lar parts at room temperature as evidenced by the line broadening of the n.m.r. signals, with average lifetimes in the neighborhood of 0.1 sec. at 35°. These systems, therefore, are quite labile, thus rendering it a hopeless task to isolate even the shorter chain molecules by ordinary separation methods under the usual conditions. Perhaps low-temperature separation methods, such as chromatography, with Dry Ice cooling, might be applied successfully. However, any isolated species when brought to room temperature undoubtedly will rearrange rapidly to the equilibrium distribution of molecules as determined by the over-all composition of the species.

Superficial inspection of the experimental data obtained on the chloro-terminated dimethylgermanium and dimethylsilicon compounds exhibiting either oxygen or sulfur bridges would indicate that the siloxanes[2] have a much lesser tendency to form ring structures than either the silthians[14] or the equivalent oxygen-(studied here) or sulfur-bridged[1] compounds of germanium. This, however, is not true since the ring–chain equilibrium constants for the oxygen-bridged molecular systems based on silicon[15] have the same

order of magnitude as the constants obtained in this work for the equivalent germanium system. The difference lies in the fact that rapid exchange between the germanium compounds forced us to study dilute systems, where the ring–chain equilibria are shifted toward the rings. The work on the silicon systems was carried out on the neat liquids.

We conclude from the study of the siloxanes and silthians and their related germanium compounds that the major difference in behavior between the silicon and germanium systems is with respect to the rate of equilibration, which is about a million times slower for silicon than for germanium. In both cases, the sulfur-bridged structures reorganize more slowly than the oxygen ones and, at equilibrium at the same dilution, exhibit a larger proportion of rings as compared to chains.

(14) K. Moedritzer, J. R. Van Wazer, C. H. Dungan, *J. Chem. Phys.*, **42**, 2478 (1965).

(15) The data of J. B. Carmichael and R. Winger, *J. Polymer Sci.*, **3A**, 971 (1965), corresponds to the following set of ring-chain constants of the form of eq. 5: $K_3° = 0.018$, $K_4° = 0.75$, $K_5° = 0.69$, $K_6° = 0.29$, $K_7° = 0.10$, and $K_8° = 0.04$. These constants are consistent with the data of ref. 2.

The Crystal Structure of Scandium Sesquitelluride

By J. G. WHITE and J. P. DISMUKES

Scandium sesquitelluride has been prepared in single crystal form by a vapor transport technique. The crystals are rhombohedral with $a_h = 4.109 \pm 0.004$ Å., $c_h = 40.59 \pm 0.05$ Å., referred to the triply primitive hexagonal unit cell. The space group is R$\bar{3}$m and the Te atoms are at $\pm 0, 0, \cdot 1247$ and $\pm 0, 0, \cdot 2918$ forming a 12-layer stacking sequence containing regions of both cubic and hexagonal close packing. All the Sc atoms are in octahedral sites, 2Sc in 0, 0, 0 and 0, 0, $^1/_2$, and $^2/_3$ Sc in $\pm 0, 0, \cdot 4150$. The structure may be regarded as being made up of alternate regions of NaCl and NiAs structure types, with the metal sites common to both regions being only one-third occupied. A nonstoichiometric scandium telluride of approximate composition $Sc_{2.3}Te_3$ has been made which also has the Sc_2Te_3 structure, presumably with a higher scandium content in the partially occupied sites.

Introduction

Men'kov, *et al.*,[1] have reported X-ray powder diffraction data for Sc_2Te_3. They describe the structure as being similar to that of γ'-Al_2O_3,[2] which is a close-packed cubic structure for the anions with the cations being distributed statistically over all the possible octahedral and tetrahedral sites in the ratio of 70% in octahedral and 30% in tetrahedral sites. During an investigation of the occurrence of the Sc_2S_3 structure[3] among the higher atomic number rare earth (including Sc and Y) chalcogenides,[4] single crystals of Sc_2Te_3 were

prepared, giving the opportunity of definitive structural investigation. Our X-ray powder pattern is quite different from that published by Men'kov, *et al.*, and it is possible that these authors had a different crystalline modification, although our experimental conditions were quite similar to theirs.

Experimental

Preparation.—Polycrystalline Sc_2Te_3 was prepared by direct reaction of the elements at 1000°, using a small amount of I_2 as a mineralizer. Single crystal plates of Sc_2Te_3 were then chemically transported with I_2 from a hot zone of 1050° to a cold zone of 950°.[4] About a 160-mg. sample was decomposed with nitric acid, and scandium was titrated by EDTA, as in the determina-

(1) A. A. Men'kov, L. N. Komissarova, Y. P. Simanov, and V. I. Spitsyn, *Dokl. Akad. Nauk SSSR*, **128**, 92 (1959).

