TABLE III (*Continued*)

$t = 40°$

$\bar{n}$	p[dien]	$\log \bar{n}/(1 - \bar{n})$	$\log k_1$
0.304	10.96	−0.36	10.60
.371	10.83	− .23	10.60
.507	10.55	+ .01	10.56
.544	10.46	+ .08	10.54
.581	10.36	+ .14	10.50
.686	10.12	+ .34	10.46
		Av.	10.54
		$\log (\bar{n} - 1)/(2 - \bar{n})$	$\log k_2$
1.292	8.15	−0.38	7.77
1.463	7.92	− .06	7.86
1.530	7.79	+ .06	7.85
1.603	7.66	+ .18	7.84
1.678	7.50	+ .32	7.82
		Av.	7.83

respectively, from (6) and from

$$\log k_2 = p[\text{dien}] + \log (\bar{n} - 1)/(2 - \bar{n}) \qquad (8)$$

The values of $\log k_1$ and $\log k_2$ at 30 and 40° are obtained from $\bar{n}$ values between 0.3 and 0.7 and between 1.3 and 1.7, respectively, and are shown in Table III.

The values of $\log k_1$ at both 30 and 40° decrease slightly with increasing concentration of dien. At first it was thought that a change of structure might be the explanation for this anomalous behavior, and the magnetic susceptibilities of the solutions were investigated. The measurements showed that all solutions had paramagnetic susceptibilities of the same magnitude indicating that no shift in structure occurred.

No explanation is offered for the trend in the values of $\log k_1$ for the nickel(II) ion. The values at the $\bar{n}$ value of 0.5 are taken as the most probable values. This value at 30° is 10.85, and at 40° is 10.56.

The heat of binding of each dien molecule by the nickel(II) ion is calculated with equation (7) to be −13 kcal. This is considerably less than the −21 kcal. calculated for the binding of dien by the copper(II) ion.

Summary

I. Formation curves and constants of the copper(II) and the nickel(II) ions with diethylenetriamine are determined at 30 and 40°.

II. Heats of binding of diethylenetriamine by the copper(II) ion and the nickel(II) ion are calculated from the formation constants of the respective complexes.

NEW ORLEANS 15, LOUISIANA RECEIVED MARCH 6, 1950

[CONTRIBUTION OF THE DEPARTMENT OF CHEMISTRY, WASHINGTON UNIVERSITY]

The Crystal Structure of Potassium Chlorochromate, $KCrO_3Cl$[1]

BY L. HELMHOLZ AND W. R. FOSTER[2]

Introduction

Potassium chlorochromate shows a slight but unmistakable dichroism which may be attributed to the polarized absorption of light by the chlorochromate ion itself. We have investigated the crystal structure of this substance for the purpose of determining the configuration of CrO_3Cl^- and in order to correlate this structure with the observed spectra. A comparison of the chromium–oxygen interatomic distances in the series chromate, chlorochromate, chromyl chloride is also of importance in a discussion of the electronic structure of these molecules.

Experimental

Procedure.—Potassium chlorochromate was prepared by heating a solution of potassium dichromate in concentrated hydrochloric acid to 70° and then allowing the resulting solution to stand for some hours. The salt deposits from the solution in the form of long lath-shaped crystals. Laue photographs with the X-ray beam perpendicular to the prism axis showed that most of the crystals were twinned on the largest face (100). Several untwinned samples were obtained and used for Laue and oscillation exposures. Both Cu $K\alpha$ and Mo $K\alpha$ radiations were used, the first for a determination of the unit cell dimensions; the second for intensity measurements in order to minimize the effect of absorption. The $hk0$ data were obtained using the method of visual estimation and the multiple film technique. The intensities of the $h0l$ reflections were determined using a Geiger counter spectrometer. A comparison of the relative intensities of the $h00$ reflections as determined by the different methods showed that the ratio of intensities of strong to weak reflections was greater for the Geiger counter technique than for the visual estimation method.

In the case of the $h0l$ spectra, the cross section of the crystal was such that absorption effects were of importance. The observed data were corrected for the effect by an integration of the function $e^{-\mu d}$ over the rectangular cross section of the crystal, d being expressed as a function of the angles between the crystal axes and the directions of the incident and diffracted beams.

