search Foundation and the Nutrition Foundation, Inc., to whom we express our sincerest thanks. We wish also to express our appreciation to Professor M. A. Peacock, Professor G. F Wright and Mr. A. Brook for the X-ray diffraction photographs, to Professor S. J. Thannhauser for a gift of the natural dipalmitoyl lecithin, to Mr. F. M. Martin for preparing some of the starting materials and to Mrs. E. Mason for the combustion analyses.

Summary

1. A method for the synthesis of both enantiomeric forms of fully saturated α-lecithins of assured constitutional and configurational purity has been developed.

2. The synthesis of three homologous α-lecithins of the L-series, namely, (distearoyl)-, (dipalmitoyl)- and (dimyristoyl)- lecithin is described.

3. The X-ray diffraction patterns, the solubilities and other physical data of these pure, individual, crystalline lecithins are reported.

4. The synthetic L-α-(dipalmitoyl) lecithin and natural (dipalmitoyl) lecithin were found to be identical, thus establishing the α-constitution and L-configuration of this natural lecithin.

TORONTO 5, CANADA RECEIVED JUNE 23, 1949

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY PASADENA 4, CALIFORNIA, NO. 1261]

The Crystal Structure of DL-Alanine. II. Revision of Parameters by Three-Dimensional Fourier Analysis[1]

BY JERRY DONOHUE

Introduction

The crystal structure of DL-alanine was determined over seven years ago by Levy and Corey.[2] Crystals of DL-alanine are isomorphous with the space group C_{2v}^9–Pna, having no center of symmetry. Because of the low symmetry of the crystal and the pecularities of its atomic arrangement, only limited use could be made of the customary Fourier projections or structure factor plots, and the refinement of the parameters of all atoms but one was carried out primarily by trial and error methods. Most use was made of reflections of the type $(hk0)$ in the determination of the structure, since for this zone alone the structure factors are real. With the exception of the methyl carbon atom, which was resolved in a Fourier projection on (001), the x- and y-parameters were arrived at by the use of plots of the trigonometric portion of the structure factors as guides in obtaining the best agreement between observed and calculated values of F_{hk0}. The z-parameters of all atoms were refined by trial and error adjustment of all six atoms in accord with intensity data from $(0kl)$ and $(h0l)$ reflections. Because of the molecular arrangement, no resolution of atomic peaks could be expected in asymmetric Fourier projections on either (100) or (010), and the calculation of a three-dimensional Fourier function was prohibited by the excessive time and labor which would have been involved.

The calculation of three-dimensional plots of interatomic vectors and electron densities has been made feasible recently through the use of punched card methods[3a] and especially by the design[3b] of a file of cards to correspond to a set of Beevers–Lipson strips. These methods have made possible the rapid calculation of one- and two-dimensional Patterson and electron density functions and have reduced to the order of several days the time required for the calculation of corresponding three-dimensional functions. In connection with a determination of the crystal structure of L-threonine[4] based on three-dimensional Fourier functions a new punched card method was devised[5] which greatly reduces the time required for the calculation of complex structure factors, a very significant item in the analysis of crystals having no center of symmetry.

The dimensions of the L-threonine molecule as determined by this very exhaustive X-ray investigation[4] are, with one exception, in good agreement with the corresponding dimensions found by Levy and Corey in the molecule of DL-alanine. In their analysis of alanine the C–N distance was found to be 1.43 Å., about 0.04 Å. shorter than that calculated from the generally accepted covalent radii.[6] In threonine the C–N distance was established as 1.49 Å., close to the normal value. Since methods are now available for the calculation of three-dimensional plots of electron density, this discrepancy in the C–N distances suggested the desirability of a redetermination of the parameters of DL-alanine so as to

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[1] Aided by a grant from the National Foundation for Infantile Paralysis.

[2] H. A. Levy and R. B. Corey, THIS JOURNAL, **63**, 2045 (1941).