(2) E. J. W. Verwey, *Z. Krist.*, **91**, 317 (1935).

(3) J. P. Dismukes and J. G. White, *Inorg. Chem.*, **3**, 1220 (1964).

(4) J. P. Dismukes and J. G. White, *ibid.*, 4, 970 (1965).

TABLE I

CALCULATED AND OBSERVED LATTICE SPACINGS FOR Sc_2Te_3

(Cu Kα RADIATION)

hkl	d_{calcd}	d_{obsd}	$I_{obsd}{}^a$
10·1	3.544 ⎫		
01·2	3.504 ⎭	3.501	vw
00·12	3.383	3.370	w+
01·5	3.258	3.243	m+
10·7	3.033	3.018	m+
01·8	2.912	2.898	w
10·10	2.675	2.663	w+
01·11	2.562	2.552	vw
10·13	2.347	2.334	vw
01·14	2.248	2.239	w+
11·0	2.054	2.046	s
01·17	1.983	1.976	m
10·19	1.832	1.828	w+
11·12	1.756	1.751	m
20·5	1.738	1.732	w
02·7	1.700 ⎫		
00·24	1.691 ⎭	1.692	w+, b
02·10	1.629	1.625	w
20·14	1.517	1.513	w
20·17	1.427	1.424	w
02·19	1.368	1.365	w
12·5	1.326	1.325	w
21·7	1.310 ⎫		
11·24	1.306 ⎭	1.305	m, b

^{a} vw, very weak; w, weak; m, medium; s, strong; b, broad.

tion of lead in lead telluride.[5]   *Anal.*   Calcd. for Sc_2Te_3:   Sc, 19.02.   Found: Sc, 18.96.

A nonstoichiometric scandium telluride was prepared by heating about 75 mg. of polycrystalline Sc_2Te_3 at 1050° in an evacuated quartz ampoule, with one end cold, for 24 hr.   From the weight of tellurium lost this material has the approximate composition $Sc_{2.3}Te_3$.

Crystal platelets of Sc_2Te_3 have a bright silvery appearance, but develop a black surface layer after several days exposure to air. The crystals prepared were not suitable for accurate density determination.

Crystal Data for Sc_2Te_3.—The crystal data are: Sc_2Te_3, mol. wt. 472.75; absent spectra, hkl with $-h + k + l \neq 3n$; rhombohedral, space group $R\bar{3}m$, $Z = 1^1/_3$; cell dimensions: $a_r = 13.72 \pm 0.02$ Å., $\alpha = 17° 12' \pm 2'$, $a_h = 4.109 \pm 0.004$ Å., $c_h = 40.59 \pm 0.05$ Å.; V (primitive cell) $= 197.8$ Å.^{3}; $d_{calcd} = 5.29$ g. cm.$^{-3}$; μ (Mo Kα) $= 186$ cm.$^{-1}$.

The crystals of Sc_2Te_3 are thin (00·1) plates, frequently twinned.   Single crystal X-ray measurements established that they are rhombohedral, and negative pyroelectric measurements indicated a centrosymmetric space group.   Data from the X-ray powder diffraction pattern are reproduced in Table I.   The cell dimensions were obtained from this pattern by extrapolation.[6]   Since the back-reflection region contains too many overlapping lines to be indexed unequivocally, the accuracy is considerably less than can be obtained from simpler patterns.   The X-ray photograph of the scandium-rich preparation is almost indistinguishable from that of Sc_2Te_3 and cell dimensions obtained by the same procedure are $a_h = 4.113$ Å., $c_h = 40.51$ Å. While the absolute differences in the cell dimensions between the two materials are within the possible experimental errors, the difference in the c/a ratios, 9.88 for Sc_2Te_3 and 9.85 for $Sc_{2.3}Te_3$, is probably real as shown by the resolution in the $Sc_{2.3}Te_3$ pattern of the line pairs 02·7, 00·24 and 21·7, 11·24 which are overlapped in the Sc_2Te_3 pattern.

Three-dimensional X-ray intensity data were obtained from one crystal, a thin needle of cross section 0.028 × 0.032 mm., using Zr-filtered Mo Kα radiation and the equi-inclination Weis-

(5) K. L. Cheng, *Anal. Chem.*, **33**, 761 (1961).