Unit Cell and Space Group.—The Laue exposures showed a symmetry C_{2h} with a monoclinic angle close to 90° in agreement with the crystallographic data.[3] The twofold axis was found to lie in the plane of the large developed face perpendicular to the long axis of the crystals which was chosen to be the c-axis. The a-axis was then very nearly perpendicular to the large face.

The dimensions of the unit cell and the angle β are given in Table I with the results of Gawrych,[4] who measured the size of the unit cell but carried through no structure determination.

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[1] For detailed data supplementary to this article order Document 2836 from American Documentation Institute, 1719 N Street, Washington 6, D. C., remitting \$0.50 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or \$0.50 for photocopies (6 × 8 inches) readable without optical aid.

[2] Du Pont Fellow, Washington University.

[3] Groth, "Chemische Krystallographie," Teil II, Leipzig, 1908.

[4] S. Gawrych, *Roczniki Chem.*, **19**, 413 (1939).

Table I

	H + F	Gawrych
a_0	= 7.79 Å. ± 0.02 Å.	7.83 Å.
b_0	= 7.50 Å. ± 0.02	7.46 Å.
c_0	= 7.80 Å. ± 0.02	7.82 Å.
β	= 91° 20′ ± 10′	91° 24′ (88° 36′)

The oscillation and Laue photographs showed the absence of reflections $h0l$ with l odd and $0k0$ with k odd. These absences are characteristic of the space group C_{2h}^5-$P2_{1/c}$.

The size of the unit cell and the observed density of potassium chlorochromate give 3.93 ≈ 4.00 as the number of molecules in the unit cell.

The possible sets of atomic positions for the space group $P2_{1/c}$ are

2: (a) 000; $0\,{}^1/_2\,{}^1/_2$ (b) ${}^1/_2\,00$; ${}^1/_2\,{}^1/_2\,{}^1/_2$
(c) $00\,{}^1/_2$; $0\,{}^1/_2\,0$ (d) ${}^1/_2\,0\,{}^1/_2$; ${}^1/_2\,{}^1/_2\,0$
4: (e) xyz; $\bar{x}, \bar{y}, \bar{z}$; $x, {}^1/_2 - y, {}^1/_2 + z$; $\bar{x}, {}^1/_2 + y, {}^1/_2 - z$

Patterson and Fourier Projections.—Employing the $h0l$ and $hk0$ data, Patterson projections were prepared on (001) and (010). These projections are shown in Fig. 1 and Fig. 2.

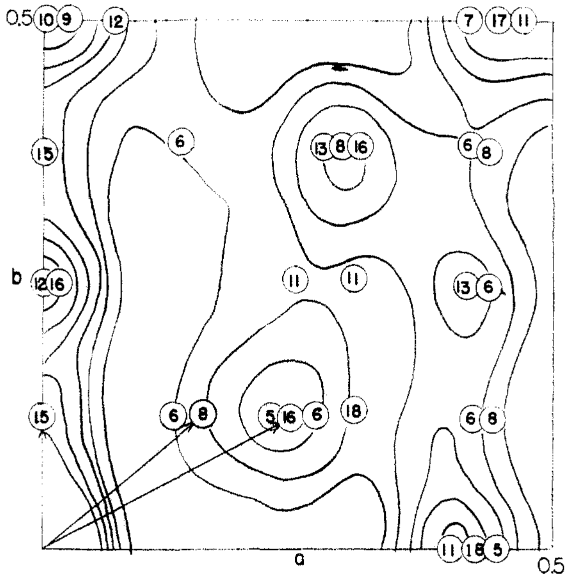

Fig. 1.—Patterson projection on plane (001): The projections of significant interatomic distances as calculated from the final structure are shown as open circles, the numbers within the circles being proportional to the product of the atomic numbers of the atoms involved multiplied by the frequency of occurrence of the vector between the atoms. The arrows correspond to interatomic distances between chromium and the other atoms within the chlorochromate ion.

There is no indication in the Patterson projections that the atoms are to be placed in the special positions,[4] a-d.

In these projections one should expect to find peaks, corresponding to the Cr–O and Cr–Cl interatomic distances within the chlorochromate ion, situated close to the origin.

