

the scatter of the experimental points and the fact that a significant change in the activity coefficients may accompany the replacement of sodium perchlorate by chromium(III) perchlorate while keeping the ionic strength constant, it does not seem justifiable to assert that the exchange in experiments 9 and 21-29 is governed by a rate law different from equation 2 coupled with equation 3.

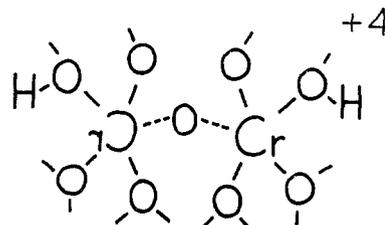
The several series of experiments were performed at different values of the ionic strength. A comparison of the results in the several series is made by calculating the value of $F([H^+])$ for $[H^+] = 0.1 M$. These values are

$I (\times 1. \text{mole}^{-1})$	0.47	0.70	0.79
Exps.	6-8	1-5	9-12
$10^6 \times F([0.1]) \times$ moles $l.^{-1} \text{ sec.}$	17 ± 1	13 ± 2	11 ± 1
$I (\times 1. \text{mole}^{-1})$	0.91	0.93	1.16
Exps.	13-20	21-29	30-33
$10^5 \times F([0.1]) \times$ moles $l.^{-1} \text{ sec.}$	8.0 ± 0.4	9.0 ± 1.3	13.0 ± 0.5

That $F([0.1])$ should show the indicated dependence upon I is consistent with the fact that the path with $n = 2$ (see reaction 5), with $(\Delta Z^2)^\ddagger = -6$, is dominant at $[H^+] = 0.1 M$. (The value of $(\Delta Z^2)^\ddagger$ is the sum of the squares of the charges on the products minus the sum of the squares of the charges on the reactants in the balanced chemical equation for the net activation process,²⁴ reaction 5 in the present study.) With this sign for $(\Delta Z^2)^\ddagger$, the rate coefficient should decrease with an increase of I at low values of I ; the opposite trend at high I is not anomalous.

the exchange of manganese(II) and manganese(VI) by A. W. Adamson (*J. Phys. Chem.*, **55**, 293 (1951)) consisting of the rate-determining exchange of manganese(III) and manganese(IV) also leads to reaction orders 3/2 and 1/2, respectively, which do not suggest the correct mean oxidation number for manganese in the transition state $1/2 ((3/2) \times 2 + (1/2) \times 7) \pm 3.5$.

The rationalization of the fact that the two reaction pathways have transition-states differing in composition by two protons may lie in the symmetry of the transition-state for exchange if such exchange occurs in a single step (*e.g.* reaction 1). If different transition-states for this reaction involve the same bridging atom (or group), the composition of these symmetrical transition states must differ from one another by an even number of atoms. For $n = 0$ and $n = 2$ (see reaction 5), these transition-states could have the geometry



with the indicated H's included for $n = 0$ and omitted for $n = 2$. The necessity of chromium(III) reducing its coordination number to 5 before forming this transition state does not impose upon the reaction



a rate too large to be consistent with the observed rate of O^{18} exchange between water and hexa-aquochromium(III) ion.²⁷ The shuffling of protons necessary in going from the predominant form of the reactants to a symmetrical transition-state such as this would be accomplished in relatively rapid equilibria and should not be considered a deterrent to the formation of the symmetrical transition-state.

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Alkaline Earth-Tantalum-Oxygen Phases Including the Crystal Structure of an Ordered Perovskite Compound, $\text{Ba}_3\text{SrTa}_2\text{O}_9$

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Further investigation of the perovskite-like phases $\text{Ba}_3\text{CaTa}_2\text{O}_9$ and $\text{Ba}_3\text{SrTa}_2\text{O}_9$ indicates that an X-ray powder pattern of the first can be indexed on a 4.17 Å. cubic cell, while for the second a hexagonal cell with $a = 5.95$, $c = 7.47$ Å. is required. The structure of the latter can be described as a repetition of three close packed BaO_3 layers with Sr and Ta in an ordered arrangement in octahedral holes. When this phase is heated in the presence of silica it changes to a $\text{Ba}_5\text{Ta}_4\text{O}_{15}$ type compound. From a plot of cell sizes for solid solutions of $\text{Ba}_5\text{Ta}_4\text{O}_{15}$ and $\text{Sr}_5\text{Ta}_4\text{O}_{15}$, it was found that the cell size of the product on heating corresponded to the composition $(\text{Ba}_{4.85}\text{Sr}_{1.15})_5\text{Ta}_4\text{O}_{15}$.

