

[CONTRIBUTION FROM THE OAK RIDGE NATIONAL LABORATORY, CHEMISTRY DIVISION]

Hydrolytic Behavior of Metal Ions. X. Ultracentrifugation of Lead(II) and Tin(IV) in Basic Solution<sup>1</sup>

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The species formed by amphoteric solutes in basic aqueous media have been described by some as colloidal aggregates and by others as monomers. By equilibrium ultracentrifugation we have established that Sn(IV) and Pb(II) exist as monomeric (mononuclear) species in basic solution.

The nature of dispersions of amphoteric solutes such as Sn(IV), Pb(II), Al(III), In(III) and Zn(II) in basic aqueous solutions is in dispute. According to one view,<sup>2</sup> the solutes form colloidal, rather than true, solutions. Others<sup>3</sup> have held that monomeric (or mononuclear) ions are formed under these conditions. Since the field has been reviewed recently by Basolo,<sup>3</sup> who discussed conflicting views on the subject, the literature will not be surveyed in detail here.

The work reported here attempts to decide the question for Pb(II) and Sn(IV) by equilibrium ultracentrifugation.

## Experimental

Experimental techniques have been described elsewhere.<sup>4-8</sup> Centrifugations were carried out with a Spinco Model E Ultracentrifuge; in all but one case the rotor used was an Analytical "E," in which two 30 mm. cells can be spun simultaneously. The concentration of solute was followed by the schlieren optical system standard with this instrument, which measures refractive index gradients ( $dn/dx$ ,  $x$  being the radius), corresponding to the concentration gradients in the solution. Two centrifugations are required with this method: one of a solution made up of solvent, supporting electrolyte and solute of interest; the other of solvent and supporting electrolyte only ("background"). The refractive index gradients displace the shadow of an inclined bar a distance  $Z$  cm., and the results are obtained in terms of  $Z^*$ , the difference between the value of  $Z$  for the two centrifugations at equilibrium. Attainment of equilibrium required usually between four and seven days.

In one experiment sedimentation was followed with the interference optical system recently developed for the Spinco machine by the manufacturer. In this method a double compartment 12 mm. cell is used in an Analytical "A" rotor. One compartment contains the solution, and the other contains solvent and supporting electrolyte. Light passing through the compartments combines to give interference fringes, and the positions of the fringes in the radial direction are measured. In the radial interval between two adjacent fringes, the change in refractive index difference between the solutions in the two compartments equals the wave length of the light (5461 Å.) divided by the height of the column of solution. Changes in concentration of the solute as a function of radius can then be computed from values of  $\Delta n/c$ , the increment of refractive index with con-

centration  $c$ . The height of the column of solution was determined by subtracting from the distance between the outside of the quartz plates in the assembled cell the total thickness of the plates. Light of the desired wave length was isolated with a Baird interference filter assembly.

Refractive index increments ( $k$ ) were measured in the appropriate media with a Brice-Phoenix differential refractometer. The increments were assumed constant over the range of concentrations involved in this study. Density measurements were made with a ca. 24-cc. pycnometer. Solutions were prepared of C.P. or reagent grade chemicals without further purification. Some Pb(II) solutions were made from PbO dissolved in HClO<sub>4</sub> and brought to the desired composition by addition of appropriate amounts of concentrated NaOH and NaClO<sub>4</sub> solutions and water. Others were prepared by dissolving PbCl<sub>2</sub> in base. The initial precipitates of hydroxide obtained on addition of base redissolved to give clear solutions. The solutions were stable over the period of time required for centrifugation, though some precipitate settled out on long standing. Sn(IV) solutions were prepared by dissolving either Na<sub>2</sub>SnO<sub>3</sub>·3H<sub>2</sub>O or SnCl<sub>4</sub>·5H<sub>2</sub>O in appropriate media. These solutions were also stable during the time necessary for attaining centrifugation equilibrium, though again precipitates were deposited on long standing.

Salts used in the preparation of solutions were analyzed for lead by precipitation of PbMoO<sub>4</sub> and for tin by precipitation of SnO<sub>2</sub>.