These peaks are readily identified in both projections and are indicated by arrows. The fact that the interatomic distances given by the peaks are in approximate agreement with the corresponding distances found in chromyl chloride[5] lends support to this assignment as does the approximately tetrahedral arrangement suggested by the projections.

Figure 2 shows peaks corresponding to the interatomic distances between chromium and a neighboring chlorochromate ion (shown by dotted arrows). This indicates that according to this analysis the x-parameter for chromium should be approximately 0.2. Referring again to Fig. 1, for x_{cr} = 0.2 there exist the possibilities y_{cr} = 0.0, 0.125 or 0.25. For the choice $y_{cr} = 0$, the assignment of the Cr–Cl peak made above leads to a Patterson projection which should show chromium–chlorine maxima placed symmetrically with respect to a line $x = 0.30$. This is clearly not in agreement with Fig. 1. For $y_{cr} = 0.25$ the chlorochromate ions lie directly above one another in the direction parallel to c and a distance $c/2$ apart. This possibility can be eliminated by steric considerations. The remaining possibility, $y_{cr} = 0.125$ is compatible with the projection (Fig. 1) and is structurally reasonable. The peaks in the region $x = 0.25$ are accounted for by Cr–Cl and Cr–O interactions. Since the chlorine atoms lie nearly above one another in the c-direction these peaks are largely due to two Cr–Cl peaks unresolved.

The strong peak at $x = 0.40$ and $y = 0.0$ and the stronger peak at $x = 0.0$, $y = 0.50$ suggest that the potassium and chromium atoms have roughly the same x-parameters and $y_{K^+} = y_{cr} + 0.50$. The simplicity of the Patterson projection lends support to the assumption and the approximate interatomic distances resulting are reasonable. The maximum at $x = 0.40$, $y = 0.25$ is then to be ascribed to K–K and Cr–Cr interactions, the two not being resolved. The magnitude of this maximum is in agreement with the assignment.

The projections of the significant interatomic distances as calculated from the final structures are shown in Fig. 1 and 2 as open circles, the numbers within the circles being proportional to the product of the atomic numbers of the atoms involved multiplied by the frequency of occurrence of the vector between the atoms.

From rough parameter values obtained from the Patterson projections the signs of the F_{hkl}'s were calculated and

Table II

	x	y	z
Cr	0.220 ± 0.003	0.127 ± 0.003	0.117 ± 0.003
Cl	.455 ± .003	.280 ± .003	.133 ± .003
O_I	.228 ± .005	.005 ± .005	.032 ± .005
O_{II}	.211 ± .005	.005 ± .005	.275 ± .005
O_{III}	.060 ± .005	.245 ± .005	.110 ± .005
K	.200 ± .005	.630 ± .005	.130 ± .005

Table III

Atom	Neighbor	Distances, Å.
Cr	Cl	2.16 ± 0.04
	O_I O_{II} O_{III}	1.529 ± 0.05, 1.539 ± 0.05
		1.528 ± 0.05
K	Cl	3.29, 3.42, 3.48
	O_I O_{II} O_{III}	3.02, 3.03, 3.08
	O_{III}	2.88, 3.02
	O_I O_{II}	2.81, 2.94
Cl	Cl	3.97, 4.22, 4.22
O_I	O_{II} O_{III}	2.40, 2.55
	O_{III} (different ion)	2.92
O_{II}	O_I O_{III}	2.40, 2.49
	O_{III} (different ion)	3.02
O_{III}	O_I O_{II}	2.49, 2.55
	∠Cl–Cr–O_I	109° 46′
	∠Cl–Cr–O_{II}	108° 56′
	∠Cl–Cr–O_{III}	112° 40′
	∠O_I–Cr–O_{II}	103° 10′
	∠O_{II}–Cr–O_{III}	108° 46′
	∠O_I–Cr–O_{III}	112° 43′

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(5) K. J. Palmer, This Journal, 60, 2360 (1938).

