oxygen reactions (1), (2), (3), (4), (5), (6) and (7) are followed. Therefore reaction (1) leads to the oxidation of four ferrous ions in the presence of oxygen and one ferrous ion in the absence of oxygen, whereas but one ferrous ion is oxidized per water molecule dissociated in reaction (2) whether oxygen is present or not. Let X equal fraction of total water molecules dissociated in (1) and $1 - X$ the fraction in (2) and we have for R: $R = 3X + 1$.

The fraction of radicals formed in the experiments of former investigators is compared in Table I with those of the present work using Co^{60} γ-rays and tritium β-rays.

TABLE I

EFFECT OF TYPE OF IONIZING RADIATION ON FREE RADICAL FORMATION IN THE OXIDATION OF FERROUS SULFATE IN 0.8 N SULFURIC ACID

	Radiation	(R)	Fraction of Radicals Formed in Reaction (1)	Fraction of Radicals Formed in Reaction: (2)
Fricke, *et al.*[3]	X-Rays	2.55	0.52	0.48
Shishacow[4]	X-Rays	2.59	0.53	.47
Krenz and Dewhurst[2]	γ-Rays	4.0	1.00	.00
Miller[5]	γ-Rays	2.7	0.57	.43
Present work	γ-Rays	2.86	0.62	.38
Present work	β-Rays	2.59	0.53	.47

It is significant that the fractions of radicals formed in reaction (1) in the Fricke and Shishacow X-ray work and the present tritium β-ray work are similar and less than the fraction of radicals obtained for γ-rays. This is the expected trend, since the 5690 ev. electron from tritium disintegration has but one per cent. the energy of the recoil electron from the Co^{60} γ-ray interaction with water. Special mention must be made of the ratio 4.0 reported by Krenz and Dewhurst, who attributed lower values to traces of oxygen in evacuated samples. Here exhaustive means were taken to insure the removal of oxygen but it is possible, as was indicated by our work and as suggested by Miller,[5] that impurities suppressing the air-free reaction were introduced by their high vacuum method.

The present work was carried out on 0.5 mN ferrous sulfate in 0.8 N sulfuric acid using an evacuation technique[6] capable of reducing the oxygen content of dilute aqueous formic acid solutions to less than 10^{-6} M. The γ-ray dose-rate was 18000 r per hour and the tritium water activity was 0.157 curies per ml. Since R is very sensitive to methods of preparation and treatment of the ferrous sulfate solutions, the γ-ray irradiation was carried out on the tritium solution of ferrous sulfate and a correction for the tritium-induced oxidation made.

With 12.46 years half-life and average β-energy of 5690 ev.[7] for tritium, these experiments show that one radial pair in water requires 17.9 ev. in the absence of oxygen and 17.6 ev. in the presence of oxygen. These values are lower than the 32.5 ev. generally assumed for ion-pair formation in gases.

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(5) N. Miller, private communication, December 2, 1950.

(6) E. J. Hart, THIS JOURNAL, **73**, 68 (1951).

(7) G. H. Jenks, F. H. Sweeton and J. A. Ghormley, ORNL-333 (March 28, 1950).

ON THE STRUCTURE OF ELEMENTARY BORON[1]

Sir:

We have found an approximate structure for one modification of elementary boron from a study of the needle-like single crystals prepared earlier in this Laboratory.[2] Complete (CuKα) Weissenberg photographic X-ray data together with the density,[2] 2.31 g./cc., establish a tetragonal unit with $a = 8.73 \pm 0.02$, $c = 5.03 \pm 0.02$ Å., containing fifty atoms. The observed symmetry and glide plane vanishings are characteristic of $D_{4h}^{14}-P4/mnm$, $C_{4v}^{4}-P4nm$, and $D_{2d}^{8}-P\bar{4}n2$, but the absence of peaks in the Patterson section P(00Z) virtually eliminates D_{4h}^{14}. In terms of D_{2d}^{8} the "ideal" structure uses the positions 2(b): 00 $^1/_2$; $^1/_2$ $^1/_2$ 0 and 8(i) with the parameters:

	x	y	z		x	y	z
I	0.328	0.095	0.395	IV	0.078	0.223	0.105
II	.095	.328	.395	V	.127	.127	.395
III	.223	.078	.105	VI	.250	.250	−.078