[3] (a) P. A. Shaffer, Jr., V. Schomaker, and L. Pauling, *J. Chem. Phys.*, **14**, 648 (1946); (b) V. Schomaker, unpublished work.

[4] D. Shoemaker, J. Donohue, V. Schomaker, and R. B. Corey, submitted to THIS JOURNAL.

[5] J. Donohue and V. Schomaker, *Acta Cryst.*, **2**, 344 (1949).

[6] L. Pauling, "The Nature of the Chemical Bond," second edition, Cornell University Press, Ithaca, N. Y., 1940. For a compilation of C–N bond distances observed in various compounds see E. W. Hughes and W. N. Lipscomb, THIS JOURNAL, **68**, 1970 (1946).

obtain a structure for that molecule based upon all available intensity data and free from the limitations imposed by the older methods of analysis. Special interest is attached to a precise knowledge of the length of the carbon-nitrogen bond in amino acids, since it should be capable of direct extrapolation to similar carbon–nitrogen distances in proteins.

Electron Density Calculations

Two calculations were made by the punched card methods of the electron density function

$$\rho(xyz) = \frac{1}{V}\sum_{h}\sum_{k}\sum_{l} |F_{hkl}| \exp 2\pi\, i(hx + ky + lz - \alpha_{hkl})$$

Each required about one week for completion. The data used for the first summation, ρ_1, comprised the 340 experimentally observed values of $|F_{hkl}|$ published by Levy and Corey[2] together with the phase angles α_{hkl} corresponding to their final structure; the latter were compiled from their original notebooks. The second summation, ρ_2, was identical with ρ_1 except that the experimentally observed values of $|F_{hkl}|$ were replaced by those calculated for Levy and Corey's final structure. This second summation was used for correcting the values of the parameters obtained from the first summation as described in the next section. Both summations were calculated at points separated by $a_0/60$, $b_0/30$, and $c_0/20$; these intervals correspond to 0.20, 0.20 and 0.29 Å., respectively. A sufficient number of points was calculated to ensure the accurate location of the centers of all the peaks. The centers of the peaks were located by an analytical method based on the assumption that the electron density closely resembles a Gaussian distribution around the center of the peak.[7]

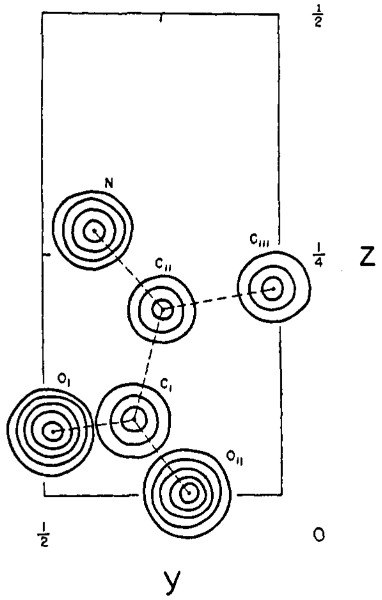

Fig. 1.—Composite drawing of electron density made from sections of $\rho_1(xyz)$ at several values of x. The contour lines are drawn at equal intervals of an arbitrary scale.

A composite drawing of the electron density distribution, ρ_1, as calculated from the experimentally observed values of $|F_{hkl}|$ is presented in Fig. 1. For each atom the contours shown are taken at that multiple of $a_0/60$ which is closest to the center of the electron density of that atom.