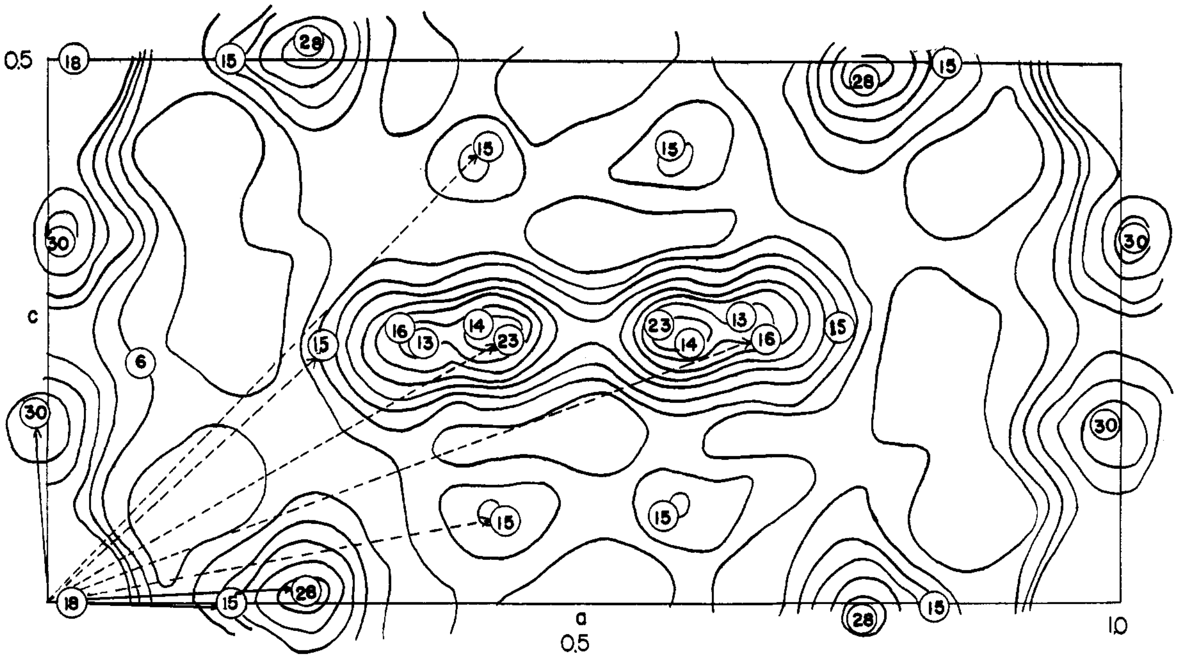

Fig. 2.—Patterson projection on plane (010): The projections of most important interatomic distances calculated from final structure are shown as circles, the enclosed numbers being proportional to product of atomic numbers of atoms involved times the frequency of occurrence of the vector between the atoms. The solid arrows represent interatomic distances between chromium and the other atoms within the chlorochromate ion. The dotted arrows correspond to interatomic distances between chromium and atoms of a neighboring chlorochromate ion.

Fourier projections prepared. These are shown in Fig. 3 (on 00*l*) and Fig. 4 (on 0*l*0). The configuration and orientation of the chlorochromate ions is clearly shown. Slight shifts in the parameters were made to improve the agreement between observed and calculated intensities. In no case were these shifts greater than 0.005 and were of importance chiefly in the case of the unresolved maxima. The final parameters are given in Table II and the interatomic distances and important angles in Table III.

The values of F_{hkl} calculated from the parameters given in Table II are in satisfactory agreement with the observed values.[6] The mean value of the percentage deviation of the F_{hkl} observed values from the calculated is 15%. Since large percentage deviations occur frequently for weak reflections and may correspond to experimental error and minor errors in the determined structure this figure, 15%, gives only a rough measure of the reliability of this determination. Reflections which were not observed were uniformly calculated very weak. This type of agreement between observed data and calculation, of course, is not reflected in the figure 15%. A relatively large temperature factor was used in obtaining the calculated F values. Atomic scattering factors from the tables of Pauling and Sherman[7] multipled by $e^{-2.5}(\sin\theta/\lambda)^2$ were used. The large value, 2.5, seemed justified by the observed rapid decline in intensities with increasing sin θ.