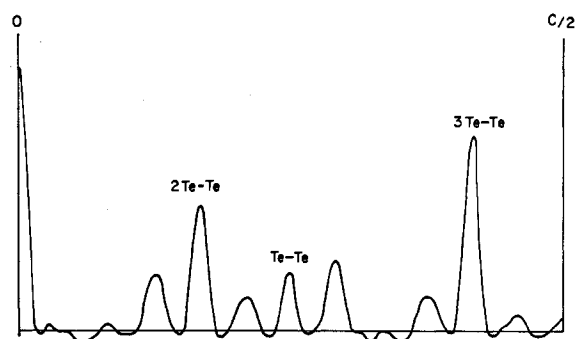(6) J. B. Nelson and D. P. Riley, *Proc. Phys. Soc.* (London), **57**, 160 (1945),

Figure 1.—The line 0, 0, z of the three-dimensional sharpened Patterson function.   Vectors between tellurium atoms are marked.
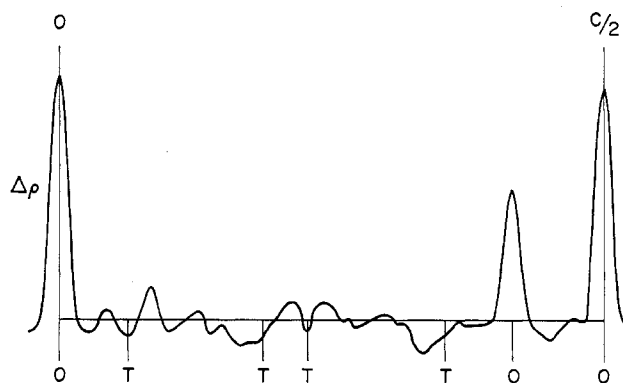

Figure 2.—The electron density line 0, 0, z computed using the phase angles determined by the tellurium atoms alone and coefficients $F_o - F_{Te}$.   The octahedral and tetrahedral sites are marked O and T, respectively.

senberg technique.   The intensities were estimated visually by comparison with a standard intensity scale.   Approximate absorption corrections were made by treating the crystal as a cylinder of equivalent cross-sectional area.

Structure Determination and Refinement

The c/a ratio in Sc_2Te_3 is 1.647 × 6, which is very close to that expected (1.633 × 6) for a close-packed tellurium sublattice with a 12-layer periodicity in the z direction. Only two 12-layer stacking sequences can give rise to a rhombohedral structure.   One of these is cubic close packing repeated four times, and this structure can be ruled out immediately on consideration of the intensity data.   The other sequence, actually found in Sc_2Te_3, is ACACBABACBCB..., which contains regions of both cubic and hexagonal close packing.   The three-dimensional Patterson function, with the data sharpened to correspond to atoms at rest, showed that this close-packed structure is indeed present with practically no distortion.   The vector concentration established that the cations also lie on the trigonal axis.   The line 0, 0, z of the three-dimensional Patterson is shown in Figure 1. The cation positions were found with greater certainty by computation of the electron density along the line 0, 0, z using the phase angles calculated from the Te positions and coefficients $F_o - F_{Te}$ (Figure 2).   The positions along this line corresponding to the octahedral and tetrahedral sites are marked and it is clear that

there are sites of high scandium occupancy at 0, 0, 0 and 0, 0, $^1/_2$ while weaker peaks occur at ± 0, 0, $^5/_{12}$. There is no evidence at all for any occupancy of the tetrahedral sites. The reflections due to scandium atoms alone were necessarily left out of this calculation, and since these all make negative contributions at ± 0, 0, $^5/_{12}$ the occupancy ratio is actually close to $1:1:^1/_3$ for these positions, respectively.