Assignment of Parameters

The centers of the peaks of ρ_2 differed slightly from the atomic parameters which were the basis for computing both the $|F_{hkl}|$ values and the corresponding phase angles used in its calculation. These differences, which are due mainly to abrupt termination of the Fourier series and omission of terms in certain regions of the reciprocal lattice, were applied, with opposite sign, to the peaks of ρ_1 in order to obtain corrected values of the positions of the atomic centers as derived from the observed data.[8] However, these corrected values still do not correspond to the true parameters of the atoms for reasons which can be indicated only briefly here. The space group of DL-alanine, C_{2v}^{9}–Pna, does not contain centers of symmetry. In the application of the Fourier method it is necessary to use not only the observed values of $|F_{hkl}|$ but, since the F values are in general complex quantities, also phase angles which are calculated from the parameters of a postulated structure. It has been shown that in Fourier syntheses of this nature the peaks occur on the average, half way between the positions of the atoms as given by the postulated structure and the positions of the atoms in the true structure. In order to obtain the parameters of the atoms in the true structure one merely has to apply a shift to the centers of the peaks of the Fourier (ρ_1), corrected as described above, equal in magnitude and of the same sign as the shift from the postulated structure to the positions of the peaks. This procedure leads to the relation $x_0 = x_1 + 2(x_2 - x_3)$ where x_0 is the true parameter, x_1 is the parameter of the trial structure, and x_2 and x_3 are the parameters obtained from the maxima of the Fourier syntheses made with the observed and calculated $|F|$ values, respectively. The proof of this "double shift rule" and a demonstration of its validity will be given in a paper on the crystal structure of L-threonine.[4] These considerations, however, apply strictly only in Fourier synthesis in which *all* the values of F_{hkl} are complex. In all but one of the asymmetric space groups, the F values of certain zones or other classes of reflections may be wholly real or imaginary, with phase angles 0°, $\pi/2$, π, or $3\pi/2$. Experience in this Laboratory has shown that in such cases, the double shift rule must be replaced by an n-shift rule, $1 < n < 2$, where n

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[7] G. B. Carpenter and J. Donohue, submitted to THIS JOURNAL.

[8] A. D. Booth, *Proc. Roy. Soc.* (*London*), **A188**, 77 (1946).

is some function of the fraction of the F values which do not have general phase angles. In the present case, where 78 out of 340 of the F values are real, a 1.7 shift rule was used, the choice of the value 1.7 being based upon largely empirical evidences of other asymmetric Fourier syntheses. The relation by which the parameters are obtained now becomes $x_0 = x_1 + 1.7\ (x_2 - x_3)$. The factor 1.7 may be in error by a maximum of ±0.10, an amount which has a very small effect on the accuracy of the parameter assignment.

The final parameters for the atoms in DL-alanine were obtained by correcting the three-dimensional Fourier summation and applying the 1.7 shift rule as outlined above. They are compared in Table I with those published by Levy and Corey. Corresponding comparisons of the interatomic distances and bond angles within the alanine molecule are given in Table II. (The unit cell dimensions, given by Levy and Corey in kX units, have been converted to Å., $\lambda\mathrm{CuK}_\alpha = 1.542$ Å.; $a_0 = 12.06$ Å., $b_0 = 6.05$ Å., $c_0 = 5.82$ Å.)

TABLE I

ATOMIC PARAMETERS IN DL-ALANINE

Atom		L. C.	Fourier peak, ρ_2 (calcd. F)	Fourier peak, ρ_1 (obsd. F)	Revised parameter	Change from L. C. in Å.
C_I	x	0.145	0.1453	0.1440	0.1428	−0.027
	y	.312	.3112	.3132	.3154	+ .021
	z	.161	.1596	.1603	.1622	+ .007
C_{II}	x	.161	.1642	.1655	.1632	+ .027
	y	.227	.2242	.2196	.2192	− .047
	z	.408	.4107	.4076	.4027	− .031
C_{III}	x	.091	.0885	.0884	.0908	− .002
	y	.017	.0165	.0178	.0192	+ .013
	z	.444	.4438	.4448	.4457	+ .010
N	x	.139	.1403	.1407	.1397	+ .008
	y	.393	.3914	.3929	.3955	+ .015
	z	.576	.5753	.5754	.5762	+ .001
O_I	x	.090	.0879	.0877	.0897	− .004
	y	.481	.4835	.4848	.4832	+ .013
	z	.134	.1330	.1339	.1355	+ .009
O_{II}	x	.186	.1863	.1852	.1841	− .023
	y	.201	.2010	.1995	.1985	− .015
	z	.000	.0005	.0016	.0019	+ .011
					Mean change, Å.	0.016

