from the combination of the heat of combustion of BN in fluorine and the heat of formation of BF<sub>3</sub>.

The heats of combustion of two forms of silica with fluorine have been measured. A combination of these with the heat of formation of SiF<sub>4</sub> yields  $-215.9_7 \pm 0.3_0$  kcal mole<sup>-1</sup> as  $\triangle H_f^\circ$  for vitreous silica and  $-217.7_4 \pm 0.3_3$  kcal mole<sup>-1</sup> as  $\triangle H_f^\circ$  for alpha-quartz.

A review of available thermochemical determinations suggests that the spectroscopically determined value of  $\Delta H_{\rm f}^{c}$  for hydrogen fluoride (-65.1  $\pm$  0.4 kcal mole<sup>-1</sup>) is probably more nearly correct than the calorimetrically determined value (-64.4  $\pm$  0.2 kcal mole<sup>-1</sup>). A COMBUSTION BOMB REACTION VESSEL FOR SPONTANEOUSLY COMBUSTIBLE MATERIALS

R. L. Nuttall, S. S. Wise and W. N. Hubbard Rev. Sci. Instr. <u>32</u> 1402 (December 1961) Note

An apparatus is described for use in burning spontaneously combustible materials in a bomb calorimeter. It utilizes a standard combustion bomb as the reaction vessel. The bomb is connected through a special valve to a separate gas tank which contains an oxidizing gas such as fluorine. At the appropriate time the valve can be opened and the gas can flow into the combustion bomb and react with the sample.

# EFFECT OF FLUX COMPOSITION ON THE REDUCTION OF URANIUM, THORIUM AND PLUTONIUM OXIDES BY ZINC-MAGNESIUM ALLOY

J. B. Knighton and R. K. Steunenberg

Trans. Am. Nuclear Soc. 4 (2) 352-353 (November 1961)

A survey has been conducted to determine the effectiveness of various halide fluxes on the rate and extent of uranium, thorium, and plutonium oxide reduction by a molten zinc-5 w/o magnesium alloy. Although reductions of this type can be performed in the absence of a flux, several advantages are offered by flux systems: 1) the rate is markedly increased by a properly chosen flux, 2) by-product magnesium oxide is effectively scavenged by the flux and separated from the metallic product dissolved in the alloy, and 3) reductions can, if desired, be conducted in an air atmosphere since the flux protects the alloy from oxidation.

The scope of this discussion is limited to the initial work on this problem, in which the only variable under investigation was the flux composition. Other variables such as temperature, mixing rate, and magnesium concentration in the zinc were arbitrarily fixed and held constant throughout the series of experiments. The effect of flux composition was then determined on the basis of the rate and extent of reduction as a function of time.

Two general conclusions can be drawn from the data from the reduction of  $U_3O_8$ : 1) that rapid and complete reduction of the uranium oxide can be achieved with certain fluxes, using simple equipment and an air atmosphere, and 2) that a systematic relationship exists between the effectiveness of reduction and the atomic weights of alkali and alkaline earth cations present in the flux, the best reductions occurring with the lighter cations. With fluxes consisting of alkali and alkaline earth halides in combination, the effectiveness of reduction decreased in the order Li, Na, K and in the order Mg, Ca, Sr, Ba. Flux systems containing 95 m/o or more alkali metal halides proved to be ineffective. While the reduction rates of thorium dioxide were slower than those of  $U_3O_8$ , the same general relationships between reduction rate and flux composition were observed.

THE KINETICS OF OXIDATION OF URANIUM BETWEEN 125° AND 250°C Leonard Leibowitz, J. G. Schnizlein, J. D. Bingle and R. C. Vogel J. Electrochem. Soc. 108 1155-1159 (December 1961)

Rates of oxidation of uranium have been measured volumetrically at constant pressure in the temperature range  $125^{\circ}-250^{\circ}C$  and at oxygen pressures from 20 to 800 mm. The oxidation is best described by two linear rate laws, a marked increase in rate occurring after an average of 50  $\mu$ g O<sub>2</sub>/cm<sup>2</sup> has been consumed. The first stage rate in  $\mu$ g/cm<sup>2</sup>-min is given by the expression

 $v_1 = 1.48 \times 10^4 P^{1/n} e^{-E/RT}$ 

where E = 10,700 cal, P is oxygen pressure in millimeters of mercury, and 1/n varies with temperature. The reaction is believed to be controlled by process occurring at the gas-oxide surface. The increase in rate leading to the second stage is not treated quantitatively, but is attributed to a net increase in surface area.

## A MICROSCOPIC STUDY OF OXIDE FILMS ON URANIUM Leonard Leibowitz, J. G. Schnizlein, L. W. Mishler and R. C. Vogel J. Electrochem. Soc. <u>108</u> 1153-1155 (December 1961)

Microscopic examination of the surface of uranium during the course of its oxidation has shown that the appearance and growth of oxide nodules coincide with the start of an increase in oxidation rate. Oxidation mechanisms are discussed, and the effects of oxide film cracking and surface area changes are considered.