Introduction

In previous work compounds of the general formula $\text{Ba}_3\text{M}^{\text{II}}\text{Ta}_2\text{V}\text{O}_9$ have been reported with $\text{M}^{\text{II}} = \text{Sr, Ca, Zn, Fe, Co, Ni}$.² An inspection of their X-ray powder photographs showed that

these compounds have structures related to that of perovskite. This relationship may be emphasized by writing the formula $\text{Ba}(\text{M}_{1/3}^{\text{II}}\text{Ta}_{2/3}^{\text{V}})\text{O}_3$ with the parentheses indicating the octahedrally coordinated cations. Further X-ray and preparation studies on the compounds with $\text{M}^{\text{II}} = \text{Ca}$ and Sr were undertaken since it seemed less likely that these large cations would occupy octahedral positions equivalent to those of tantalum.

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(2) Francis Galasso, Lewis Katz and Roland Ward, *J. Am. Chem. Soc.*, **81**, 820 (1959).

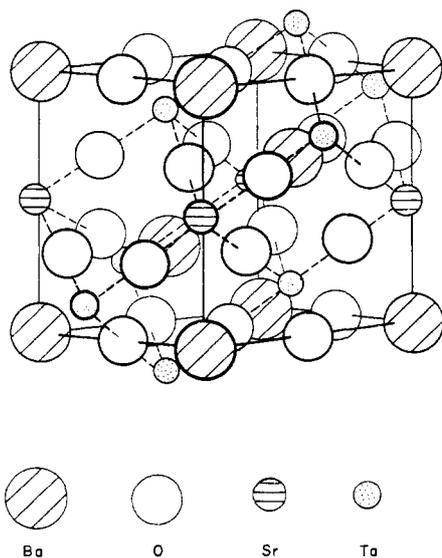


Fig. 1.—Structure of $\text{Ba}_3\text{SrTa}_2\text{O}_9$: the related perovskite units are shown in dotted outline.

Experimental

Initial attempts to prepare $\text{Ba}_3\text{CaTa}_2\text{O}_9$ left doubt that a compound of the same composition as the starting mixture was obtained.² Further work with this preparation has shown that it is possible to obtain an X-ray powder pattern indexable on the basis of a small cubic cell with $a = 4.17 \text{ \AA}$ but that other phases are also present. The most persistent of these is a hexagonal phase of the $\text{Ba}_5\text{Ta}_4\text{O}_{15}$ type.³

The phase $\text{Ba}_3\text{SrTa}_2\text{O}_9$ was also examined, with a variety of results. The best patterns, from the standpoint of simplicity and probable purity, were obtained by starting with BaO , SrO and Ta_2O_5 and heating in a sealed, evacuated, 10 mm. i.d. silica capsule for 24 hr. at 1100° . Two weak lines on the pattern corresponded to the strongest lines of $\text{Ba}_5\text{Ta}_4\text{O}_{15}$. All but three of the remaining lines could be indexed by assuming a small rhombohedral distortion of the basic perovskite cube. In order to account for all of the remaining lines, however, it was necessary to assume a

TABLE I

COMPARISON OF OBSERVED AND CALCULATED INTENSITIES AND $\text{SIN}^2 \theta$ VALUES

All non-observed reflections had calculated intensities smaller than the smallest of those observed. They are therefore not included in this table.

<i>hkl</i>	$\text{SIN}^2 \theta \times 10^4$		Intensities	
	obsd.	calcd.	obsd.	calcd.
001	106	106	w	3
100	224	223	w	3
101,011	328	329	w	4
102,012	648	649	vs	98
110	670	670	vs	100
202,022	1318	1319	s	55
104,014	1925	1926	iii ⁺	20
212,122	1992	1988	s	62
300		2009		
204,024	2596	2596	iii	18
220	2684	2678	m ⁻	16
214,124	3259	3265	m	18
312,132	3333	3328	m	16
006	3832	3832	w	3
402,042	3998	3997	w ⁺	9
116	4484	4502	w ⁺	12
410,140	4688	4687	w ⁺	10
404,044	5281	5274	w	6

(3) Francis Galasso and Lewis Katz, to be published.