TABLE II

BOND LENGTHS AND BOND ANGLES FOUND IN THE DL-ALANINE CRYSTAL

	L. C., Å.	This work, Å.	Δ, Å.
C_I–C_{II}	1.539	1.536	0.003
C_{II}–C_{III}	1.540	1.513	.027
C_I–O_I	1.229	1.211	.018
C_I–O_{II}	1.255	1.273	.018
C_{II}–N	1.427	1.496	.069
N-H...O_I	2.885	2.883	.002
N-H...O_{II}	2.850	2.840	.010
N-H...O_{II}	2.786	2.801	.015
		Mean Δ	0.020
O_I–C_I–O_{II}	124.2°	125.4°	1.2°
O_I–C_I–C_{II}	117.1	121.3	4.2
O_{II}–C_I–C_{II}	118.0	113.2	4.8
N–C_{II}–C_I	112.4	108.3	4.1
N–C_{II}–C_{III}	112.7	110.4	2.3
C_I–C_{II}–C_{III}	109.5	111.2	1.7
		Mean Δ	3.0°

Discussion of the Results

The structure factors, $|F_{hkl}|$, of all reflections were calculated from the new parameters for comparison with the observed structure factors and with those calculated from the parameters of the earlier determination. Inasmuch as the observed structure factors and those calculated from the earlier structure were in good agreement generally and showed no individual examples of serious disagreement, the superiority of the new parameters cannot be strikingly demonstrated by inspection, as can be seen by reference to Table III, where data are presented for all planes the calculated values of $|F_{hkl}|$ of which were changed by more than 1.0 electron unit by the parameter revision. If, on the other hand, the average discrepancy $\Sigma||F_{\text{calcd.}}| - |F_{\text{obsd.}}||/\Sigma|F_{\text{obsd.}}|$ is used as a criterion for agreement, the new parameters represent a small but definite im-

TABLE III

OBSERVED AND CALCULATED STRUCTURE FACTORS[a]

		$\|F_{\text{calcd.}}\|$				$\|F_{\text{calcd.}}\|$	
hkl	$\|F_{\text{obs.}}\|$	L. C.	This work	*hkl*	$\|F_{\text{obs.}}\|$	L. C.	This work
020	5.1	3.4	5.4	604	7.7	6.4	7.5
120	6.7	8.8	7.0	10.1.1	7.2	8.6	7.2
221	14.7	11.6	12.7	234	8.0	7.9	6.6
402	26.3	22.4	23.6	205	20.1	15.2	17.6
130	3.7	3.7	4.9	740	6.8	5.7	7.9
601	18.5	17.0	15.6	930	3.9	2.4	4.0
330	5.2	3.5	5.2	10.1.2	7.4	7.3	8.7
213	12.1	8.5	10.1	405	17.0	13.3	15.1
430	16.7	17.0	15.5	550	6.8	6.8	8.0
602	10.5	10.2	11.7	452	3.2	4.6	3.4
403	24.1	20.5	22.8	10.0.3	11.1	9.3	11.3
621	3.6	5.1	3.4	060	4.3	5.9	7.1
223	18.1	15.2	16.4	10.1.3	4.9	5.9	4.8
332	14.5	12.5	14.1	261	8.8	8.2	9.4
040	16.7	17.5	16.0	11.3.0	9.7	9.1	10.2
323	17.4	14.5	15.6	10.2.3	5.9	7.3	8.4
800	4.4	4.8	6.7	453	3.3	4.4	3.2
340	2.1	1.1	2.2	006	6.0	6.2	5.0
811	9.0	10.3	9.0	206	5.0	4.2	5.4
603	16.3	13.9	15.0	12.0.2	3.2	4.1	5.3
613	6.8	5.6	6.9	254	1.6	4.1	2.7
042	6.1	6.7	5.5	950	3.4	2.9	4.5
802	12.4	10.6	12.5	12.0.3	5.3	6.1	7.7
540	3.3	2.1	4.0	13.2.0	7.1	6.0	7.2
414	3.9	5.2	4.0	606	9.6	6.8	9.3
640	7.4	7.7	8.8	270	2.6	3.7	4.8
803	7.7	8.3	10.7	207	14.3	13.5	15.6
250	6.1	6.3	5.0	745	2.9	3.6	2.4

