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.[6]

The monomer units could, for example, have been taken as $Na_2Sn(OH)_6$ or as $NaSnOOH$. The former, for which there is structural evidence in the solid state,[11] differs from Na_2SnO_3 only in that it contains three molecules of water of hydration. Non-ideality stemming from hydration cannot be distinguished from other non-ideality,[12] and the present results thus can not be used to distinguish between, e.g., SnO_3^-, as assumed for $z' = 2$, or $Sn(OH)_6^-$. To be sure, the component $Na_2Sn(OH)_6$ has a higher molecular weight M_2' than the component Na_2SnO_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, $NaSnOOH$,[13] differs from Na_2SnO_3 more fundamentally since it contains one less mole of 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).

$Sn(IV)$ 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 $Sn(IV)$ might be that the monomeric species SnO_3^- is partially complexed by 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 $Pb(II)$ and $Sn(IV)$ 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 $Sn(IV)$ are in general agreement with diffusion measurements,[14] which also indicated a plateau at low molecular weights for 0.05 M Sn(IV) in basic solutions.

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

Oak Ridge, Tenn.

Cesium Ion Catalysis of the Manganate–Permanganate Isotopic Exchange Reaction[1]

By Liv Gjertsen[2] and Arthur C. Wahl

The greater rate[3] of exchange between MnO_4^{--} and MnO_4^- in aqueous CsOH than in aqueous NaOH is shown to be due to catalysis by Cs^+, not by an impurity. At 0° and ionic strength 0.16 (adjusted with NaOH) the rate dependence on Cs^+ concentration is consistent with the law, Rate $= (MnO_4^{--})(MnO_4^-)[k_0 + k'(Cs^+)]$. The value[3] of k_0 is 710 $\pm$ 30 M^{-1} sec.$^{-1}$, and the value of k' is 12,000 $\pm$ 3000 M^{-2} sec.$^{-1}$.

Sheppard and Wahl[3] 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 CsOH was $\sim$3.5 times greater than in 0.16 f 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-

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

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" Cs_2SO_4 was further purified by the $CsICl_2$ method of West and Anderson[4] for one CsOH preparation, and Fairmont C.P. Cs_2SO_4 was used without purification for another. Mallinckrodt U.S.P. IX Ag_2O was used for preparation of one NaOH solution.

The apparatus and procedures described by Sheppard and Wahl[3] were used, except measurements of the Mn^{54} γ-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[3] 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 perrhenate–permanganate. To

(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.

reduce systematic errors caused by this effect, points were run so as to obtain both "short-" and "long-time" points early and late in the run. In drawing exchange curves, we have weighted more heavily the points run early.

For estimation of limits of uncertainty in the half-time values, exchange curves were drawn with maximum and minimum slopes consistent with the data after allowance for a 3% uncertainty in the fraction-exchange values. These uncertainties are quite large, 10 to 30%, due partly to the effect discussed in the preceding paragraph and partly to the large zero-time exchange associated with the very rapid reaction. In 0.16 f CsOH at 0° the half-time was 1.4 ± 0.4 sec.; ~60% exchange occurred during the mixing and quenching procedures.

Results and Discussion

The data summarized in Table I show that the rate of exchange is not affected appreciably by the presence of the silver(I) in solution resulting from reaction of aqueous sodium iodide and excess silver(I) oxide. We conclude, therefore, that the large rate[3] in cesium hydroxide solution prepared by reaction of aqueous cesium iodide and excess silver(I) oxide was due mainly to catalysis by cesium ion.

TABLE I

EXCHANGE RATE IN 0.16 f NaOH AT 0°

Method of prepn. of NaOH soln.	(MnO_4^{--}) + (MnO_4^-), $M \times 10^4$	$t_{1/2}$, sec.	k_0, M^{-1} sec. $^{-1}$
NaOH pellets	1.87	5.5	680
NaOH pellets	1.85	5.5	680
NaI + Ag₂O	1.98	5.0	700
NaI + Ag₂O	1.95	5.0	710
Sheppard–Wahl[3] av. value			710 ± 30

In support of this conclusion we have found that exchange rates in cesium hydroxide solutions prepared by reaction of aqueous solutions of barium hydroxide and cesium sulfate (in small excess)[5] agreed, within experimental errors, with the rates measured by Sheppard and Wahl.[3] The data are summarized in Fig. 1.

The linear increase in rate with cesium ion concentration is consistent with the rate law

Rate = $(MnO_4^{--})(MnO_4^-)[k_0 + k'(Cs^+)]$

At 0° and ionic strength 0.16 (adjusted with NaOH) the value of k_0 is 710 ± 30 M^{-1} sec.$^{-1}$ (S. and W.[3])

(5) Sheppard and Wahl[3] showed that substitution of SO_4^{--} and other anions for OH$^-$ affected the rate very little.
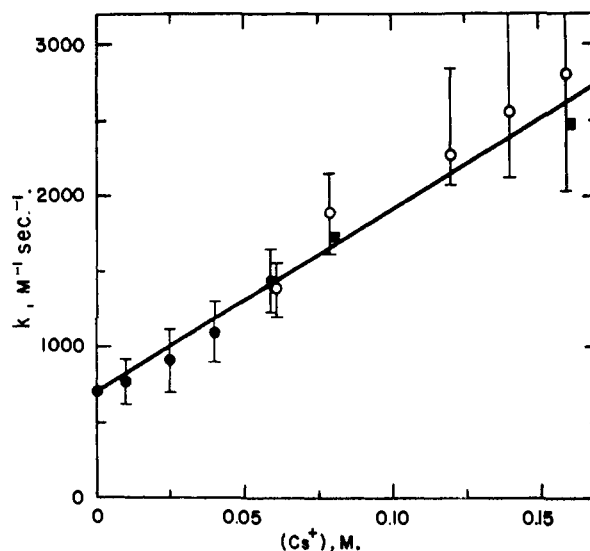

Fig. 1.—Rate dependence on cesium ion concentration; 0°; ionic strength adjusted to 0.16 with NaOH; 0.016 M OH$^-$: ●, cesium purified[4] before CsOH preparation; ○, C.P. Cs₂SO₄ used in CsOH preparation; ■, Sheppard and Wahl[3] values.

and the value of k' is 12,000 ± 3,000 M^{-2} sec.$^{-1}$. The rate law supports the suggestion[3] that Cs$^+$ may be incorporated into the activated complex, possibly forming a bridge between the manganate and permanganate ions.

A somewhat poorer fit of the data is obtained with the equation log $k/k_0 = \alpha(Cs^+)$, suggested by numerous observations[6] on activity coefficients in mixed strong electrolyte systems. However, the value of α is ~4, which is unreasonably large.

One run at 0° in 0.08 f CsOH (no NaOH added) gave a rate constant of 1680 M^{-1} sec.$^{-1}$, which is the same, within experimental errors, as the values 1730 M^{-1} sec.$^{-1}$ (S. and W.[3]) and 1880 M^{-1} sec.$^{-1}$ obtained from runs in 0.08 f CsOH, 0.08 f NaOH.

(6) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., pp. 595–616.

St. Louis, Missouri