## Results and Discussions

1. Interpretation of Results.—The interpretation of centrifugation results for charged solutes in supporting electrolytes has been described in detail elsewhere for schlieren<sup>5,7</sup> and for interference<sup>6</sup> optics. Briefly, sedimentation depends on the degree of ionization of the polymeric solute as well as on its molecular weight, and determination of molecular weight requires an estimate of charge  $z$ . The effect of charge on sedimentation varies with concentration of both polymeric solute (component 2) and supporting electrolyte (component 3); in favorable cases, centrifugation as a function of concentration allows estimation of both quantities. Though in principle the charges could be estimated from the centrifugation results, the low accuracy of the results obtained with schlieren optics precludes this for these low molecular weight solutes. The results, therefore, will be presented as apparent degrees of polymerization  $N$  computed for the maximum and minimum plausible values of the charge per monomer unit,  $z'$ .

The degree of polymerization  $N$  for an assumed  $z'$  may be computed by the equation<sup>8</sup>

$$N = M_2/M_2' = \frac{S/A_2'}{1 - z'\eta(S - \sigma)/A_2'} \quad (1)$$

where

$$S = d \ln c_2'/d(x^2) \\ \sigma = d \ln c_2/d(x^2)$$

(7) J. S. Johnson, K. A. Kraus and G. Scatchard, *J. Phys. Chem.*, **58**, 1034 (1954).

(1) This paper is based on work done for the U. S. Atomic Energy Commission at the Oak Ridge National Laboratory, Oak Ridge, Tennessee, operated by Union Carbide Corporation. Presented in part at the 131st Meeting of the American Chemical Society, Miami, Florida, April, 1957. Previous paper in series, J. S. Johnson and K. A. Kraus *J. Phys. Chem.*, **63**, 440 (1959).

(2) See *et. al.*, A. F. Wells, "Structural Inorganic Chemistry," 2nd Ed., The Clarendon Press, Oxford, England, 1950, pp. 226, 411, 420.

(3) F. Basolo in "The Chemistry of Coordination Compounds," Chapter 12, edited by J. C. Bailar, Jr., and D. H. Busch, Reinhold Publ. Corp., New York, N. Y., 1956.

(4) J. S. Johnson, K. A. Kraus and T. F. Young, *THIS JOURNAL*, **76**, 1436 (1954).

(5) J. S. Johnson, K. A. Kraus and R. W. Holmberg, *ibid.*, **78**, 26 (1956).

(6) J. S. Johnson, G. Scatchard and K. A. Kraus, *J. Phys. Chem.*, in press.

TABLE I  
 ULTRACENTRIFUGATION OF Sn(IV) AND Pb(II) IN BASIC SOLUTION

Solute and formula wt.	Concn. (M)	Supporting electrolyte	S <sub>e</sub> or S	Conditions <sup>a</sup>	Temp., °C.	-N <sub>w</sub> computed for		
						z' = 0	z' = 2	
Na <sub>2</sub> SnO <sub>3</sub>	0.101	0.5 M NaOH	0.0405	C-4-a	25	0.75	1.41	
	212.68	.5 M NaCl						
		.7 M NaOH	.0299	A-2-b	32	.82	1.32	
		.2 M NaCl						
		.1 M NaOH	.0309	A-2-a	30.5	.85	1.29	
	.9 M NaCl							
	.057	1.0 M NaCl	.0555	A-4-a	30	1.53	3.38	
	.024	1.0 M NaCl	.0325	A-4-a	30	0.89	1.22	
	Na <sub>2</sub> PbO <sub>2</sub>	.050	0.5 M NaOH	.0412	B-3-c	31.5	.68	1.05
285.19		.5 M NaClO <sub>4</sub>						
	.050	.25 M NaOH	.0368	B-5-c	31.5	.60	0.95	
	.75 M NaClO <sub>4</sub>							
	.018	.95 M NaOH	.0382	B-1-d	29	.65	0.81	
	.04 M NaCl							
	.014	.44 M NaOH	.0520	B-3-d	29	.86	1.17	
	.03 M NaCl							
	.015 <sup>b</sup>	.42 M NaOH	.0262	B-6-d	25	.54	0.86	
		.03 M NaCl						

<sup>a</sup> Conditions: approximate speed (r.p.m.): A, 27,690; B, 31,410; C, 33,450; bar angle: 1, 40°; 2, 45°; 3, 50°; 4, 55°; 5, 60°; 6, interference; solute introduced as: (a) Na<sub>2</sub>SnO<sub>3</sub>·3H<sub>2</sub>O; (b) SnCl<sub>4</sub>·5H<sub>2</sub>O; (c) PbO; (d) PbCl<sub>2</sub>. <sup>b</sup> Interference: 12 mm. cell; all others schlieren, 30 mm. cell.