The same arrangement with a different grouping of equivalent atoms is obtainable from C_{4v}^{4} (but not from D_{4h}^{14}). The forty-eight atoms in general positions are arranged at the vertices of four nearly regular icosahedra centered at $^1/_4$ $^1/_4$ $^1/_4$; $^3/_4$ $^3/_4$ $^1/_4$; $^1/_4$ $^3/_4$ $^3/_4$; $^3/_4$ $^1/_4$ $^3/_4$. These icosahedra are linked together so that every boron atom of a group forms six bonds directed toward the corners of a pentagonal pyramid. The two atoms in 2(b) form only four tetrahedrally directed bonds, but are needed to complete in detail the three-dimensional network.

This structure accounts remarkably well for numerous Patterson sections. A Fourier synthesis of (hk0) amplitudes, $h + k$ even, nearly reproduces the ideal structure in projection on (001). The phases of the few weakly observable (hk0) reflections with $h + k$ odd differ for C_{4v}^{4} and D_{2d}^{8}, but no basis for a choice is as yet apparent. A second Fourier projection along [1$\bar{1}$0], assumed centrosymmetric on the basis of D_{2d}^{8}, also shows the structure to be approximately correct. This projection, however, could be interpreted as an approximation to the real part of a complex synthesis based on C_{4v}^{4}, the imaginary contribution being small. To resolve the space-group ambiguity and to improve the quality and range of the data we plan to measure intensities on our spectrometer with MoKα radiation. We have begun also a study of the more complex plate-like crystals obtained in the earlier study.[2] It seems probable that this modification, with a unit volume about four times that of the tetragonal form, is present in the usual microcrystalline preparations.

The average bond distance in tetragonal boron appears to lie in the range 1.75–1.80 Å., somewhat smaller than Godfrey and Warren's 1.89 Å. (obtained from a Fourier integral analysis of powder data[3]), but agreeing with the data for boron car-

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(1) Supported in part by a grant from the Research Corporation, in part by the Atomic Energy Commission under contract with Cornell University.

(2) A. W. Laubengayer, D. T. Hurd, A. E. Newkirk and J. L. Hoard, THIS JOURNAL, **65**, 1924 (1943).

(3) T. N. Godfrey and B. E. Warren, *J. Chem. Phys.*, **18**, 1121 (1950)

bide[4] and decaborane.[5] The linked icosahedra in boron and boron carbide give strong network structures in which surprisingly large holes are interspersed among the very compact icosahedral groups.

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[4] H. K. Clark and J. L. Hoard, THIS JOURNAL, **65**, 2115 (1943).

[5] J. S. Kasper, C. M. Lucht and D. Harker, *Acta Cryst.*, **3**, 436 (1950).

[6] Du Pont Post-Doctoral Fellow, 1949–1950.

CHROMATOGRAPHY OF PROTEINS. RIBONUCLEASE

Sir:

It has been demonstrated that elution analysis is capable of extremely high resolving power when either starch columns[1] or ion exchange resins[2] are used for the fractionation of mixtures of amino acids. The advantages of bringing proteins within the scope of such chromatographic methods are too obvious to require elaboration. After many unsuccessful attempts, employing several different proteins and numerous adsorbents, satisfactory chromatograms have been achieved with ribonuclease and with lysozyme on columns of the carboxylic acid resin IRC-50. A finely ground preparation of the resin (XE-64, 250 to 500 mesh) was employed, for which we are greatly indebted to Dr. James C. Winters of The Rohm and Haas Company. It should be mentioned that Paléus and Neilands[3] have employed columns of IRC-50 for the purification of cytochrome C.

