Inorganic Chemistry

Kinetics of the Exchange of Water between Oxygen-18-Labeled Solvent and Aquorhodium(III) Cation

BY W. PLUMB[1] AND G. M. HARRIS

A kinetic study was made of the exchange reaction between $Rh_{aq}{}^{+3}$ ion and O^{18}-labeled solvent water, using conventional isotopic dilution technique. Data were obtained on the dependence of the exchange on complex ion concentration, acidity, temperature, and ionic strength. The hydration number was also evaluated, and is 5.9 ± 0.4. The exchange reaction obeys a rate law of the form

$$R = k_1[Rh(H_2O)_6{}^{+3}] + k_2 K_a[Rh(H_2O)_6{}^{+3}]/[H^+]$$

where k_1 and k_2 are first-order rate constants for the dissociation of a water molecule from the hexaaquo and pentaaquo-hydroxo ions, respectively, and K_a is the first acid dissociation constant of hexaaquorhodium(III) cation. At $64.4°$ and $\mu = 12$, the magnitudes of the three constants are 1.3×10^{-3} min.$^{-1}$, 2×10^{-1} min.$^{-1}$, and 4×10^{-3} M, respectively. The Arrhenius activation energy for the acid-independent process is 33 ± 3 kcal./mole.

Studies of the rate at which "free" solvent water exchanges with the "bound" water of hydrated transition metal cations are of value for several reasons. They provide information concerning the relative lability of the aquo ions and the number of water molecules retained in the primary coordination sphere. Further, if the necessary rate parameters can be determined with sufficient accuracy, some conception can be formed of the detailed mechanism of the water exchange process and of its relation to other types of ligand replacement reactions undergone by the aquo ion in question. Slow water exchange reactions were first studied by an isotopic dilution technique using oxygen-18, developed in the pioneer investigations of the $Cr_{aq}{}^{+3}$ ion by Taube and co-workers.[2a,b] This method has the disadvantage that the complex ion must be present at relatively high concentration (and thus high ionic strength), but, if separation of "free" and "bound" water is not possible, it is the only practical way. Slow exchanges which have proven amenable to the separation technique include a later study of $Cr_{aq}{}^{+3}$ ion[2c] and that of the $Co(NH_3)_5H_2O^{+3}$ ion,[3] the $Co(en)_2(H_2O)_2{}^{+3}$ ion,[4] and the $Co(en)_2NH_3$-H_2O^{+3} ion.[5] Moderately rapid exchanges have been investigated by a flow system modification of the dilution procedure, as was done[6] for $Al_{aq}{}^{+3}$. All other aquo ion–water exchanges so far examined are of the extremely rapid variety, for which information is best obtained by nuclear magnetic resonance relaxation techniques utilizing O^{17}-labeled water.[7,8] In the pres-

ent work, one is dealing with an unusually slow exchange system which could be studied only by the isotopic dilution method. The objectives of the research were not only those stated earlier, but to provide yet another basis for comparison of the kinetic behavior of Cr(III) and Rh(III) octahedral coordination compounds. As such, the work is a sequel to previously reported studies[9-12] of oxalate exchange and aquation reactions of the complex ions $Cr(C_2O_4)^{-3}$ and $Rh(C_2O_4)_3{}^{-3}$.

Experimental

Materials and Equipment.—Solid $Rh(ClO_4)_3 \cdot 6H_2O$ was prepared from $RhCl_3 \cdot 3H_2O$ in a manner similar to that of Ayres and Forrester,[13] freed of traces of $HClO_4$ by heating at $80°$ under high vacuum, and stored over anhydrous $Mg(ClO_4)_2$. Reagent grade $HClO_4$ and $Al(ClO_4)_3$ were used as obtained.[14] Isotopic analyses were performed on a C.E.C. Model 21-401 isotope ratio mass spectrometer,[15] pH determinations on a Cambridge Model R pH meter, and spectrum measurements on Beckman DK-2 and DU spectrophotometers. Temperature readings were calibrated against an N.B.S. thermometer, accurate to $\pm 0.02°$.