# THE EFFECT OF AN ELECTRIC DISCHARGE ON THE OXIDATION KINETICS OF URANIUM

J. G. Schnizlein, J. D. Bingle and Leonard Leibowitz

J. Electrochem. Soc. 108 1166-1167 (December 1961) Note

It has been observed that a variety of gas-solid reactions will proceed at an enhanced rate if the gas is activated by an electric discharge. A 1-cm uranium cube was placed in a reaction chamber at a pressure below  $10^{-5}$  mm Hg and heated to 200°C. Oxygen was admitted and its rate of uptake measured while an oxygen pressure of 20 mm was maintained. A marked increase in oxygen consumption resulted from the application of the discharge.

### A RECORDING EFFUSION BALANCE FOR PHASE DIAGRAM INVESTIGATIONS: U-Cd, U-Zn AND Ce-Zn SYSTEMS Ewald Veleckis, C. L. Rosen and H. M. Feder J. Phys. Chem. 65 2127-2137 (December 1961)

Abstract in ANL-6445, p. 49

### THERMODYNAMICS OF THE URANIUM-CADMIUM SYSTEM Irving Johnson and H. M. Feder Trans. A.I.M.E., in press

Galvanic cell measurements with uranium and alloy electrodes were used to obtain the thermodynamic functions for dilute solutions of uranium in liquid cadmium. Even at concentrations as low as  $5 \times 10^{-3}$  atom fraction deviations from Henry's law were observable. The excess thermodynamic functions could be described in terms of "sub-regular" behavior. The unusually large negative values for the partial molar heat of mixing and excess entropy of uranium (at 800°K in infinitely dilute solution,  $H_1^M = -10.7 \text{ kcal}/\text{mole}$ ,  $S_1^E = -20.1$  cal deg/mole with reference to sub-cooled liquid uranium) suggest the occurrence of partial ordering of cadmium atoms around each solute atom. For one gram-atom of the intermetallic UCd<sub>11</sub> the standard heat and entropy of formation from  $\alpha$ -uranium and liquid cadmium were found to be -2280 cal and -3.03 cal deg<sup>-1</sup>, respectively.

The emf investigation independently verified the temperature  $(473^{\circ}C)$  at which peritectic decomposition of UCd<sub>11</sub> into melt +  $\alpha$ -uranium takes place. The known retrograde solubility of uranium in cadmium above this temperature was shown to be attributable to the observed negative partial molar heat of mixing of uranium at the liquidus.

## FLUORINATION OF URANIUM AND PLUTONIUM IN SOLID MIXTURES L. J. Anastasia, Jack Fischer and L. E. Trevorrow Trans. Am. Nuclear Soc. 4 (2) 353-354 (November 1961)

The efficiency of removal of uranium and plutonium by fluorination from mixtures containing solid solutions of plutonium dioxide in uranium dioxide and various inert solids has been determined.

The fluorination experiments were carried out in nickel and Monel apparatus, contained in a glove box. Materials used were fluorine, the mixed oxides of plutonium and uranium, and the inert solids zirconium tetrafluoride, calcium fluoride, and crystalline alumina. Solid solutions of uranium and plutonium dioxides were prepared following the procedure recommended by Wilson.

In a typical fluorination experiment a weighed quantity of solids was spread in a layer,  $\frac{1}{32}$  to  $\frac{1}{8}$  in. deep, on the flat bottom of a shallow, nickel reaction boat which was placed inside a horizontal, tubular furnace. After the system was evacuated and heated to the fluorination temperature, it was filled with fluorine to a pressure of about one atmosphere. Fluorine was then circulated over the sample at a rate of about 800 cc/min. The residual solids were mixed thoroughly. Samples were taken from this mixture and dissolved completely prior to analysis. The solutions were analyzed for plutonium by alpha counting and for uranium by a fluorophotometric analysis.

Adequate removal of uranium was achieved for each solid. Inadequate removal of plutonium resulted when reactions with fluorine were made at 350°, 450° and 550°C, using zirconium tetrafluoride or calcium fluoride as solids. Pure crystalline aluminum oxide (Norton's Blue Label 60 mesh Alundum) has been shown to be better for use as an inert solid than calcium fluoride and zirconium tetrafluoride. PLUTONIUM HEXAFLUORIDE THER MAL DECOMPOSITION RATES Jack Fischer, L. E. Trevorrow, G. J. Vogel and W. A. Shinn Ind. Eng. Chem. Process Design & Development <u>1</u> (1) 47-51 (January 1962)

The Direct Fluorination Volatility Process is being developed at Argonne National Laboratory to recover uranium and plutonium from spent uranium dioxide power reactor fuels. After removal of the cladding, the fuel will be treated with fluorine to convert the oxides to the respective fluorides. Uranium can be separated from plutonium by taking advantage of the difference in rates of fluorination of the tetrafluorides and the difference in chemical reactivities of the hexafluorides. Uranium and plutonium will be recovered separately and highly decontaminated from fission products.

