These, when plotted against the concentration of hydrogen ion, should give a straight line whose slope is equal to K_1 and whose zero intercept is equal to $2K_1K_2$. Such a plot is shown as Fig. 1: from it we conclude that the hydrolysis constants of vanadic ion are

$$K_1 = [VOH^{++}][H^+]/[V^{+++}] = (1.2 \pm 0.3) \times 10^{-3}$$
$$K_2 = [VO^+][H^+]/[VOH^{++}] = (3 \pm 1.5) \times 10^{-4}$$

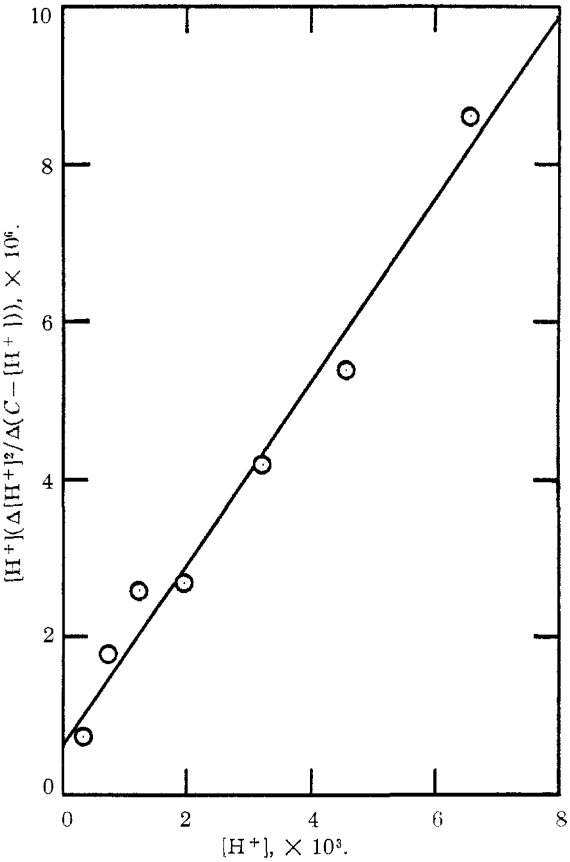

Fig. 1.—Plot of $[H^+](\Delta[H^+]^2/\Delta(c - [H^+]))$ *vs.* $[H^+]$ for the data of Jones and Ray on the *p*H values of vanadic sulfate solutions at concentrations between 0.0004 and 0.040 *M* in +3 vanadium.

The data on which these calculations were based were secured by Jones and Ray,[1] who measured the *p*H values of solutions of carefully purified vanadic sulfate at a number of concentrations from 0.0001 to 1 *M* in +3 vanadium. They assumed that VO^+ was the only hydrolysis product and attempted to compute a hydrolysis constant from their data, but failed because their equations could not correctly describe the relationship between the concentration of hydrogen ion and that of unhydrolyzed vanadic ion.

Two assumptions were made in these calculations: that the measured *p*H is equal to $-\log[H^+]$, and that all activity coefficients may be set equal to unity. In the range of ionic strengths used in constructing Fig. 1, these assumptions probably do not lead to errors much greater than those corresponding to the uncertainties in the data themselves.

In addition to its use in the calculation of consecutive hydrolysis constants, this method is in principle also suitable for the calculation of the dissociation constants of any dibasic acid from data on $[H^+]$ and *c*. In practice, however, it is useful only if K_1 and K_2 are not too widely separated: if this is not the case, the terms representing the contribution of the second dissociation or hydrolysis step become relatively very small and the experimental errors are enormously magnified in the calculation of K_2.