Water Exchange Experiments.—Preliminary attempts to effect separation of the "free" and "bound" water by precipitation and flash evaporation methods failed, due to the fact that the water cannot be removed from solid hexaaquorhodium(III) salts without extensive decomposition, involving oxidation-reduction reactions. The isotopic dilution procedure was therefore adopted, as follows: Samples of solid hexaaquorhodium perchlorate of normal isotopic content were dissolved in water containing 1.6 atom % oxygen-18. Rhodium was determined on an aliquot of the solution by reduction with magnesium chips and H_2SO_4, filtering off the black rhodium powder, igniting the latter after thorough washing with water in a Rose crucible under a hydrogen atmosphere, and weighing the purified metal obtained. Total perchlorate was found by potentiometric titration of a

(1) Work done by W. Plumb as part of the Ph.D. requirement of the University of Buffalo, 1961. Complete report available from University Microfilms, Ann Arbor, Mich.

(2) (a) J. P. Hunt and H. Taube, *J. Chem. Phys.*, **18**, 757 (1950); *ibid.*, **19**, 602 (1951); (b) R. A. Plane and H. Taube, *J. Phys. Chem.*, **56**, 33 (1952); (c) J. P. Hunt and R. A. Plane, *J. Am. Chem. Soc.*, **76**, 5960 (1954).

(3) (a) A. C. Rutenberg and H. Taube, *J. Chem. Phys.*, **20**, 825 (1952); (b) H. R. Hunt and H. Taube, *J. Am. Chem. Soc.*, **80**, 2642 (1958).

(4) W. Kruse and H. Taube, *ibid.*, **83**, 1280 (1961).

(5) D. F. Martin and M. L. Tobe, *J. Chem. Soc.*, 1388 (1962).

(6) H. W. Baldwin and H. Taube, *J. Chem. Phys.*, **33**, 206 (1960).

(7) (a) R. E. Connick and R. E. Poulson, *ibid.*, **30**, 759 (1959); (b) R. E. Connick and E. D. Stover, *J. Phys. Chem.*, **65**, 2075 (1961); (c) T. J. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 307 (1962).

(8) J. A. Jackson, J. F. Lemons, and H. Taube, *ibid.*, **32**, 553 (1960).

(9) F. D. Graziano and G. M. Harris, *J. Phys. Chem.*, **63**, 330 (1959).

(10) K. V. Krishnamurty and G. M. Harris, *ibid.*, **64**, 346 (1960).

(11) D. Barton and G. M. Harris, *Inorg. Chem.*, **1**, 251 (1962).

(12) K. V. Krishnamurty, *ibid.*, **1**, 422 (1962).

(13) G. H. Ayres and J. S. Forrester, *J. Inorg. Nucl. Chem.*, **3**, 365 (1957).

(14) The $Al(ClO_4)_3$ (G. F. Smith Chemical Co.) was found to contain 0.254 mole of $HClO_4$ per mole of Al(III). This was allowed for in making up the solutions to the specified acidity.

(15) Use of instrument by courtesy of Roswell Park Memorial Institute, Buffalo, N. Y.

second aliquot of the reactant solution with NaOH, the method being confirmed by an experiment in which the salt solution was passed through a column of Dowex 50 cation-exchange resin in the hydrogen form and subsequent titration of the eluted $HClO_4$. Known additions to the exchange samples of labeled water, $HClO_4$, and $Al(ClO_4)_3$ were made as required. The resulting reaction mixtures, totaling 10 ml. in volume, were weighed (to provide a density determination), placed in a 50-ml. round-bottom flask fitted with a stopcock,[16] frozen to Dry Ice temperature, and evacuated. On warming up, two 25–40-mg. water samples were distilled off under vacuum and retained for isotopic assay as "zero-time" samples. The reaction flask was then placed in the constant temperature bath and additional small water samples were withdrawn at convenient intervals while water exchange occurred. The oxygen-18 assay, expressed in terms of atom fraction, N, was done by equilibrating the small water samples with measured amounts of normal CO_2 gas (this required several days at room temperature in the absence of catalyst) and then obtaining the mass spectrometric data on the CO_2 requisite for calculation of N by the procedure of Doestrovsky and Klein.[17] The values of N were used[18] to calculate fractions of reaction $F = (N_0 - N_t)/(N_0 - N_\infty)$, and reaction half-times, $t^{1/2}$, were determined from the usual linear $\ln (1 - F)$ vs. time plots, as illustrated in Fig. 1. Rates of reaction were then calculated from the conventional isotopic exchange equation