and

$$A_2' = M_2'(1 - \bar{v}_2\rho)\omega^2/2RT$$

the subscripts indicate the components in question, primes refer to quantities expressed in terms of the monomer unit. In equation 1,  $M$  is molecular weight;  $c$ , concentration in molarity;  $\bar{v}$ , partial specific volume;  $\rho$ , solution density;  $R$ , gas constant;  $T$ , absolute temperature;  $\omega$ , angular velocity of centrifugation; and  $\eta = z'c_2'/2c_3$ . Activity coefficients, partial specific volumes, and densities are assumed constant. The value of  $\sigma$  may be computed with sufficient accuracy from the known molecular weight and partial volume of component 3.<sup>7</sup>

With schlieren optics, the value of  $S$  for an assumed  $z'$  is computed by the equation<sup>5</sup>

$$S_o - S = - \frac{(z'\eta/A_2')(S - \sigma)^2}{1 + (z'\eta/A_2')\sigma} \quad (2)$$

where  $S_e = d \ln (dc_2/x \, dx)/d(x^2)$ . With polymeric systems, the approximation that  $S_e = S_e \equiv d \ln (Z^*/x)/d(x^2)$  usually may be made with minor error. With the light solutes involved here, the error may be significant; we have therefore computed a correction by the equation

$$S_o - S_e = \frac{(A_3/2) - NA_2'/(1 + Nz'\eta)^2}{1 + 4k_2'NA_2'/z'k_3A_3(1 + Nz'\eta)} \quad (3)$$

Values of  $N$  were computed by iteration of equations 1, 2 and 3. The approximations made in obtaining equation 3 are the same as those of equation 21, ref. 6, and the derivation of the two equations is similar. The correction of  $S_e$  by this equation though significant affected the computed values of  $N$  by less than 4% in the centrifugations discussed here.

With interference optics, the concentration distribution of component 2, computed from the fringe position, and consequently the value of  $S$ , is also affected by the assumed magnitude of  $z'$ ; the computational procedure described in Reference 6 was used, and  $N$  was computed by equation 19 of that

reference, rather than the more approximate Equation 1 given here.

2. Conditions.—The conditions of the centrifugations are summarized in Table I. Centrifugations of Pb(II) were carried out for concentrations of NaOH (in excess of the component Na<sub>2</sub>PbO<sub>2</sub>) from 0.25 to 0.95  $M$ , for supporting electrolyte concentrations from about 0.5 to 1  $M$  total, and for initial Pb(II) concentrations of *ca.* 0.015 and 0.05  $M$ . For Sn(IV), the range of base concentration (NaOH) was approximately from 0 to 0.7  $M$  (in excess of the component Na<sub>2</sub>SnO<sub>3</sub>), and the initial Sn(IV) concentrations were between approximately 0.024 and 0.1  $M$ .

3. Centrifugation Results.—The centrifugation results are presented in Fig. 1, a deviation plot of  $(\log (Z^*/x) - (S_e/2.303)x^2)$  (schlieren) or  $(\log n^* - (S/2.303)x^2)$  vs.  $x^2$  (interference). Values of  $S_e$  and  $S = d \log n^*/d(x^2)$  used in computing the deviations are listed in Table I. The essential linearity or concavity downward of the graphs in the figures indicates that, over the concentration range of single experiments, the weight average degree of polymerization,  $N_w$ , does not change greatly with radius. Equation 1 may therefore be used without extended terms.<sup>8</sup>

The greater precision attained with the interference system is seen in the smaller scatter associated with the 0.015  $M$  Pb(II) results obtained with this optical system compared with those for other centrifugations with schlieren optics. Actually, the comparison is even more favorable to the fringe method, since with the interference optics a 12 mm. cell was used, while a 30 mm. cell was used for the schlieren optics; results with the 30 mm. cell should be 2.5 times as precise, other things being equal.

4. Density and Refractive Index Results.—Apparent volumes are listed in Table II. Scatter in the volumes is rather high, owing to uncer-

(8) J. S. Johnson and K. A. Kraus, *THIS JOURNAL*, **78**, 3937 (1956).

tainties of composition, but since the term  $(1 - \bar{v}_2\rho)$  is close to unity, the resulting uncertainty in computation of molecular weights will be only about 2%. For the same reason, the use of apparent volumes, rather than the partial volumes, entails little error. The apparent molal volumes of  $\text{Na}_2\text{SnO}_3$  given in Table II are in sharp disagreement with those computed from literature values of solution densities (*ca.* 36 cc.).<sup>9</sup>

For  $\text{Na}_2\text{PbO}_2$ , we obtained a molar refractive index increment of 0.0383 and for  $\text{Na}_2\text{SnO}_3$ , 0.0344. These values, though somewhat uncertain, are sufficiently accurate for present purposes. Literature values<sup>10</sup> were used to compute the refractive index increments of the supporting electrolytes.