We have also used the data of Jones and Ray[1] on the *p*H values of vanadyl sulfate solutions to calculate the hydrolysis constant of VO^{++}. As the calculations are perfectly straight-forward, we shall record only the final result. For $0.0001 \leqslant c \leqslant 0.050$

$$K = [VOOH^+][H^+]/[VO^{++}] = (4.4 \pm 0.4) \times 10^{-6}$$

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Some Observations on High Temperature Gallate (III) Formation

BY THERALD MOELLER AND GLENDALL L. KING

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Physicochemical studies[1] on gallium(III) salt solutions have shown the gallium ion to be comparatively acidic. Further information on the acidic properties of gallium in this oxidation state might be expected from investigations of reactions of the oxide with more basic oxides and hydroxides. Although gallate(III) formation in aqueous solution is well recognized,[1,2] the species present are somewhat difficult to characterize. On the other hand, high temperature reactions yield easily studied products. The preparation and properties of spinel-like gallates of the type $M^{II}Ga_2O_4$, where M^{II} is magnesium,[3,4] zinc[5] or cadmium,[6] have been described. These observations have been checked and extended to materials derived from other basic oxides. All products have been examined by X-ray diffraction techniques.

Experimental

Gallium metal, containing only spectroscopic traces of impurities, was converted to the oxide by dissolution in acid, precipitation with ammonia, and ignition. Weighed samples (0.05–0.10 g.) of gallium(III) oxide were sintered with sufficient quantities of various chemically pure metal oxides or nitrates to give 1:1 mole ratios of the two oxides. Heating was effected in porcelain containers, the conditions being summarized in Table II. The cooled products were stirred thoroughly and sampled carefully for X-ray diffraction studies. Powder patterns were obtained with Hayes powder diffraction cameras of 7 cm. radius, using Machlett,

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[1] T. Moeller and G. L. King, *J. Phys. Colloid Chem.*, **54**, 999 (1950).

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[5] F. Buschendorf, *Z. physik. Chem.*, **B14**, 297 (1931).

[6] W. Rüdorff and B. Reuter, *Z. anorg. Chem.*, **253**, 194 (1947).

Hayes and Picker tubes. In all cases, copper targets with nickel filters were operated at 40 kv. and 15 ma.

Results and Discussion

An analysis of the powder patterns obtained[7] gave the d spacings summarized in Table I as characteristic of the gallates formed, other lines of low intensity in the patterns being those of small quantities of unreacted starting materials. Spinel formation is indicated with copper(II), magnesium, zinc and cadmium, results for the last three agreeing well with those previously reported.[3-6] Data for the lanthanum compound, $LaGaO_3$, indicate a perovskite type of structure, a structure characteristic of the comparable compounds $LaFeO_3$, $LaMnO_3$ and $LaCrO_3$.[8] The perovskite structure appears probable for the strontium compound as well (compare SrV_2O_4[9]), but the data for the barium compound are completely different and do not indicate a cubic structure by the "slide-rule test." An apparently hexagonal structure is tentatively assigned to this material. No evidences of gallate formation were obtained with calcium materials.

TABLE I

SUMMARY OF d VALUES FOR GALLATES

Mg-Ga_2O_4	Cu-Ga_2O_4	Zn-Ga_2O_4	Cd-Ga_2O_4	La-GaO_3	Sr-Ga_2O_4	Ba-Ga_2O_4
4.78	4.81	4.83	4.96	2.73[a]	2.86[a]	3.15[a]
2.93[d]	2.94[d]	2.96[d]	3.05[d]	1.93[c]	2.02[c]	2.68[b]
2.50[a]	2.51[a]	2.52[a]	2.59[a]	1.58[b]	1.65[b]	2.17[f]
2.07	2.08	2.09	2.15	1.37	1.43	2.04[d]
1.69	1.70	1.71	1.77	1.22	1.28	1.97[f]
1.60[c]	1.60[c]	1.60[c]	1.66[c]	1.12	1.17	1.82[f]
1.47[b]	1.47[b]	1.48[b]	1.52[b]	1.03	1.08	1.70[e]
1.32	1.32	1.33	1.37	0.966	1.01	1.68[e]
1.25	1.25	1.26	1.30	0.865	0.952	1.63[e]
1.20	1.20	1.21	1.24		.903	1.55[e]
1.11	1.11	1.12	1.15		.862	1.50[f]
1.08	1.08	1.09	1.12		.824	1.44[f]
1.04	1.04	1.04	1.07		.791	1.28[f]
						1.24[f]

[a] First intensity. [b] Second intensity. [c] Third intensity. [d] Fourth intensity. [e] Weak (W). [f] Very weak (VW).