[a] The table includes all reflections, the calculated values of which were changed by more than 1.0 by the parameter revision.

provement. This quantity, calculated for various types of reflections, is compared in Table IV.

TABLE IV

COMPARISON OF THE AGREEMENT BETWEEN OBSERVED AND CALCULATED STRUCTURE FACTORS

Planes	$\Sigma\|\|F_{\text{calcd.}}\| - \|F_{\text{obsd.}}\|\|/\Sigma\|F_{\text{obsd.}}\|$ L. C.	This work
(*hk*0)	0.102	0.104
(0*kl*) and (*h*0*l*)	.132	.115
(*hkl*)	.192	.177
All	.157	.146

It is interesting that for the (*hk*0) reflections, which are amenable to structure factor map refinement and were therefore more thoroughly examined by Levy and Corey, the new parameters do not give better agreement. On the other hand, the improvement in the agreement of the other prism reflections and of the general (*hkl*) reflections is ample confirmation of the greater precision with which the atomic positions have been determined by use of the three-dimensional Fourier treatment, doubtless because of its capacity to utilize for the analysis of the structure all of the experimental intensity data.

From the data in Table II it appears that the limits of error of 0.03 Å. and 3° reported for the bond lengths and bond angles respectively by Levy and Corey were a bit too optimistic. In the present work the C_{II}–N distance has been revised by +0.069 Å. and three bond angles have been changed by 3° or more, the remaining changes in bond angles and distances being within the limits set in the original investigation.

The probable error of a revised parameter is estimated to be about 0.007 Å. The probable error in an interatomic distance is therefore about 0.01 Å., making it very unlikely that any distance is in error by more than 0.03 Å.

Discussion of the Structure

The shape of the alanine molecule and its dimensions as determined in this revision are shown in Fig. 2. With the exception of two items, the original discussion of the structure is unaltered. First, attention should be called to the revision of the C–N bond distance to 1.496 Å. This distance, formerly thought to be anomalously shorter than the expected distance 1.47 Å. given by the sum of the covalent radii, is now in agreement with C–N distances in other compounds,[6] and, in particular, is substantially equal to the C–N distance of 1.49 Å. found in threonine.[4]

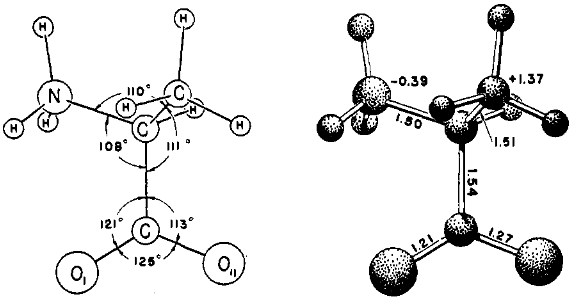
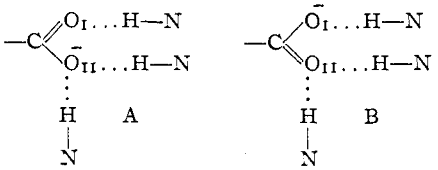


Fig. 2.—Projection of the alanine molecule on the plane of the carboxyl group. The bond angles are shown in the left hand drawing; the bond distances and the distances of the nitrogen atom below and the methyl carbon atom above the reference plane are shown in the right-hand drawing.