Uranium hexafluoride is relatively stable at elevated temperatures, whereas plutonium hexafluoride undergoes thermal decomposition to plutonium tetrafluoride and fluorine. Knowledge of the equilibrium constant and rate of thermal decomposition of plutonium hexafluoride are of prime importance in many steps of the direct fluorination volatility process. Both the stoichiometry and the equilibria involved in the decomposition of plutonium hexafluoride have been investigated previously.

The rate of thermal decomposition of plutonium hexafluoride vapor has been studied by a static method at initial pressures of 17 to 98 cm at a temperature of 161°C. The rate has also been studied by a flow method at lower partial pressures and at temperatures from 150° to 250°C. Laboratory work has been carried out on the fluorination of plutonium dioxide and tetrafluoride and also on the efficiency of transport of plutonium hexafluoride which illustrates the use of equilibriums and kinetic data and their importance to the process.

The rate of decomposition is dependent both on the surface area of plutonium tetrafluoride and on the pressure of plutonium hexafluoride. Experimental results on the thermal decomposition have been fitted to a rate equation assuming concurrent first and zero orders with respect to plutonium hexafluoride pressure. Maximum recovery of plutonium hexafluoride from a fluorination reactor was obtained by cooling the effluent rapidly to a temperature below  $150^{\circ}$ C. Plutonium hexafluoride has been transferred with recoveries of greater than 99.3% at temperatures of 25° to 70°C. The transfers were made by distillation and by transpiration in fluorine or helium.

#### VERSATILE SCRUB TOWER REMOVES HALOGEN OFF-GAS

#### J. T. Holmes

Chem. Eng. 68 94 (December 25, 1961)

A simple, versatile and very efficient scrub system can be constructed of standard flanged glass pipe for the disposal of halogen or halogen acid off-gases from small scale pilot plants. The halogen gases react with anhydrous ammonia in the space below the column packing to form a smoke of ammonium halide. Water is sprayed into the top of the column and dissolves the solid ammonium halide from the column walls and packing.

### SOME METALLURGICAL APPLICATIONS OF AUTORADIOGRAPHY M. D. Adams and R. K. Steunenberg ANL-6412 (October 1961)

Macro- and high-resolution methods for autoradiography were used to investigate a number of problems concerning the distribution of uranium and other active elements in metal specimens. Illustrations are presented of the behavior of some of these materials with various heating and cooling treatments and in the presence of metals with which intermetallic phases are formed. Techniques are discussed for handling and examining autoradiographic stripping films by means of various types of metallurgical and conventional microscopic equipment.

# A FAMILY OF INTERMEDIATE PHASES HAVING THE $\mathrm{Si}_2\mathrm{Mo-TYPE}$ STRUCTURE

M. V. Nevitt and J. W. Downey A.I.M.E. Trans., in press Note

Eight binary compounds isostructural with  $Ti_2Cu$  [having the  $Si_2Mo-$ type (Cllb) structure] have been found. They are  $Zr_2Cu$ ,  $Hf_2Cu$ ,  $Ti_2Pd$ ,  $Zr_2Pd$ ,  $Hf_2Pd$ ,  $Zr_2Ag$ ,  $Zr_2Au$  and  $Hf_2Au$ . The lattice parameters were determined by a least squares analysis of the back reflection lines of patterns made with Co radiation. The evidence supporting the large tetragonal cell containing six atoms involves the presence of the reflections 002, 101, 004, 112, 114, 202 and other reflections with higher indices for which  $l \neq 3n$ . Three or more reflections corresponding to these indices, which cannot be indexed on the basis of a small body-centered tetragonal cell containing two atoms, are observed in the patterns of all the compounds. They are strongest and most numerous when the case in  $Ti_2Pd$ ,  $Zr_2Cu$  and  $Hf_2Cu$ .

Values of the z parameter were selected on the basis of the best agreement between the observed intensities of two pairs of closely spaced powder pattern lines (004):(112) and (114):(202) and the corresponding intensities calculated for several values of z. An ordering scheme was assumed in which Ti, Zr or Hf atoms occupy the Ti positions of Ti<sub>2</sub>Cu and Cu, Ag, Pd or Au atoms occupy the Cu positions.

THE EFFECT OF MANGANESE AND SILICON CONTENT ON THE HOT WORKABILITY OF TYPE 304 STAINLESS STEEL CONTAINING 2 w/o BORON

L. C. Hymes and Nicholas Balai\* ANL-6393 (October 1961)

Increased hot workability of Type 304 stainless steel containing approximately 2 w/o boron was obtained by maintaining the manganese and silicon contents of the alloy above minimum levels of 1.40 w/o and 0.60 w/o, respectively. Close control of the range of temperatures over which hot working was carried out was also demonstrated to be of importance. However, over the range investigated variation in the temperature of hot working was of secondary significance as compared with alloy composition.