$$R = 0.693ab/(a + b)t^{1/2}$$

where a is the molar concentration of "bound" water ($\equiv 6$ $[Rh^{+3}]$) and b is the molar concentration of "free" water.[19] The assumed hexacoordination of the aquorhodium ion was confirmed from the known N_∞ figures and a knowledge of the rhodium:water ratio for several of the runs. The average hydration number calculated for twelve runs chosen randomly with respect to reaction variables was 5.9 ± 0.4, with no trends evident in conditions of equilibration.

Acid Dissociation of the Rh $(H_2O)_6^{+3}$ Ion.—The published data on the acid properties of the aquorhodium(III) cation are contradictory, in spite of the use of identical potentiometric titration methods. Jørgensen[20] reported in favor of a double dissociation process, which produced the intermediate ion $Rh(H_2O)_4$-$(OH)_2^+$. Forrester and Ayres,[21] however, found evidence for only a singly-deprotonated soluble species, the ion $Rh(H_2O)_5OH^{+2}$. This latter finding was confirmed in the present work, in which it was noted by potentiometric titration that precipitation of hydrated rhodium oxide commences as soon as the $(OH^-):(Rh^{+3})$ ratio exceeds unity. This establishes a self-buffered solution of practically constant pH, with no further end point appearing until the sharp one corresponding to complete formation of $Rh(OH)_3$. The redetermined pK_a value of 3.2 is in reasonable agreement with the earlier figure[21] of 3.4 at 25°.

Results and Discussion

Series of experiments were run to test the dependence of the exchange rate on complex concentration, acidity, temperature, and ionic strength. Figure 2 summarizes the data obtained at 64.4° and ionic strength of $\sim$12. The cluster of points close to 2 M acid concentration

(16) Dow-Corning silicone high vacuum stopcock grease was found to hold fast for many hours at 64°.

(17) I. Doestrovsky and F. S. Klein, *Anal. Chem.*, **24**, 414 (1952).

(18) A test was made of the reproducibility of the N-values by assaying ten identical H_2O^{18} samples in separate experiments. The standard deviation was ±0.008% in samples containing about 1.6 atom % oxygen-18 (*i.e.*, ±0.5% on a relative basis). The response of the mass spectrometer was checked over the range 0.5 to 1.6 atom % oxygen-18 and found to be completely linear.

(19) This latter value was calculated from the measured density of the solutions and the known concentration of solutes. The "free" water concentration varied between the limits 30.4 and 45.4 M, depending on the total ionic strength of the reaction mixture.

(20) C. K. Jørgensen, *Acta Chem. Scand.*, **10**, 502 (1956).

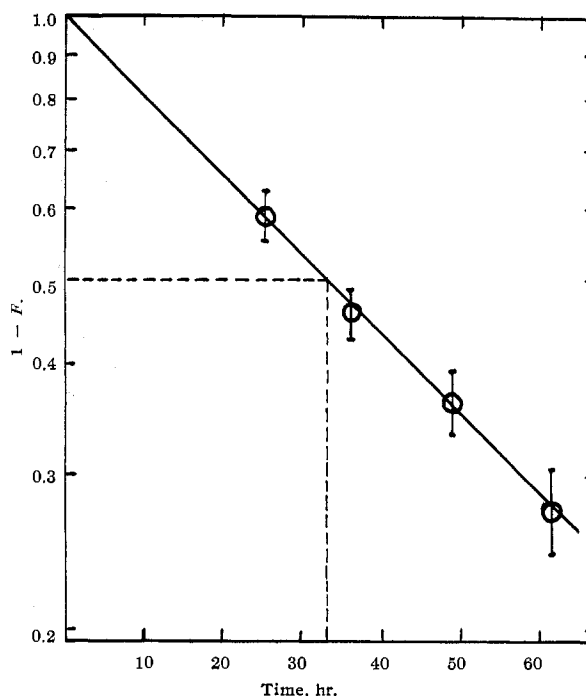(21) J. S. Forrester and G. H. Ayres, *J. Phys. Chem.*, **63**, 1979 (1959).