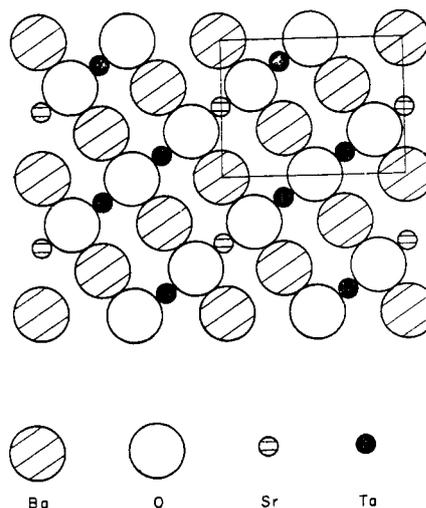


Fig. 2.—Three-layer repeat sequence in $\text{Ba}_3\text{SrTa}_2\text{O}_9$: ions shown lie in the (11.0) plane.

hexagonal cell ($a = 5.95 \text{ \AA}$, $c = 7.47 \text{ \AA}$) of volume three times that of the small rhombohedral cell. This larger cell permits an ordered arrangement of the Sr and Ta in the octahedrally coordinated positions. The structure postulated may be based on space group $\text{P}\bar{3}\text{m1}$ with atoms at the following locations: 1 Ba at $0,0,0$. 2 Ba at $1/3, 2/3, z$ and $2/3, 1/3, \bar{z}$ with $z = 2/3$. 1 Sr at $0,0,1/2$. 2 Ta at $1/3, 2/3, z$ and $2/3, 1/3, \bar{z}$ with $z = 1/6$. 6 O at x, \bar{x}, z ; $x, 2x, z$; $2\bar{x}, \bar{x}, z$; \bar{x}, x, \bar{z} ; $\bar{x}, 2\bar{x}, \bar{z}$; $2x, x, \bar{z}$ with $x = 1/6$, $z = 1/3$. 3 O at $1/2, 0, 0$; $0, 1/2, 0$; and $1/2, 1/2, 0$. The structure is illustrated in Figs. 1 and 2; note how it would revert to the perovskite structure on replacing both Ta and Sr by M^{IV} ions. In Table I the $\text{sin}^2 \theta$ values for the observed reflections are recorded, together with the indices and calculated and observed intensities. The intensity agreement is good and supports the postulated structure.

It should be pointed out that most of the attempts to prepare this $\text{Ba}_3\text{SrTa}_2\text{O}_9$ phase resulted in different products. It was therefore decided to examine the effects of continued heating. For this purpose a sample was mounted on a silica fiber using starch as an adhesive, and photographs were taken at 850° in a high temperature X-ray powder camera. The $\text{Ba}_3\text{SrTa}_2\text{O}_9$ pattern gradually disappeared, and the $\text{Ba}_5\text{Ta}_4\text{O}_{15}$ pattern grew stronger until finally, after some 60 hr., a complete conversion was effected. The new phase was stable at room temperature also.

The presence of the $\text{Ba}_5\text{Ta}_4\text{O}_{15}$ phase needed clarification. Only a little of this phase was present in the $\text{Ba}_3\text{SrTa}_2\text{O}_9$ prepared at 1100° in the silica capsule. However, when the $\text{Ba}_3\text{SrTa}_2\text{O}_9$ was heated at 850° on a silica fiber using starch adhesive, there was considerable conversion to the $\text{Ba}_5\text{Ta}_4\text{O}_{15}$ phase even after 8 hr. The following experiments were conducted:

- $\text{Ba}_3\text{SrTa}_2\text{O}_9$ was heated in a combustion boat in air, no silica or starch present. No conversion resulted.
- The compound was mixed with starch and heated in a boat, no silica present. No conversion resulted.
- The compound was placed in silica capillaries and heated, no starch present. Conversion to the $\text{Ba}_5\text{Ta}_4\text{O}_{15}$ phase resulted.

It would appear from the above that the silica was necessary for the conversion. Perhaps it reacts with the BaO and SrO that, according to



have to be accounted for. That only a small amount of this reaction was observed in the silica capsule can be explained by the fact that relatively little of the compound is in contact with the silica in the capsule. On the fiber, or in the capillary, however, there is intimate contact between the silica and a large fraction of the compound present. Whether other substances besides silica would have the same effect has not been determined.

Although the lines of the end-product pattern indicated a compound of the $\text{Ba}_5\text{Ta}_4\text{O}_{15}$ type, they were displaced from

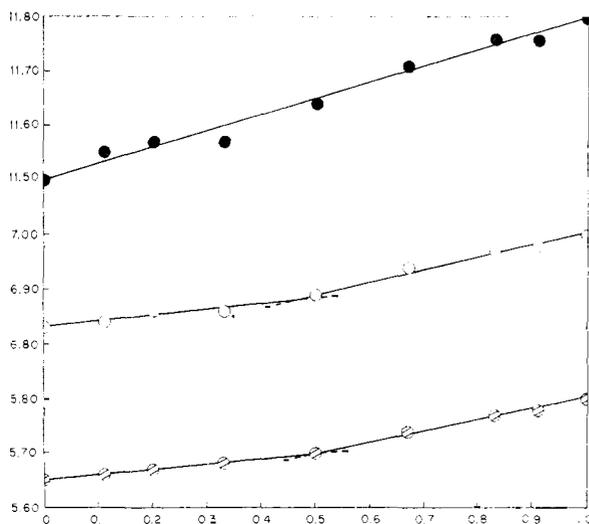


Fig. 3.—Cell dimensions versus composition for $(\text{Ba}_{1-x}\text{Sr}_x)\text{Ta}_4\text{O}_{15}$.