The second point of special interest is the configuration of the carboxyl group. The two resonating structures of the carboxyl group and the disposition of the hydrogen bonds as they occur in the DL-alanine crystal may be represented as:



The formation of two hydrogen bonds by O_{II} should tend to stabilize structure A over structure B. The distances C_I–O_I = 1.21 Å. and C_I–O_{II} = 1.27 Å. lend support to this contention, which is further strengthened by the values of the angles, $\angle$ C_{II}–C_I–O_I = 121° and $\angle$ C_{II}–C_I–O_{II} = 113°. The revised structure of DL-alanine thus indicates strongly that hydrogen bond formation affects the resonance character of the carboxyl group. The possibility of the presence of this effect was suggested by Levy and Corey in their original paper, although the evidence for it on the basis of their parameters was not strong. An effect of this sort has not been observed, on the other hand, in the dicarboxylic acid dihydrates,[9] where one of the oxygen atoms of the carboxyl group is involved in one hydrogen bond, the other in two. Unlike DL-alanine, however, in which the N-H...O bonds are all roughly the same in length, the O-H...O bonds in the dicarboxylic acids are markedly different: the hydrogen bond to the oxygen atom which forms one such bond is decidedly stronger, being approximately 0.3 Å. shorter, than the two hydrogen bonds formed by the other oxygen atom. Consequently, neither of the two resonance structures is favored and the two C–O distances in the carboxyl group are found to be equal.

Acknowledgments.—The assistance of Miss Lillian Casler and Miss Jean Mainwaring with the calculations is gratefully acknowledged. I also wish to thank Dr. Robert B. Corey for the use of the original notebooks and for advice and discussion.

Summary

The X-ray diffraction data published by Levy and Corey in their determination of the crystal structure of DL-alanine have been used for a redetermination of the atomic parameters of this

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[9] J. D. Dunitz and J. M. Robertson, *J. Chem. Soc.*, 142, 148, 1145 (1947).

crystal by means of three-dimensional Fourier summations. The revised parameters yield structure factors which are in better agreement with the observed data. Two features of the structure are significantly different from those of the original determination: The C–N bond distance is 1.50 Å. and is no longer anomalously short; and the two C–O distances in the carboxyl group differ by 0.06 Å., indicating that hydrogen bond formation causes one of the resonating structures to be favored over the other, an effect which is substantiated by the inequality of the C–C–O bond angles.

PASADENA, CALIF. RECEIVED AUGUST 22, 1949

[CONTRIBUTION FROM THE CHEMISTRY DIVISION OF THE ARGONNE NATIONAL LABORATORY]

The Polarographic Behavior of the Neptunium(III)–Neptunium(IV) Couple in Chloride and Perchlorate Solution

BY J. C. HINDMAN AND EVELYN S. KRITCHEVSKY

It has been reported previously[1] that the uranium(III)-uranium(IV) couple is reversible at the dropping mercury electrode in acid chloride and perchlorate solutions and, further, that the potential of the couple is independent of hydrogen ion concentration at acidities above 0.05 molar. These data have been interpreted as showing that the U^{+4} (hydrated) ion exists in acid solution in the absence of a complexing agent. Confirmation of this conclusion has been obtained by direct measurement of the amount of acid liberated on the addition of anhydrous uranium tetrachloride to an aqueous chloride solution.[2] Since plutonium(IV) is known to exist as Pu^{+4} (hydrated) in acid perchlorate solutions[3] and thorium(IV) is present as Th^{+4} (hydrated) under similar conditions,[4,5] the only tetrapositive ion in the actinide series for which data were not available was the neptunium(IV) ion. Potential measurements of the hydrogen ion dependence of the neptunium(III)-neptunium(IV) couple were therefore considered.