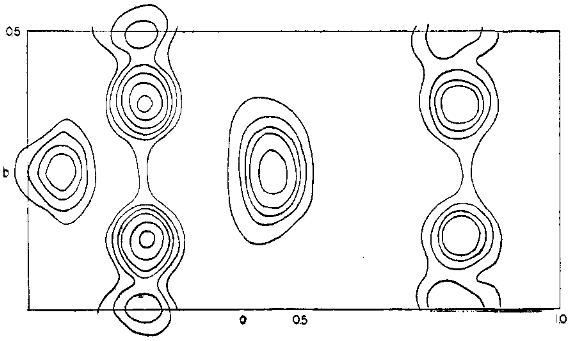

Fig. 3.—Fourier projection on plane (001).

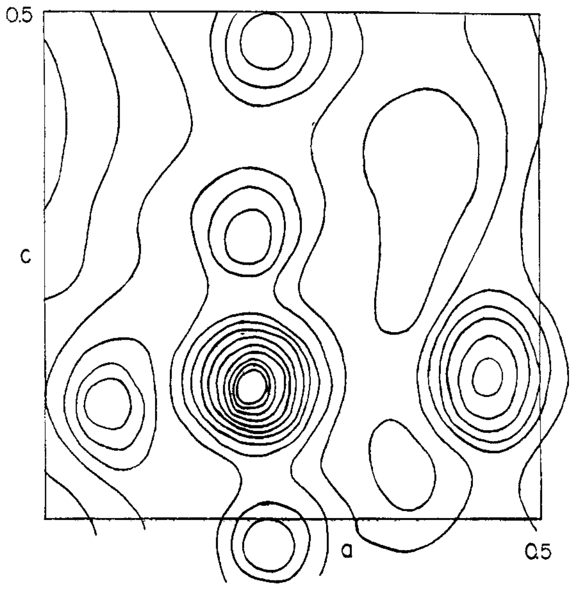

Fig. 4.—Fourier projection on plane (010).

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[6] A comparison of calculated and observed values of F_{hkl} is available from the American Documentation Institute, see ref. 1.

[7] L. Pauling and J. Sherman, *Z. Krist.*, **81**, 1 (1932).

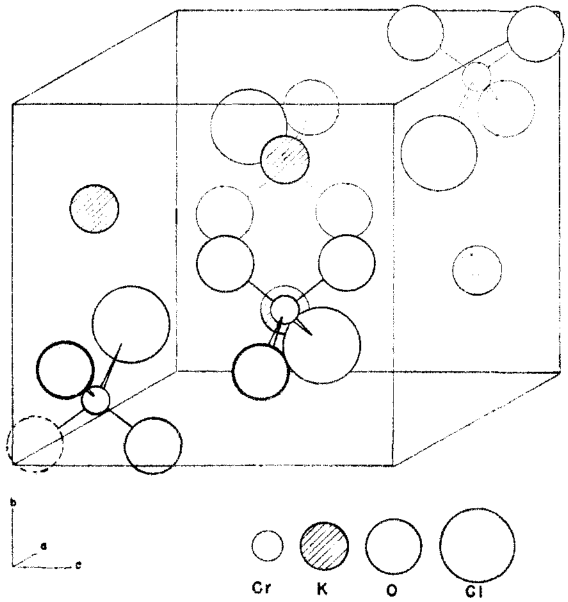

Fig. 5.—Unit cell of potassium chlorochromate: dotted circles indicate that the atom lies outside the unit cell.

Discussion of Structure.—The structure, shown in Fig. 5, may be thought of as derived from the scheelite structure. Potassium fluochromate crystallizes in this arrangement with a random arrangement of the CrO_3F^- "tetrahedra."[8] If one identifies the *b*-axis of potassium chlorochromate with the *c*-axis of the tetragonal scheelite structure, the deformations are as follows: the substitution of a chlorine for an oxygen atom forces a lengthening of the scheelite a_1 and a_2 axes and a consequent shortening of the *c*-axis. This brings the potassium ions (at $00^1/_2$ in scheelite) into contact with the negative ions above and below them in the *c*-direction and increases the coördination number from eight to ten. There is a rotation of the negative ions around the *c*-axis and a displacement parallel to a_1 to give a more satisfactory packing of the large chlorine atoms. The ions maintain their relative spacing along the *b*-axis (*c*-axis in scheelite).

The contact distances are roughly what would be anticipated. The potassium–oxygen contacts seem on the average to be larger than the sum of the ionic radii. The coördination number of potassium is ten—three chlorine and seven oxygen atoms being situated close enough to be regarded as making contact.