those of pure $\text{Ba}_5\text{Ta}_4\text{O}_{15}$. Since Sr was present, it was assumed that the product was $(\text{Ba}_{1-x}\text{Sr}_x)_5\text{Ta}_4\text{O}_{15}$. To test this possibility $\text{Sr}_5\text{Ta}_4\text{O}_{15}$ was prepared, and attempts were made to obtain solid solutions of $\text{Ba}_5\text{Ta}_4\text{O}_{15}$ and $\text{Sr}_5\text{Ta}_4\text{O}_{15}$.

These attempts were successful. Figure 3 shows plots of cell dimensions versus composition for this series. The cell size for the end product of the $\text{Ba}_5\text{SrTa}_2\text{O}_9$ conversion corresponded to the composition $(\text{Ba}_{0.85}\text{Sr}_{0.15})_5\text{Ta}_4\text{O}_{15}$. No theoretical significance is attached to the straight lines drawn through the points. A smooth curve could have been used to indicate a continuous change in cell dimensions.

Conclusion

Of the various divalent cations substituted in the octahedrally coordinated positions, all except Sr^{II} , the largest ion of the series, substituted for tantalum in a random way. This result is consistent with the general observation that large size difference, as well as large charge difference, leads to ordered arrangements. In the perovskite-like compounds $\text{Ba}_2\text{M}^{IV}\text{W}^{VI}\text{O}_6$, ordering was observed regularly.⁴ In the $\text{Ba}_3\text{M}^{IV}\text{Ta}_2\text{O}_9$ series, on the other hand, the smaller charge difference (+2 vs. +5) leads to ordering only when combined with the large size of Sr^{II} .

Acknowledgments.—We are grateful for assistance provided by the National Science Foundation, Grant NSF-G6214. We also wish to thank Professor Roland Ward for helpful discussions.

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Magnetic and Thermodynamic Properties of Potassium Ferricyanide at Low Temperatures

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The heat capacity and magnetic susceptibility of potassium ferricyanide have been measured from 0.6° to 20°K. There is a small peak in the heat capacity below 2°K. whose maximum is at 1.2°, and $\chi_m T$ decreases sharply below 2°. The susceptibility obeys a Curie-Weiss law between 20° and 2°K. The entropy removed by isothermal magnetization to 7040 oersteds at 1.245°K. was 0.122 e.u. Adiabatic demagnetization from this point lowered the temperature to 0.52°K.

Introduction

This paper reports the latest in a series of investigations by this Laboratory of the magnetic and thermodynamic properties of compounds involving the first transition series (iron group) elements. Previous studies²⁻⁴ have reported a variety of effects due to interactions of the magnetic ions with surrounding ions and molecules. These interactions usually result in deviations of the magnetic susceptibility from Curie or Curie-Weiss law behavior and in heat capacity anomalies at low temperatures.

In potassium ferricyanide, the $\text{Fe}(\text{CN})_6^{-3}$ ion is an octahedral complex. Two of the five 3d orbitals of the ferric ion are used in the $d\gamma^2sp^3$ bonding orbitals, leaving three d_e orbitals for the five remaining electrons. Two electrons each are paired in two d_e orbitals, leaving a single unpaired

electron. The magnetic susceptibility accordingly is much closer to that corresponding to a single unpaired electron than to that of the normal $^6S_{5/2}$ ground state of Fe^{+3} . Although the crystal structure of $\text{K}_3\text{Fe}(\text{CN})_6$, space group $C_{2h}^5\text{-P2}_1/c$, is monoclinic, the angle between the c -axis and the plane of the a - and b -axis is 90°6', so that the structure is pseudo-orthorhombic.⁵ Crystal structure data indicate that there are two non-equivalent ferricyanide ions per unit cell.⁶

The principal susceptibilities of $\text{K}_3\text{Fe}(\text{CN})_6$ were measured by Jackson⁷ from 14° to 290°K. The susceptibility is distinctly anisotropic, and for the powdered salt is twice the amount expected for a single unpaired electron. At 14°K. the powder susceptibility is close to the value for a single unpaired electron. The anisotropy observed by Jackson was explained by Howard⁸ in terms of a rhombic, almost axial, crystal field acting on the d_e orbitals. Howard's treatment succeeded in re-

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