\*Reactor Engineering Division

THE MORPHOLOGY OF SURFACE REACTION PRODUCTS ON ALUMINUM

R. K. Hart and W. E. Ruther

J. Nuclear Materials 4 (3) 272-280 (August-September 1961)

Abstract in ANL-6394, p. 67

NEUTRON DIFFRACTION STUDY OF Zn<sub>X</sub>Mn<sub>1-x</sub>Fe<sub>2</sub>O<sub>4</sub> Jerome Woyci,\* Victor Hicks\* and S. S. Sidhu Structure de la Matiere <u>22</u> (6) 411 (1961)

Abstract in ANL-6298, p. 63

α-MANGANESE PHASES CONTAINING TECHNETIUM-99 D. J. Lam, J. B. Darby, Jr., J. W. Downey and L. J. Norton Nature 192 744 (November 25, 1961) Letter

During the course of investigation of alloy phases involving technetium-99 with transition metals,  $\alpha$ -manganese phases were found in the binary systems scandium-technetium, titanium-technetium, hafnium-technetium and tantalum-technetium. The alloys were made by arc-melting transition metals of high purity with technetium-99. X-ray data were obtained from specimens in the as-cast condition with a powder camera of 114.6-mm diameter using filtered copper radiation.

In the present investigation lattice dimensions of technetium-99 were obtained from an annealed needle of high purity technetium-metal. The dimensions are as follows:  $a_0 = 2.743 \pm 0.001$  A,  $c_0 = 4.400 \pm 0.001$  A, and c/a = 1.604. These lattice parameters are probably more accurate than those recently reported by Mooney who had a slight impurity in his mixed sample.

NUCLEAR MAGNETIC RESONANCE OF  ${\rm Tc}^{99}$  IN Tc METAL AND  ${\rm Tc}^{99}$  AND  $V^{51}$  IN Tc-V ALLOYS

D. O. Van Ostenburg, H. D. Trapp and D. J. Lam Bull. Am. Phys. Soc. <u>6</u> 444 (November 1961) Abstract Phys. Rev., in press

The nuclear magnetic resonance of  $Tc^{99}$  has been observed in Tc metal and its Knight shift measured relative to a solution of  $CsTcO_4$ . The  $Tc^{99}$  and  $V^{51}$  resonances have been studied in 50-50 atomic per cent TcV and TcV<sub>3</sub> alloys as a function of field and temperature. The  $Tc^{99}$  resonance curves in TcV and TcV<sub>3</sub> have a Lorentzian shape while  $V^{51}$  is Gaussian in TcV and Lorentzian in TcV<sub>3</sub>. Probable causes for the shape changes and excess widths encountered are discussed.

\*Allen-Bradley Company

### NEUTRON DIFFRACTION STUDIES OF THE ZIRCONIUM-DEUTERIUM SYSTEM

S. S. Sidhu, LeRoy Heaton and M. H. Mueller Structure de la Matiere 22 (6) 411 (1961)

Abstract in ANL-6298, p. 66

ZIRCONIUM ALLOYS FOR USE IN SUPERHEATED STEAM

Sherman Greenberg

J. Nuclear Materials 4 (3) 334-335 (August-September 1961)

Abstract in ANL-6394, p. 63

# ADIABATIC ELASTIC MODULI OF SINGLE CRYSTAL ALPHA ZIRCONIUM

E. S. Fisher and C. J. Renken

J. Nuclear Materials 4 (3) 311-315 (August-September 1961)

Abstract in ANL-6445, p. 54

# PRECIPITATION OF ZIRCONIUM HYDRIDE IN ALPHA ZIRCONIUM CRYSTALS

D. G. Westlake and E. S. Fisher Trans. A.I.M.E., in press

The habit planes for zirconium hydride precipitation in crystals of alpha zirconium have been determined at various hydrogen concentrations. The  $\{10.0\}$  planes are the predominant habit planes; some  $\{10.5\}$  and  $\{10.1\}$  planes were observed after charging conditions which permitted formation of a surface layer of hydride. No platelets were observed parallel to any of the twinning planes. Mechanisms for embrittlement due to hydride precipitation are discussed.

THE EFFECT OF ADDITIVES ON THE DENSIFICATION OF URANIA-THORIA COMPOSITIONS

G. D. White

ANL-6375 (November 1961)

An investigation is reported of the effect of several oxide additives on the densification of  $UO_2$ -ThO<sub>2</sub> compositions in which  $U_3O_8$  is the initial uranium oxide. The investigation also determined the effects on densification of variation of the compaction pressure and of the pretreatment of the oxide powders. The validity of results were checked by two forming techniques, dry pressing and extrusion. The results are indicated as follows:

- Additives had an increasing effect on densification with decreasing ThO<sub>2</sub> content.
- 2. The oxides of transition elements were most effective as additives for improving the densification.
- 3. Varying the forming pressure had little effect on densification.
- 4. Precalcination of the initial powders was effective in improving densification.
- 5. Similar results as above can be achieved with extruded as well as dry-pressed specimens.