However, since the arrangement of the tellurium atoms is itself centrosymmetric, the electron density map must contain a center of symmetry whether this exists for the scandium atoms or not. Thus, since the negative observation of a pyroelectric effect might be due to multiple twinning, two arrangements are possible. These are: (1) with the atoms in the following positions of the space group R$\bar{3}$m[7] referred to the triply primitive hexagonal cell: 6Te in (c) ± 0, 0, $^3/_{24}$, 6Te in (c) ± 0, 0, $^7/_{24}$; 3Sc in (a) 0, 0, 0; 3Sc in (b) 0, 0, $^1/_2$; 2Sc in (c) ± 0, 0, $^5/_{12}$, (2) with all atoms located in the corresponding positions of the space group R3m except the fractional Sc atoms, which could be located entirely in (a) 0, 0, $^5/_{12}$. These alternative structures are extremely difficult to distinguish since the only difference between them is the vector between the two $^1/_3$Sc atoms in structure (1) which is overlapped in the Patterson function by a strong Te–Te vector peak, and in fact the over-all structure factor agreement is not significantly different for the two cases. However, it was possible to make the distinction by examining a particular set of reflections. The permitted 00·l reflections with l odd are calculated close to zero for structure (1) and very weak but observable for structure (2). Very long exposures were taken such that if structure (2) were correct the first seven of the odd 00·l reflections would be clearly visible. Actually none of these was observed, and it was concluded that the centrosymmetric structure (1) is correct.

This structure was refined by three-dimensional difference synthesis using isotropic temperature factors since no pronounced anisotropic effects were observed in the residual density maps. Unfortunately, it was not possible to refine the occupancy factors of the scandium sites simultaneously with individual temperature factors since these variables are highly correlated. However, if it is assumed that the temperature factors of the scandium atoms are all equal, then refinement of the site occupancies gives differences of less than 2% from the most ordered ratio of $1:1:^1/_3$. The refined atomic positions and their standard deviations[8] are given in Table II, and the structure factors calculated using temperature factors with $B = 1.50$ Å.[2] for the Te atoms and $B = 1.69$ Å.[2] for the Sc atoms are listed in Table III. The scattering factors used are those given in the literature[9] corrected for anomalous dispersion.[10] For 131 observed reflections the reliability coefficient R is 0.063.

(7) International Tables for X-ray Crystallography, Kynoch Press, Birmingham, Vol. I, 1952, p. 273.

(8) D. W. J. Cruickshank, *Acta Cryst.*, **2**, 65 (1949).

(9) International Tables for X-ray Crystallography, Kynoch Press, Birmingham, Vol. III, 1962.

(10) C. H. Dauben and D. H. Templeton, *Acta Cryst.*, **8**, 841 (1955).

TABLE II

COORDINATES OF THE ATOMS IN Sc$_2$Te$_3$ WITH FREE z PARAMETER

Atom	z	σ_z, Å.
Te$_I$	0.1247	0.001
Te$_{II}$	0.2918	0.001
Sc$_{III}$	0.4150	0.008