TABLE II  
APPARENT MOLAL VOLUMES

Solute	Concn. (wt. %)	Solvent	$\bar{v}_2$ (cc.)	Apparent specific vol.
$\text{Na}_2\text{SnO}_3$	3.81	1 M NaCl	-6	-0.03
$\text{Na}_2\text{SnO}_3$	3.94	1 M NaOH	-3	-.02
$\text{Na}_2\text{PbO}_2$	1.38	0.7 M NaOH 0.2 M $\text{NaClO}_4$	6	.02
$\text{Na}_2\text{PbO}_2$	1.01	0.86 M NaOH	10	.03
$\text{Na}_2\text{PbO}_2$	1.36	1.3 M NaOH 0.14 M NaCl	2	.01

5. Lead(II).—The values of apparent degrees of polymerization computed from the centrifugation results are reported in Table I for  $z'$  assumed 0 and 2. Those reported for Pb(II) with  $z' = 0$  are all considerably lower than unity; with  $z' = 2$  they scatter about this value. No significant trend of molecular weight (or degree of polymerization) with increasing Pb(II) concentration, or with increasing basicity, is observed. The schlieren experiment at *ca.* 0.5 M supporting electrolyte concentration gave a higher result, but this is apparently not significant since a value of  $N$  less than unity was obtained in the presumably more precise duplicate experiment with interference optics. We thus conclude that under the conditions of the experiments the bulk of the Pb(II) in solution is monomeric (mononuclear) and charged. Though the charge could not be established with certainty, our results are consistent with the assumption that the lead species in basic solutions is  $\text{PbO}_2^-$  or a hydrate of this species (see also Section 7).

6. Sn(IV).—The degrees of polymerization  $N$  computed for  $z' = 0$  are less than unity, except for a 0.06 M stannate solution without added base where the computed value of  $N$  is *ca.* 1.5. For  $z' = 2$ , presumably a more reasonable value, the computed values of  $N$  are somewhat larger than unity. The difference between the computed values and unity, except for the same 0.06 M Sn(IV) run, however, is not necessarily significant. Since, in the presence of base, there is a lack of dependence of  $N$  on Sn(IV) concentration, the "high" values are probably not due to reversible, low molecular weight polymers in the solutions.

(9) J. Traube, *Z. anorg. allgem. Chem.*, **8**, 12 (1895).

(10) NaOH: A. Heydweiller, *Physik. Z.*, **26**, 526 (1925); NaCl: A. Krus, *Z. physik. Chem.*, **B34**, 13 (1936);  $\text{NaClO}_4$ : H. Kohnner, *ibid.*, **B1**, 427 (1928).