# EFFECTS OF ROLLING AND HEAT TREATMENT ON ANISOTROPIC IRRADIATION GROWTH OF URANIUM

J. H. Kittel

ANL-6344 (November 1961)

An investigation was made to determine the effect of rolling temperature, roll pass design, amount of reduction, and heat treatment before and after rolling on the anisotropic growth rate of uranium under irradiation. The growth rate was found to increase with decreasing rolling temperature and with increasing reduction of area at 300°C. The rate of elongation was proportional to the amount of (010) component present or, where shortening occurred, to the amount of (100) component. Ovaledge-oval roll passes resulted in somewhat higher irradiation growth rates than did round roll passes. Recrystallization after rolling effectively reduced the irradiation growth rate of uranium rolled at temperatures of 500°C and lower. Irradiation caused length shortening in uranium which was beta quenched after being round-rolled at temperatures of 400°C and above, and which was beta quenched after being oval-rolled at temperatures of 300°C and above. IRRADIATION OF METAL-FIBER-REINFORCED THORIA-URANIA

L. A. Neimark, J. H. Kittel and C. L. Hoenig ANL-6397 (December 1961)

Bull, Am. Ceram. Soc. 40 587 (1961)

#### Abstract

Randomly oriented fibers of either molybdenum or niobium have been incorporated into hot-pressed pellets of 10, 30, and 50 w/o UO<sub>2</sub> in ThO<sub>2</sub> to improve thermal conductivity and thermal shock resistance. Pellets, 9.5 mm in diameter and 9.5 mm in length, were irradiated in NaK capsules, both bare and jacketed with Zircaloy-2, with the annulus between pellet and jacket filled with lead or helium. They were irradiated to burnups ranging up to 34,500 MWD/T ( $1.0 \times 10^{21}$  fiss/cc) at central temperaturess of the order of 3000°C. Integral kd $\theta$  values ranged from 34 to 129 w/cm.

Fracture and metallographic sections of the irradiated specimens confirmed out-of-pile measurements that the molybdenum fibers increased the effective thermal conductivity of the mixed oxides. It was possible to give the fibered pellets higher heat ratings than unfibered pellets before comparable thermal effects occurred. The fibers tended to reduce central void formation, retard recrystallization, and maintain the integrity of the pellet. In some helium-bonded specimens, the molybdenum fibers coalesced into a central sphere after melting during irradiation. The coalescence did not occur in lead-bonded specimens. The niobium fibers were found to react with the oxide.

Fission gas release from unclad fibered pellets was a maximum of 15.3% of theoretical at a burnup of 31,500 MWD/T (8.3 x  $10^{20}$  fiss/cc) and an integral kd $\theta$  value of 57 w/cm. Gas release from similarly irradiated unfibered pellets was a maximum of 6.3% at 21,800 MWD/T (6.6 x  $10^{20}$  fiss/cc) and an integral kd $\theta$  value of 92 w/cm. The disparity in gas release is attributed to the breaking into pieces of the unfibered pellets early in the irradiation and their consequent operation at significantly lower temperatures than the fibered pellets.

EXAMINATION OF URANIUM FROM THE FIRST CORE OF THE EBR-I W. F. Murphy, A. C. Klank and S. H. Paine ANL-6113 (September 1961)

The changes due to neutron irradiation which occurred in the highly enriched uranium fuel slugs of the first core of the EBR-I have been related to burnup (0 to 0.3 a/o) and to temperature (285 to  $395^{\circ}\text{C}$ ). Initially, the slugs increased in length with increase in burnup, but at higher burnups the direction of growth reversed itself, and the slugs tended to shrink to less than their original lengths. Temperature became an important factor at the higher levels of burnup in that the ratio of length change to burnup decreased with increasing temperature. Diameter changes were the inverse of the changes in length. Density decreased almost linearly with burnup and was not affected by temperature. Hardness increased with increasing burnup but the rate of increase decreased both with increasing burnup and temperature.

#### US AND THS BODIES

P. D. Shalek

Industrial Heating 28 2260 (1961)

Abstract

Abstract in ANL-6349, p. 63

OXIDATION AND PHASE STABILITY IN THE SYSTEM URANIUM OXIDE-LANTHANUM OXIDE

D. C. Hill

Industrial Heating 28 2260 (1961)

Abstract

Abstract in ANL-6349, p. 64

#### PRELIMINARY STUDIES IN THE SYSTEM UC-PuC

R. C. Lied and G. D. White

Bull. Am. Ceram. Soc. <u>40</u> 588 (1961) Abstract

Plutonium monocarbide, uranium monocarbide, and 20 weight per cent plutonium-uranium monocarbide solid solution were prepared by reacting the respective oxides with carbon. Data are given on the densification, vaporization, chemical analyses, and x-ray diffraction for the materials. Microphotographs of microstructures are also presented.