Unit cell lengths (a_0) for the spinel and perovskite structures are summarized in Table II.

TABLE II

HIGH TEMPERATURE GALLATE(III) FORMATION

Material sintered with Ga_2O_3	Sintering conditions, hr.	°C.	Results from powder patterns	a_0, Å.	Cation radius Å.
MgO	5	1250	$MgGa_2O_4$:spinel	8.29 ± 0.05	0.65
CuO	22	900	$CuGa_2O_4$:spinel	8.31 ± .05	.70
ZnO	22	900	$ZnGa_2O_4$:spinel	8.37 ± .05	.74
CdO	20	900	$CdGa_2O_4$:spinel	8.59 ± .05	.97
$Sr(NO_3)_2 \cdot 4H_2O$	12	850	$SrGa_2O_4$:perovskite(?)	*ca.* 4.04	1.13
	20	900			
$Ba(NO_3)_2$	12	850	$BaGa_2O_4$:hexagonal(?)		1.35
	20	900			
La_2O_3	7	1250	$LaGaO_3$:perovskite	3.86 ± 0.05	1.15

Where other data are available for comparison, agreement is excellent. It is apparent that unit cell length varies directly with dipositive cation radius in the spinels. Increase in cation radius beyond a certain value destroys the spinel structure. From the data presented here, it appears that spinel-like gallates can result only when this radius is below 1.00 Å. Increase in cation radius beyond this limit gives first the perovskite (also cubic) and then a non-cubic arrangement. Cation radius is not, of course, the only structure-determining factor, but it appears to be of importance.

Although high basicity in general promotes reaction between a metal oxide and gallium(III) oxide, factors such as surface effects, previous treatment and volatility may nullify this trend. Thus, cadmium oxide reacts readily at 900°, but magnesium oxide reacts scarcely at all even on sintering for 72 hr. at 1000°. This is in agreement with the observations of Hauptmann and Novák[3] and is paralleled by similar observations on the magnesium oxide–indium(III) oxide system.[10]

Acknowledgment.—Support received from the Office of Naval Research is gratefully acknowledged.

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The Diffusion Coefficient and Molecular Weight of Alkaline Phosphatase

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In 1935, Albers and Albers[1] reported diffusion experiments on alkaline phosphatase from swine kidneys, from which they calculated the molecular weight of the enzyme to be 6,000 to 10,000. This is an exceptionally low value for the molecular weight of an enzyme. Kraemer, *et al.*,[2] observed that serum alkaline phosphatase was associated with serum globulins in the ultracentrifuge. Hence a redetermination of the diffusion coefficient of the enzyme appeared of value.

Experimental

Diffusion coefficient determinations were carried out using the diaphragm cell method of Anson and Northrop,[3] as described by Northrop, *et al.*[4] Two cells were used having capacities of 42.4 and 47.7 ml., respectively. They were fabricated with Corning grade "F" fritted glass discs. The cells were calibrated with 2 *N* NaCl at both 5.0 and 25.0° in the manner described by Northrop.[4] The cell constants of 0.301 and 0.272, respectively, were repeatedly redetermined over the two-year period of use and the values obtained were constant within ±0.3%. Only differential diffusion coefficients were determined. Each determination with enzyme consisted of 4 to 5 consecutive 24-hour diffusion intervals. Constancy in the rate of diffusion was usually observed after 48 hours, indicating adequate equilibration of the membrane after this time.

Enzyme assays and preparations were made as previously

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