Hindman, Magnusson and LaChapelle[6] have reported that the reversible oxidation potential of this couple is −0.137 ± 0.005 volt in molar hydrochloric acid. Since this potential is within the range of polarographic determination, this method of measurement was used. Investigations of perchlorate as well as chloride solutions were undertaken since there is some evidence that chloride forms weak complexes with these tetrapositive ions.[1,2,7]

Experimental

The polarograms described in this report were obtained with a Sargent Model XX potentiometric pen chart recording polarograph calibrated according to the method of Lingane.[8] The diffusion currents reported were determined from a line drawn through the mid-point of the recorder pen oscillations using either damping position 1 or 2 of the polarograph. Operation of the present instrument under these conditions gave a value of the diffusion current constant for the lead ion in 1 *M* potassium chloride within ±1% of that reported by Lingane and Loveridge.[8a] The experimental procedure and apparatus were, in general, similar to those previously described.[1] Electromotive force values in the vicinities of the half-wave potentials were determined with a Leeds and Northrup type K_2 potentiometer. All values of half-wave potentials reported in this work have an experimental error of ±0.004 volt. This error includes any error in measurement caused by the *iR* drop in the solutions. An H-cell[9] was used with a sintered glass disc and an agar-agar plug separating the two compartments. A saturated ammonium chloride agar bridge[10] was used for the perchlorate solutions. A saturated KCl-agar bridge was used for the chloride solutions. The reference electrode and anode was a saturated calomel electrode.

Air was removed from the solutions with pre-purified nitrogen. Redistilled water was used. All measurements were carried out at 25.0 ± 0.2°. Al values of the current reported have been corrected for the residual current.

Neptunium(IV) solutions in 5 *M* perchloric acid were prepared by hydrogen reduction from neptunium(V) solutions using a platinum black catalyst. Neptunium(IV) solutions in 1 *M* perchloric acid were prepared by the dissolution of solid anhydrous neptunium tetrachloride in the acid. Neptunium(IV) solutions in hydrochloric acid were prepared by precipitation of the hydroxide with ammonia from perchloric acid solutions of neptunium(IV) and redissolution in concentrated acid. The neptunium(III) chloride and perchlorate solutions were prepared by hydrogen reduction of the neptunium(IV) solutions. All of the polarograms were made on solutions approximately 0.007 *M* in neptunium except where otherwise noted. The concentrations of the neptunium solutions were determined by radiometric assay.

Results and Discussion

Analyses of the polarographic reduction waves were made by the equation of Heyrovsky and Ilkovic.[11]

$$E_{\text{d.e.}} = E_{1/2} - \frac{0.05915}{n}\log\frac{i}{i_{\text{d}}-i} \qquad (1)$$

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(1) E. S. Kritchevsky and J. C. Hindman, THIS JOURNAL, **71**, 2096 (1949).

(2) J. C. Hindman and E. S. Kritchevsky, unpublished data.

(3) J. C. Hindman, to appear as Paper No. 4.4 Vol. 14B of the Plutonium Project Record of the National Nuclear Energy Series.

(4) J. Kasper, Ph.D. Thesis, Johns Hopkins Univ., Baltimore, Md., 1941.

(5) J. C. Hindman and E. S. Kritchevsky, unpublished data.

(6) J. C. Hindman, L. B. Magnusson and T. J. LaChapelle, THIS JOURNAL, **71**, 687 (1949).

(7) J. C. Hindman, data to appear in Chapter IV, Vol. 14A of the Plutonium Project Record of the National Nuclear Energy Series.

(8) J. J. Lingane, *Ind. Eng. Chem., Anal. Ed.*, **18**, 734 (1946).

(8a) J. J. Lingane and B. Loveridge, THIS JOURNAL, **66**, 1425 (1944); **68**, 395 (1946).

(9) J. J. Lingane and H. A. Laitinen, *Ind. Eng. Chem., Anal. Ed.*, **11**, 504 (1939).

(10) C. N. Murray and S. F. Acree, *Bur. Stds. Jour. Research*, **7**, 713 (1931).

(11) J. Heyrovsky and D. Ilkovic, *Coll. Czechoslov. Chem. Comm.*, **1**, 198 (1935).