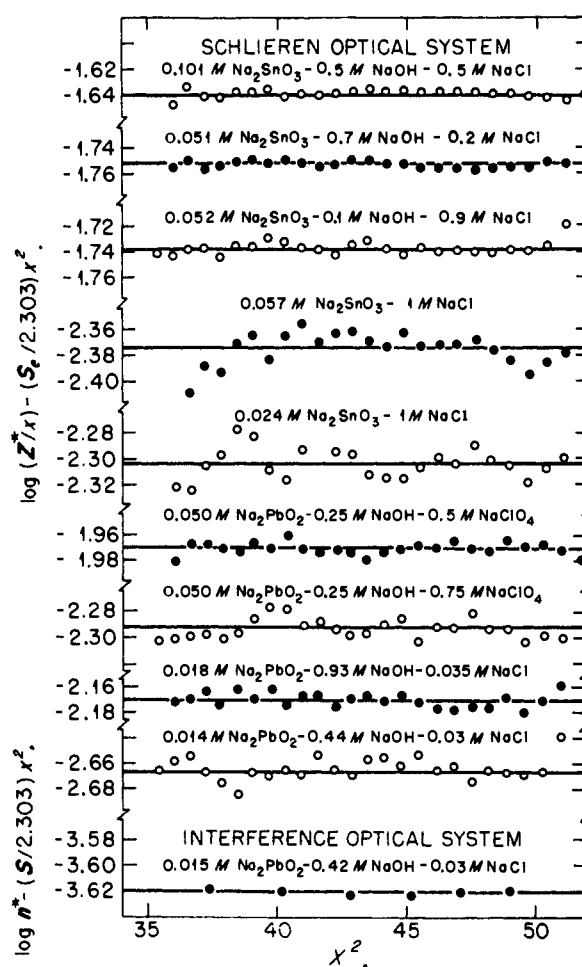


Fig. 1.—Ultracentrifugation of Sn(IV) and Pb(II) in basic solution (values of  $S$  and  $S_0$  in Table I).

They might be due to small amounts of low molecular weight polymers not in equilibrium with the monomer. This, however, is unlikely since in studies with other systems we have not observed irreversible aggregation at degrees of polymerization close to one. Irreversibly-formed, high molecular weight polymers would be essentially completely centrifuged out of the solutions at the speeds of rotation used here, or at least the results would have indicated significant polydispersity (concavity upward of the graphs in Fig. 1). Thus, we believe that except for the 0.06 M Sn(IV) solution in absence of excess base, the degree of polymerization of Sn(IV) is unity; further, there is no evidence of colloidal aggregates in any of these solutions.

7. General Discussion.—The computations of degrees of polymerization were based on the assumption that  $\text{Na}_2\text{PbO}_2$  and  $\text{Na}_2\text{SnO}_3$  are the monomer units, which implies that the metal species have the formula  $(\text{PbO}_2)_{N-2N}$  or  $(\text{SnO}_3)_{N-2N}$  except for possible complexing by  $\text{Na}^+$  ions and that the maximum plausible charge per monomer unit  $z'$  is 2. One might ask whether our conclusions might have been different had other monomer units been assumed. The question is especially pertinent with Sn(IV), where all values of  $N$  computed for  $z' = 2$  were higher than unity, even though not to an extent beyond possible experi-

mental error for any one case. The extent of the average deviation from unity seems somewhat more than might be expected from neglect of activity coefficient derivatives.<sup>6</sup>

The monomer units could, for example, have been taken as  $\text{Na}_2\text{Sn}(\text{OH})_6$  or as  $\text{NaSnOOH}$ . The former, for which there is structural evidence in the solid state,<sup>11</sup> differs from  $\text{Na}_2\text{SnO}_3$  only in that it contains three molecules of water of hydration. Non-ideality stemming from hydration cannot be distinguished from other non-ideality,<sup>12</sup> and the present results thus can not be used to distinguish between, e.g.,  $\text{SnO}_3^{2-}$ , as assumed for  $z' = 2$ , or  $\text{Sn}(\text{OH})_6^{2-}$ . To be sure, the component  $\text{Na}_2\text{Sn}(\text{OH})_6$  has a higher molecular weight  $M_2'$  than the component  $\text{Na}_2\text{SnO}_3$ , but a larger volume  $\bar{v}_2$  would also be computed from density measurements; the terms  $M_2'(1 - \bar{v}_2\rho)$  thus do not differ significantly for the two components, and the computed values of  $N$  will be essentially the same (within about 2%).

The other component suggested,  $\text{NaSnOOH}$ ,<sup>13</sup> differs from  $\text{Na}_2\text{SnO}_3$  more fundamentally since it contains one less mole of  $\text{NaOH}$  per mole of

(11) C. O. Björling, *Arkiv. Kemi., Mineral. Geol.*, **15B**, Paper 2 (1941); J. Krc, *Anal. Chem.*, **23**, 675 (1951).

(12) See e.g., R. L. Baldwin and A. G. Ogston, *Trans. Faraday Soc.*, **50**, 749 (1954).

(13) There is some evidence against this species; see, e.g., G. E. Collins and J. K. Wood, *J. Chem. Soc.*, **121**, 441 (1922).

$\text{Sn}(\text{IV})$  and thus has a maximum plausible charge  $z'$  of unity. Degrees of polymerization computed for this component, with  $z' = 1$ , were substantially lower but still considerably above unity.

Another explanation for the consistently "high" results for  $\text{Sn}(\text{IV})$  might be that the monomeric species  $\text{SnO}_3^{2-}$  is partially complexed by  $\text{Na}^+$  to give a charge  $z'$  less than its maximum value of two. Although the results computed on the basis of  $z' = 1$  scatter close to  $N = 1$ , the experimental uncertainty precludes any conclusion on sodium complexing at this time.