Within the limits of error, the chlorochromate ion has the symmetry C_{3v}. The chromium to oxygen distance is found to be short compared to the values reported for chromate,[9,10] (1.60 Å.), and chromyl chloride[6] (1.57 Å.). We believe that there is considerable shortening of the Cr–O bond in chlorochromate relative to the distance in chromate ion, though perhaps not as much as indicated by our results, which are subject to considerable error. No assumptions were made about the configuration of the ion in obtaining the parameter values and the fact that the bond distances calculated from independent sets of parameters agree gives us some confidence in the value of 1.53 ± 0.05 Å.

The chromium–chlorine distance is the same as that found in chromyl chloride within the limits of error, and probably corresponds to a single bonded distance. If one assumes this to be the case one obtains a single bond radius for chromium, 1.15, and 1.81 Å. for the Cr–O single bond distance. The shortening is then 0.28 Å. which may be compared with 0.21 Å. in sulfate (single bond radius sum—observed distance) and 0.21 Å. in chromate.

The chromium–oxygen distance in fluochromate was found to be 1.58 Å. Since the potassium fluochromate structure must be assumed to be a random one, this value must be a weighted mean of the chromium oxygen and chromium fluorine distances. If one assumes that the shortening of the Cr–F bond in this compound is the same as in SO_2F_2 one obtains from the average distance (1.58 Å.) a Cr–O distance equal to 1.55 Å. The abnormal axial ratio in potassium fluochromate may well be related to the fact that the Cr–F and Cr–O distances are not equal.

Optical Properties.—The absorption spectrum of the chlorochromate ion in solution shows a strong maximum on the ultraviolet side of the chromate ion absorption and a weak maximum displaced toward the visible. The darker color of chlorochromate is certainly due to the small maximum on the low energy side of the large chromate maximum. We have examined the dichroism of the crystals at 5400 Å. With the electric vector parallel to the *b*-axis the absorption coefficient was a minimum. As the crystal was rotated about the *a*-axis the absorption coefficient increased to a value 2.5 times the minimum value when the light was polarized along the *c*-axis. The results are given in Table IV.

TABLE IV

$\vec{E}$	μd (obs.) $[I/I_0 = 10^{-\mu d}]$	μd (calcd.)
Parallel to *c*	0.854	0.854
Perpendicular to *a* 45° to *c*	.481	.720
Parallel to *b*	.347	.58

There is no component of the Cr–Cl bond parallel to the *c*-axis while there is a component of the Cr–Cl bond along the *b*-axis. The dichroism then indicates that the polarization of the first absorption maximum is not along the three-fold axis of the ion and must be in the plane of the three oxygen atoms. The values of μd calculated from $\mu d_{\max}$ and the orientation of the ion in the crystal are included in Table IV. The assumption is made that the value of μ is the same for both components of the transition $A_1 \rightarrow E$. This is not required by the crystal symmetry and may account for the discrepancy between calculated and observed values of μd. Since the electronic ground state of the ion is probably A_1, this result means that the first excited level observed in the solution spectra must have the symmetry E.[11]

Summary

The structure of potassium chlorochromate has been determined. The substance crystallizes in a monoclinic lattice with four molecules in a unit cell, the dimensions of which are: a_0 = 7.79 Å., b_0 = 7.50 Å, c_0 = 7.80 Å., with β = 91°20′. The chlorochromate ion is found to have approximately the symmetry C_{3v} with approximately tetrahedral angles between the bonds. The Cr–O distance is found to be 1.53 Å. and the chromium chlorine distance 2.16 Å. The dichroism of the crystal is discussed on the basis of the determined structure.

ST. LOUIS 5, MO. RECEIVED MARCH 27, 1950

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[8] J. A. A. Ketelaar and E. Wegerif, *Rec. trav. chim. Pays-bas*, **57**, 1269 (1938).

[9] W. H. Zachariasen and G. E. Zeigler, *Z. Krist.*, **80**, 164 (1931).

[10] J. H. Clouse, *ibid.*, **83**, 161 (1932).

[11] For symmetry designation of molecular states and polarization properties see for example Eyring, Walter and Kimball, "Quantum Chemistry," John Wiley and Sons, New York, N. Y., 1948, p. 384.