TABLE III

CALCULATED AND OBSERVED VALUES OF THE STRUCTURE FACTORS FOR Sc$_2$Te$_3$

| hkl	F_c	F_o	hkl	F_c	F_o	hkl	F_c	F_o	hkl	F_c	F_o	hkl	F_c	F_o
00· 3	0	<6	01·35	-19	26	20·17	100	103	21·31	60	60	13·13	-19	19
00· 6	24	21	10·37	-25	25	02·19	-84	81	12·32	28	26	31·14	41	45
00· 9	-1	<10	01·38	45	44	20·20	-12	<19	21·34	40	41	13·16	24	21
00·12	-129	121	10·40	24	22	02·22	-25	27	12·35	-14	18	31·17	59	64
00·15	1	<14	01·41	64	62	20·23	14	<19	21·37	-18	17	13·19	-50	46
00·18	23	21	10·43	-52	48	02·25	21	26	12·38	32	33	31·20	-9	<15
00·21	-2	<17	01·44	-9	<15	20·26	-23	27	21·40	18	15	13·22	-16	15
00·24	156	169	10·46	-15	14	02·28	-10	<20	12·41	47	48	31·23	9	<14
00·27	2	<20	01·47	0	<13	20·29	-67	66	30· 0	113	102	13·25	13	13
00·30	7	<22	10·49	14	11	02·31	69	64	30· 3	0	<17	31·26	-15	16
00·33	-2	<23	01·50	-13	9	20·32	33	30	30· 6	9	<17	13·28	-6	<11
00·36	-70	63	11· 0	179	171	02·34	48	44	30· 9	-0	<17	31·29	-42	45
00·39	2	<24	11· 3	6	<16	20·35	-16	<19	30·12	-70	70	13·31	43	40
00·42	13	<23	11· 6	15	19	02·37	-21	20	30·15	1	<16	40· 1	12	<18
00·45	-1	<21	11· 9	-1	<19	20·38	38	36	30·18	11	<16	04· 2	-16	<18
00·48	69	63	11·12	-99	98	02·40	21	17	30·21	-1	<16	40· 4	-8	<17
10· 1	30	30	11·15	1	<22	20·41	55	56	30·24	90	91	04· 5	-50	47
01· 2	-37	32	11·18	17	23	02·43	-44	44	30·27	1	<14	40· 7	54	54
10· 4	-15	15	11·21	-1	<24	21· 1	19	27	30·30	3	<12	04· 8	24	20
01· 5	-134	129	11·24	125	125	12· 2	-26	30	30·33	-1	<11	40·10	38	37
10· 7	149	139	11·27	1	<26	12· 5	-11	<25	30·36	-44	53	04·11	-15	<15
01· 8	69	65	11·30	5	<26	12· 5	-82	79	22· 0	94	103	40·13	-17	<15
10·10	107	105	11·33	-1	<26	21· 7	91	93	22· 3	32	33	04·14	35	33
01·11	-41	40	11·36	-60	55	12· 8	40	43	22· 6	7	<19	40·16	20	16
10·13	-44	40	11·39	1	<24	21·10	63	61	22· 9	0	<19	04·17	51	51
01·14	95	91	11·42	11	<22	12·11	-25	28	22·12	-59	63	40·19	-44	46
10·16	55	46	11·45	-1	<18	21·13	-28	28	22·15	1	<18	04·20	-7	<12
01·17	126	128	11·48	60	55	12·14	58	58	22·18	9	<17	40·22	-14	<13
10·19	-103	101	02· 1	23	23	21·16	34	36	22·21	-1	<16	32· 1	10	<13
01·20	-14	<18	20· 2	-30	31	12·17	82	79	22·24	75	84	23· 2	-14	17
10·22	-29	30	02· 4	-13	<18	21·19	-70	65	13· 1	14	<21	32· 4	-7	<13
01·23	17	23	20· 5	-102	102	12·20	-11	<26	31· 2	-19	25	23· 5	-43	46
10·25	25	26	02· 7	113	112	21·22	-21	27	13· 4	-9	<20	32· 7	47	60
01·26	-27	28	20· 8	51	49	12·23	10	<26	31· 5	-58	56	23· 8	20	18
10·28	-11	<22	02·10	80	80	21·25	18	25	13· 7	64	57	32·10	33	41
01·29	-81	80	20·11	-32	36	12·26	-20	22	31· 8	28	29	23·11	-13	17
10·31	83	80	02·13	-34	35	21·28	-9	<24	13·10	44	45	32·13	-14	15
01·32	40	41	20·14	72	73	12·29	-58	61	31·11	-18	23	23·14	30	29
10·34	57	56	02·16	42	39									
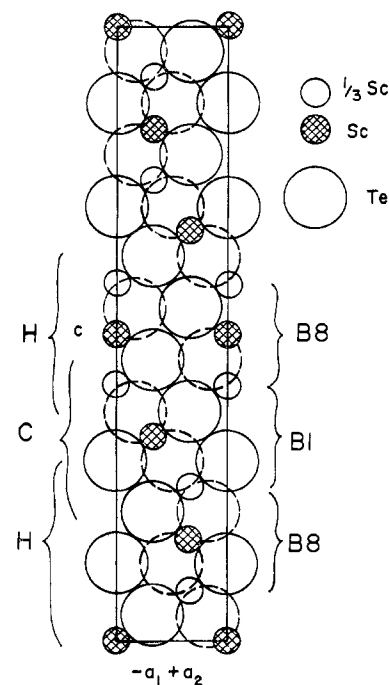
Figure 3.—The structure of Sc$_2$Te$_3$ viewed in the [11·0] direction. Full circles indicate atoms lying in the (11·0) plane, dotted circles are tellurium atoms located a distance $a/2$ behind and in front of this plane.

Discussion

A diagram of the structure is shown in Figure 3, where the full circles represent atoms within the (11·0) plane. The broken circles represent Te atoms behind and in front of this plane. For simplicity Sc atoms outside the (11·0) plane have been omitted.