#### THE UNIT CELL OF U2Ru

A. F. Berndt

Acta Cryst. 14 1301-1302 (December 1961) Note

The compound  $U_2Ru$  is monoclinic (space group either  $P_{2/m}$  or  $P_{2_1/m}$ ) with a = 13.106 ± 0.0014A, b = 3.343 ± 0.002A, c = 5.202 ± 0.0009A,  $\beta = 96^{\circ} 9.6^{\circ} \pm 2.8^{\circ}$ . There are 4 formula units per unit cell. The structure may be considered to consist of layers of atoms parallel to (001). Alternate layers contain only U atoms with the intermediate layers having the atomic composition 1/3 U, 2/3 Ru. The interatomic distances compare favorably with the sum of Pauling's metallic radii.

### GROOVE ETCHING IN URANIUM MONOSULPHIDE

J. P. Hugo and P. D. Shalek

J. Inst. Metals, in press

The microstructure of high-density, high-purity, sintered uranium monosulphide bodies consists of a matrix, which is the monosulphide US of fairly large grain size and an intergranular phase, which is the oxysulphide UOS. Etching generates a Widmanstatten structure in the US matrix. At high magnification it is seen that this structure consists of a series of grooves seldom traversing more than a fraction of the grain diameter and rarely extending to a grain boundary. In many cases one set of parallel grooves etches to greater width, and these grooves appear to contain a series of parallel steps. A number of the wide grooves show apparent curvature, notably in the neighborhood of pores or grain boundaries. Electron micrographs established definitely that the pattern consisted of etching grooves and not a dispersed phase and also revealed that the wide grooves do not contain steps; they are, in fact, shallow, plain, flat-faceted grooves. The Widmanstatten character of the groove etching indicates that in all probability the (111) planes of the f.c.c. US are suffering the preferential attack. This consideration and other characteristics of the grooves yield the clue that the grooves represent the selective etching of stacking faults.

### QUELQUES PROBLEMES DE LA METALLURGIE PHYSIQUE DE L'URANIUM

### Bernhard Blumenthal

Revue Universelle de Mines de la Metallurgie de la Mecanique, 9th Ser., Vol. 17, January 1961. pp. 13-20

Abstract in ANL-6425, p. 64

# THE VOLATILITY BEHAVIOR OF LANTHANA-URANIA SOLID SOLUTIONS

D. C. Hill

J. Am. Ceram. Soc., in press Note

The oxidation and volatilization characteristics of  $UO_2$  have limited its use as a reactor fuel to temperatures far below the material's ultimate capability. This note is concerned with the volatility behavior of urania-lanthana solid solutions subjected to oxidizing environments at high temperatures. Sintered compacts of known metal atom content and stoichiometry were heat-treated in a gas fired furnace at 1675°C for 25, 136, and 310 hours. Combustion gases, slightly rich in oxygen were passed over the specimens during firing. Weight, density and microstructural changes were used as indications of urania loss by vaporization.

Lanthana-urania specimens containing 60 to 80 mole per cent  $LaO_{1.5}$  had very low weight losses, and their loss rates were nearly constant. Examination of their microstructure indicated that grain growth and densification had occurred and that the specimen surfaces were relatively inert to attack by the furnace gases.

High urania specimens containing 20 to 50 mole per cent  $LaO_{1.5}$ , however, had much higher weight losses, and their exposed surfaces appeared to be attacked by the furnace gases. Attack of high urania specimens appears to occur by urania vaporization along grain boundaries. A decrease in the volatility rate, possibly due to vapor saturation within the porosity channels was noted after long exposure.

The transition between volatile and nonvolatile compositions (55 to 60 mole per cent  $LaO_{1.5}$ ) had intermediate surface attack and weight losses.

Solid solutions containing more than 65 mole per cent  $LaO_{1.5}$  have analyzed oxygen to metal atom ratios below the stoichiometric  $MO_{2.00}$  composition. Specimens exhibiting appreciable vaporization, however, have stoichiometries in excess of 2.00. The change from an oxygen deficient to an oxygen excess structure appears to be a significant factor in the volatility behavior of these solid solutions.