The results obtained with ribonuclease are given in Curve A of Fig. 1. About 3 mg. of crystalline ribonuclease (assaying 44 units per mg.), kindly supplied by Dr. M. Kunitz, was chromatographed. The protein concentration (solid circles) in the effluent was measured by the photometric ninhydrin method[4] and the ribonuclease activity (open circles) by the spectrophotometric method of Kunitz.[5] It can be seen that about three-fourths of the ninhydrin positive material emerges as a sharp peak around 18 effluent cc. Ahead of this peak, however, beginning at about the column volume (6 cc.), approximately one-fourth of the material appears as a spread out zone. The position of the main peak may be changed at will by variations in the *p*H of the eluting buffer. With phosphate buffers of lower *p*H the protein travels more slowly; with a higher *p*H, more rapidly.

It is of interest that ribonuclease emerges from the column with its enzyme activity undiminished, and further, that the amount of activity and the ninhydrin color value parallel one another very closely. If the material in the two peak fractions of Curve A is pooled and rechromatographed, a single symmetrical peak (Curve B) is obtained.

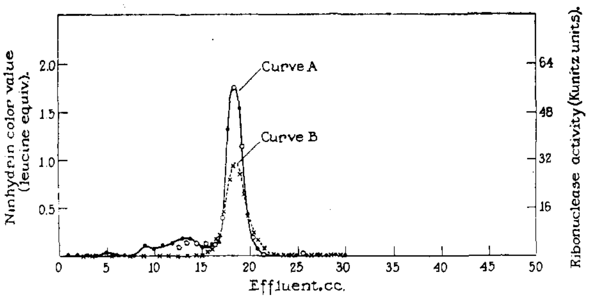

Fig. 1.—Chromatography of ribonuclease. The column of IRC-50 was 0.9 × 30 cm. Elution was performed with a 0.2 *M* sodium phosphate buffer of *p*H 6.45 at a rate of 1 to 1.5 cc. per hour. The effluent was collected in 0.5-cc. fractions. Curve A, crystalline ribonuclease; ●—● ninhydrin color; ○—○ ribonuclease activity. Curve B, rechromatography of material from peak of Curve A; ×—×, ninhydrin color.

Although the results obtained thus far suggest inhomogeneity, it will be necessary to isolate and characterize the material from various parts of Curve A before it can be concluded with certainty that the sample of ribonuclease employed in these experiments is impure.

When crystalline lysozyme carbonate was chromatographed on a column similar to the one described in Fig. 1, the protein appeared in the effluent as two well-separated symmetrical peaks at about 25 cc. and 40 cc. Elution was performed with a 0.2 *M* phosphate buffer of *p*H 7.2. The sample of lysozyme carbonate was kindly supplied by Dr. C. A. Stetson, Jr. Experiments of Dr. Harris H. Tallan, which will form the basis of a subsequent communication, have indicated that lytic activity resides in both protein peaks.

Because success has attended the chromatography of relatively stable low molecular weight proteins, it should not be inferred that the same experimental conditions will prove applicable to numerous other more fragile proteins. The present results do indicate, however, that substances with a molecular weight as high as 15,000 to 20,000 distribute themselves sufficiently rapidly between a solution and an ion exchange resin to permit near equilibrium conditions to be attained in a chromatogram flowing at an appreciable rate.

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[1] S. Moore and W. H. Stein, *J. Biol. Chem.*, **178**, 53 (1949).

[2] W. H. Stein and S. Moore, *Cold Spring Harbor Symposia on Quant. Biol.*, **14**, 179 (1950); S. Moore and W. H. Stein, to be published.

[3] S. Paléus and J. B. Neilands, *Acta chem. Scand.*, **4**, 1024 (1950).

[4] S. Moore and W. H. Stein, *J. Biol. Chem.*, **176**, 367 (1948).

[5] M. Kunitz, *ibid.*, **164**, 563 (1946).

RELATION OF MOVEMENT TO TIME IN IONOGRAPHY

Sir:

In recent reports on ionography, that is, the migration of ions or charged particles on paper in an electric field, it has been reported that the movement of certain substances was not a linear function of time.[1,2] However, it has been found possible, under proper conditions, to obtain the same mobility, *i. e.*, the migration computed on the basis of cm./sec. per volt/cm., for relatively long periods of time. This indicates a linearity of movement with

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[1] E. L. Durrum, THIS JOURNAL, **72**, 2943 (1950).

[2] E. L. Durrum, *Science*, **113**, 66 (1951).