In any case, the present results indicate that at least in freshly prepared basic solutions the solute species of both  $\text{Pb}(\text{II})$  and  $\text{Sn}(\text{IV})$  are monomeric. The possibility that other amphoteric metals exist as colloids in base is not, of course, precluded, though it seems questionable. The centrifugation results for  $\text{Sn}(\text{IV})$  are in general agreement with diffusion measurements,<sup>14</sup> which also indicated a plateau at low molecular weights for 0.05  $M$   $\text{Sn}(\text{IV})$  in basic solutions.

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(14) G. Jander, F. Busch and T. Aden, *Z. anorg. allgem. Chem.*, **177**, 345 (1929).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WASHINGTON UNIVERSITY]

## Cesium Ion Catalysis of the Manganate-Permanganate Isotopic Exchange Reaction<sup>1</sup>

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The greater rate<sup>3</sup> of exchange between  $\text{MnO}_4^{2-}$  and  $\text{MnO}_4^-$  in aqueous  $\text{CsOH}$  than in aqueous  $\text{NaOH}$  is shown to be due to catalysis by  $\text{Cs}^+$ , not by an impurity. At 0° and ionic strength 0.16 (adjusted with  $\text{NaOH}$ ) the rate dependence on  $\text{Cs}^+$  concentration is consistent with the law, Rate =  $(\text{MnO}_4^{2-})(\text{MnO}_4^-)[k_0 + k'(\text{Cs}^+)]$ . The value<sup>3</sup> of  $k_0$  is  $710 \pm 30 M^{-1} \text{sec.}^{-1}$ , and the value of  $k'$  is  $12,000 \pm 3000 M^{-2} \text{sec.}^{-1}$ .

Sheppard and Wahl<sup>3</sup> observed that the rate of the manganate-permanganate isotopic exchange reaction was dependent on which of the alkali metal ions was present, the rate being largest in the presence of cesium ion, less in the presence of potassium ion and still less in the presence of sodium or lithium ions. The surprisingly effective catalysis by cesium ion (the exchange rate in 0.16  $f$   $\text{CsOH}$  was  $\sim 3.5$  times greater than in 0.16  $f$   $\text{NaOH}$ ) was open to some question because the cesium hydroxide solution had been prepared by reaction of aqueous cesium iodide with excess silver(I) oxide, and the small amount of silver(I) going into solution could have been the effective catalyst.

We have checked this possibility by measuring the exchange rate in sodium hydroxide solution prepared by reaction of aqueous sodium iodide with excess silver(I) oxide and in cesium hydroxide solu-

tion prepared by reaction of aqueous solutions of barium hydroxide and cesium sulfate.

### Experimental

Mallinckrodt A.R. chemicals were used without purification except for the following. Fisher "purified"  $\text{Cs}_2\text{SO}_4$  was further purified by the  $\text{CsICl}_2$  method of West and Anderson<sup>4</sup> for one  $\text{CsOH}$  preparation, and Fairmont C.P.  $\text{Cs}_2\text{SO}_4$  was used without purification for another. Mallinckrodt U.S.P. IX  $\text{Ag}_2\text{O}$  was used for preparation of one  $\text{NaOH}$  solution.

The apparatus and procedures described by Sheppard and Wahl<sup>3</sup> were used, except measurements of the  $\text{Mn}^{54}$   $\gamma$ -ray intensity were made with a sodium iodide well-type scintillation crystal.

The reactant concentrations were kept approximately constant, each at  $\sim 10^{-4} M$ . The assumption was made that the second-order rate law observed by Sheppard and Wahl<sup>3</sup> applied.

During the course of most runs, which required several hours, the specific activity of the permanganate fraction increased slightly with time. We think the effect was probably due to the slow decomposition of the tagged manganate ion and coprecipitation of a decomposition product with tetraphenylarsonium perchlorate-permanganate. To

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(2) Fellow from Norway supported by an American-Association-of-University-Women International Grant during the 1957-1958 academic year.

(3) J. C. Sheppard and A. C. Wahl, *This Journal*, **79**, 1020 (1957).

(4) R. West and R. P. Anderson, in "Inorganic Syntheses," Vol. IV, edited by J. C. Bailar, Jr., McGraw-Hill Book Co., New York, N. Y., 1953, pp. 9-11.