## INFLUENCE OF GAS FLOW ON DTA CURVES OF UO<sub>2</sub> Drago Kolar, E. D. Lynch and J. H. Handwerk

J. Am. Ceram. Soc., in press Note

Differential thermal analysis (DTA) has been used to study the oxidation behavior of UO2. The DTA curves, supported by thermogravimetric analysis, in general show two exothermal peaks, identifying the two step reaction  $UO_2 \longrightarrow U_3O_7 \longrightarrow U_3O_8$ . However, the shapes of the peaks and peak temperatures differ with samples of different origin. A correlation of temperature separation between the two peaks and surface areas of samples has been shown and used as a measure of reactivity for various UO<sub>2</sub> preparations. The previously reported investigations of UO<sub>2</sub> have been made under static conditions in air. The diffusion of gases, in particular oxygen, within the sample may alter the DTA results significantly. Accordingly, DTA curves for UO, were made using a flowing-gas technique. The DTA curve using the standard "static air" technique differed considerably from the curve for the same powder in which oxygen was passed through the sample bed at a flow rate of about 25 cc/min. The observed differences can be explained on the basis of suggested mechanisms for oxidation of UO<sub>2</sub>. The shape of the first peak  $(UO_2 - U_3O_7)$  corresponding to a diffusion controlled reaction is not appreciably affected by flowing oxygen, as may be expected. The second peak, reported to indicate the break up of particles with subsequent oxidation to  $U_3O_8$ , is strongly affected by oxygen flow. It is obvious that oxygen availability plays an important role for the  $U_3O_7 - U_3O_8$  oxidation step.

### PLUTONIUM METALLURGY AT ARGONNE NATIONAL LABORATORY F. G. Foote

The Metal Plutonium, ed. A. S. Coffinberry and W. N. Miner. Chicago: The University of Chicago Press, 1961. pp. 63-69

Plutonium is one of the three major fissionable isotopes, and although it occurs in nature only in minute amounts, it is potentially a relatively abundant material since it can be made by a series of nuclear reactions from  $U^{238}$ , the major isotope of natural uranium. The most attractive use of plutonium is as fuel in fast breeder reactors. Also, since plutonium is a fissionable material, it can be burned in a thermal reactor much as  $U^{235}$ . Although plutonium has many advantages and can be used in many types of fuel it is not more widely used because of its extraordinary toxicity and the precautions which must be taken to handle safely even small amounts of plutonium and plutonium-containing materials. At Argonne a philosophy of complete confinement has been adopted; the facilities for plutonium handling at Argonne are described.

### THE PREPARATION OF HIGH PURITY PLUTONIUM

Bernhard Blumenthal and M. B. Brodsky

Proc. Conf. Intern. sur la Metallurgie du Plutonium, Grenoble, April 19-22, 1960. London: Cleaver-Hume, 1961. pp. 171-186

Abstract in ANL-6197, p. 49

### CORROSION OF ZIRCONIUM ALLOYS IN SUPERHEATED STEAM

R. D. Misch and Sherman Greenberg

Proc. Tenth Ann. AEC Corrosion Symp., San Diego, May 9-11, 1961, ed. M. T. Simnad. General Atomic Division of General Dynamics, San Diego, September 1, 1961. p. 23 Abstract

Fifty-nine binary zirconium alloys containing twenty different elements were studied in 350°C water and 540°C, 600 psi steam for comparison with previous data in 700°C oxygen. In addition, the EMF of the growing scale was measured in 700°C oxygen. The EMF is dependent upon the resistance of the  $ZrO_2$  scale and approaches the theoretical EMF as the electronic resistance becomes large. The most favorable alloying combinations in steam were those where the alloys obey a cubic law in oxygen (up to 1400 min) and have low film resistance. Theoretical considerations based on these data are described.

# THE KINETICS OF THE CORROSION OF 1100 ALUMINUM IN 70°C, OXYGEN SATURATED DISTILLED WATER

J. E. Draley and Shiro Mori

Proc. Tenth Ann. AEC Corrosion Symp., San Diego, May 9-11, 1961, ed. M. T. Simnad. General Atomic Division of General Dynamics, San Diego, September 1, 1961. p. 25 Abstract

The corrosion curve for 1100 aluminum in 70°C, oxygen saturated water has been obtained, using the eddy current-thickness gauge. This method has several advantages over both weight gain and corrosion coat stripping methods. A number of equations have been applied to the data. One based on a two film theory, and similar to Haycock's equation, fitted the data. Equations derived by considering that individual sites corrode logarithmically in cycles are being studied.

# ELECTRICAL MEASUREMENTS ON THE GROWING SCALE ON ZIRCONIUM-TITANIUM ALLOYS

R. D. Misch and G. W. Iseler ANL-6434 (October 1961)

The corrosion rates of low-titanium zirconium alloys increase with titanium content when exposed to water at 290°C or to 1-atm oxygen at 290, 350, 400, and 500°C. The scaling rate reaches a maximum (approximately 3000 mg/dm<sup>2</sup> for 3-hr exposure) at 15 a/o Ti in 1-atm oxygen at 500°C and then decreases with increasing titanium content. Under the same conditions, pure zirconium and titanium had much lower weight gains, 10 and 4 mg/dm<sup>2</sup>, respectively.