The 12-layer rhombohedral anion stacking sequence has been described in detail for In_2ZnS_4.[11] The anion arrangement may be divided into overlapping regions of cubic and hexagonal close packing as shown on the left-hand side of Figure 3. On the basis of the distribution of the cations among the octahedral sites of the close-packed anion structure, the unit cell may be divided into alternate layers, in the z direction, of cation-deficient B1 (NaCl) and B8 (NiAs) structure types as shown on the right-hand side of Figure 3. The cation layers at the boundaries of the B1 and B8 regions are only one-third occupied. Since the configuration of the scandium atoms around each tellurium atom in the B8-type regions is that of a trigonal prism, the Sc centered octahedra in these regions are linked along c by sharing faces. In other directions in these regions, and in all directions of the B1 type regions, the octahedra share edges only. A rather similar situation has been found in the system $Ti_{2+x}S_4$,[12] where the structure is based on the simpler anion stacking sequence ABAC.. The Ti atoms are all in octahedral sites while half the S atoms are in octahedral coordination and half have the trigonal prism configuration.

ScTe has been prepared by Men'kov, *et al.*,[13] and is reported to have a B8-type structure with $a = 4.122$ Å. and $c = 6.753$ Å. It would appear that in the nonstoichiometric material $Sc_{2.3}Te_3$ some filling of the partially occupied metal sites has occurred, but this cannot be established by direct comparison of the X-ray powder photographs since the intensity differences would be quite small. On further increasing the scandium proportion it is to be expected that at some point a phase transition will occur to a scandium-deficient B8-type structure.

(11) F. Lappe, A. Niggli, R. Nitsche, and J. G. White, *Z. Krist.*, **117**, 146 (1962).

(12) A. D. Wadsley, *Acta Cryst.*, **10**, 715 (1957).

(13) A. A. Men'kov, L. N. Komissarova, Y. P. Simanov, and V. I. Spitsyn, *Dokl. Akad. Nauk SSSR*, **141**, 364 (1961).

The interatomic distances in Sc_2Te_3 are given in Table IV. The Sc–Te distances are all close to the value 2.88 Å. calculated from the ionic radii 0.731 Å. for Sc^{3+} and 2.151 Å. for Te^{2-} used in comparing the rare earth sesquichalcogenides.[4] However, the occurrence of NiAs-like regions in the structure suggests that a high proportion of covalent bonding is actually present. From the cell dimensions quoted for ScTe the distances may be calculated as 2.92 Å. for Sc–Te and 3.37 Å. for Sc–Sc in this compound. If the Sc_2Te_3 structure were undistorted the Sc–Sc distance would be almost identical with that in ScTe. However, the fractional Sc atoms at ± 0, 0, $^5/_{12}$ are distorted away from the atom at 0, 0, $^1/_2$ so that the Sc–Sc distance is increased to 3.45 Å. The average first neighbor distance in scandium metal is 3.28 Å.

TABLE IV

INTERATOMIC DISTANCES IN Sc_2Te_3

Atoms	d, Å.
Sc_I–Te_{II}	2.91
Sc_{II}–Te_I	2.92
Sc_{III}–Te_I	2.94
Sc_{III}–Te_{II}	2.88
Sc_{II}–Sc_{III}	3.45

The rather complex structure found in Sc_2Te_3 is clearly an intermediate one between a B1 (or a disordered Sc_2S_3) structure and a B8 structure. In such cases the arrangement adopted is probably a consequence of a small energy minimization with respect to alternative arrangements and is not easily predictable. However, the fact that the $Sc_{2+x}Te_3$ structure occurs over the range $2 \leq x \leq 2.3$ suggests that it is a particularly stable one.

The Acid-Catalyzed Hydrolysis of Pyrophosphoric Acid[1]

By C. A. Bunton and Hernan Chaimovich[2]

The hydrolysis of undissociated pyrophosphoric acid in water is catalyzed by strong acids. Plots of the first-order rate constant against acid concentration curve upward slightly, but are very similar for hydrochloric, perchloric, and sulfuric acids. Added salts slightly increase the reaction rate. The kinetic form of the hydrolysis, and the values of the Arrhenius parameters, suggest that the mechanism falls into the A2 category. Experiments in aqueous methanol, in acid and at pH 4, show that no methyl phosphate is formed, suggesting that metaphosphate ion is not a reaction intermediate, or more probably is not partitioned indiscriminately between methanol and water.

The hydrolysis of inorganic pyrophosphate has been studied very extensively in the pH region $1-10^{3-5}$ and

the over-all rate constants have been dissected into the individual rate constants relating to the undissociated

(3) S. L. Friess, *J. Am. Chem. Soc.*, **74**, 4027 (1952).

(4) D. O. Campbell and M. L. Kilpatrick, *ibid.*, **76**, 893 (1954).

(5) R. K. Osterheld, *J. Phys. Chem.*, **62**, 1133 (1958), and references cited.