In oxygen at 500°C, the oxidation rate law is initially cubic or parabolic for alloys containing 3.75, 15.0, and 50.0 a/o Ti, and then changes to approximately a linear one. The transition times are 17,7, and 54 min for the 3.75, 15.0, and 50.0 a/o Ti alloys, respectively.

Transition in the rate law and the rise in EMF and resistance appear to be independent variables. The electrical changes are attributed to changes in defect structure, and the rate law transitions are attributed to structural changes.

The results provide an explanation for the maximum oxidation rate at 15 a/o Ti and for the differences in the influence of additives on the corrosion rates of zirconium and titanium in high temperature water.

The EMF of the corrosion cell consisting of  $[alloy | oxide | O_2]$  was a function of the resistance of the oxide layer. The 3.75 and 15.0 a/o Ti alloys had small EMF's and resistances initially, but EMF and resistance increased appreciably and rapidly at times after the transition stage. The 50 a/o Ti alloy had a very small EMF which was relatively constant while the resistance showed a slight increase with time.

### EFFECT OF OXYGEN CONCENTRATION ON THE AQUEOUS CORROSION OF IRON AND STEEL

W. E. Ruther and R. K. Hart

Proc. Tenth Ann. AEC Corrosion Symp., San Diego, May 9-11, 1961, ed. M. T. Simnad. General Atomic Division of General Dynamics, San Diego, September 1, 1961. p. 28 Abstract

The corrosion behavior of pure iron in water containing concentrations of oxygen from < 0.1 to 540 ppm has been determined for a range of temperatures from 50°C to 315°C.

When sufficient oxygen is present at temperatures from 100° to 260°C a smooth, tightly adherent corrosion film is formed, and no pitting or accelerated attack is noted. If slightly less than adequate oxygen is present in the water, the temper film forms but pitting and undercutting of the film take place at numerous sites. The average metal loss rates are still low with marginal oxygen but pit sites are deep.

As the oxygen concentration is decreased further, depending on the temperature, the attack becomes general and, by comparison, quite rapid. Finally, as the oxygen content is reduced to about 0.1 ppm, the attack is uniform and the corrosion rate is low.

Evaluation of binary alloys made from the pure iron and many of common constituents of low alloy steels indicates that chromium and carbon are particularly useful in the formation of tight protective films under marginal oxygen conditions.

The corrosion rates of iron and selected alloy steel are compared for deoxygenated and adequately oxygenated tests at 260°C.

Electron micrographs have been obtained showing the morphology of the corrosion product.

Identification of some of the constituents of the corrosion product has been accomplished through interpretation of selected area electron diffraction patterns.

THE USE OF NUCLEAR NULL-MATRIX IN NEUTRON DIFFRACTION STUDIES OF CRYSTAL STRUCTURES AND MAGNETIC STRUCTURES S. S. Sidhu, LeRoy Heaton and M. H. Mueller Structure de la Matiere 22 (7-8) 511 (1961)

Abstract in ANL-6298, p. 64

### AN INFORMATIVE RADIOGRAPH FROM THE SCATTERED BEAM

N. S. Beyer, N. P. Lapinski and R. B. Perry

Nondestructive Testing 19 (6) 408-409 (November-December 1961)

An example of a radiograph produced by scattered radiation, which displays desired detail unobtainable by conventional techniques, is presented. The problems requiring the scattered radiograph and technique used to produce it are described. Reproductions of a scatter and conventional radiograph are presented for comparison.

GLASSY MATERIALS FOR NUCLEAR REACTOR APPLICATIONS J. H. Handwerk, E. D. Lynch and V. K. Moorthy Industrial Heating 28 2258 (1961) Abstract

Abstract in ANL-6445, p. 57

# VISUALIZATION OF INTERNAL STRUCTURE IN METALS USING NEUTRON RADIOGRAPHY

Harold Berger Trans. ASM, in press

A means of visualizing the grain and crystal structure differences within a metal sample can be achieved by the use of neutron radiographic techniques. A radiographic study of a nickel sample is presented in which comparisons are made between surface structure, as shown by metallographic methods and internal structure, as shown by neutron and xradiographic methods. Similarities between the metallographic pictures and the neutron radiographs are evident, although differences are noted and expected because the metallographic picture shows only the surface structure while the neutron radiograph displays the structure throughout the thickness of the sample. Other metals in which grain structure differences have been found by neutron radiography include chromium, iron and molybdenum-tungsten alloy. A note on the techniques used to obtain the neutron radiographs is also presented.

# RADIATION RESISTANT, REMOTELY OPERATED, HIGH CAPACITY SPRING BALANCE

J. E. Ayer and G. J. Pokorny

Rev. Sci. Instr. <u>32</u> 1114-1116 (October 1961)

Abstract in ANL-6445, p. 59