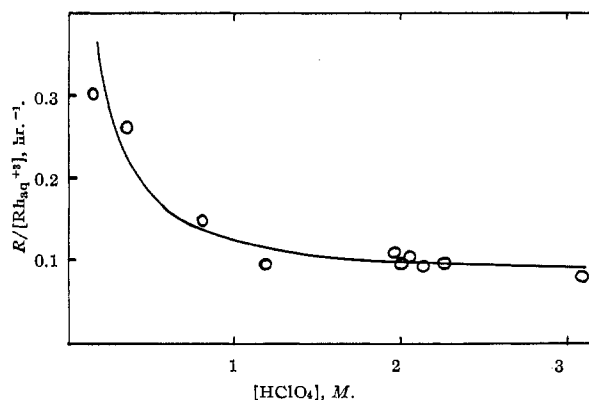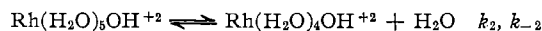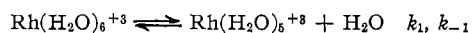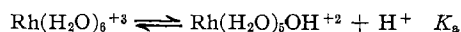Fig. 1.—Typical aquo ion exchange plot. $t^{1/2} = 33$ hr.

Fig. 2.—Variation of exchange rate with acid concentration at 64.4°.

were obtained from runs in which the $[Rh_{aq}^{+3}]$ was varied between 0.6 and 1.7 M, satisfactorily proving a first-order dependence on this reactant, as expected.[22] The variation of rate with acidity is in accordance with the relation $R/[Rh_{aq}^{+3}] = R_1 + R_2/[H^+]$, the smooth curve shown being calculated by use of the values $R_1 = 0.075$ hr.$^{-1}$ and $R_2 = 0.05$ M hr.$^{-1}$. A simple rationale for this rate law derives from the following mechanism of water exchange.

$$Rh(H_2O)_6^{+3} \rightleftharpoons Rh(H_2O)_5OH^{+2} + H^+ \quad K_a$$

$$Rh(H_2O)_6^{+3} \rightleftharpoons Rh(H_2O)_5^{+3} + H_2O \quad k_1, k_{-1}$$

$$Rh(H_2O)_5OH^{+2} \rightleftharpoons Rh(H_2O)_4OH^{+2} + H_2O \quad k_2, k_{-2}$$

Making the usual assumption of instantaneous acid-base proton equilibration in aqueous systems, so that

(22) At the high acidities of these experiments, there is little likelihood of formation of a binuclear oxo-bridged complex, nor was there any evidence for this possibility from the ultraviolet spectra, since clearly defined peaks occurred at 396 and 311 mμ, with a rather low minimum at 260 mμ. Strong structureless absorption in the ultraviolet is generally observed for binuclear species.

the "primary-sphere" water dissociation reactions are rate-determining, the rate law is[23,24]

$$R = k_1[\text{Rh}(\text{H}_2\text{O})_6{}^{+3}] + k_2 K_a[\text{Rh}(\text{H}_2\text{O})_6{}^{+3}]/(K_a + [\text{H}^+])$$

This expression reduces to the experimental form provided $K_a \ll [\text{H}^+]$, as is true here. Accepting an average experimental value at 25° for pK_a of 3.3 (see Experimental section), and assuming that K_a changes with temperature in much the same way as does that for $\text{Co}(\text{H}_2\text{O})_6{}^{+3}$ ion,[25] one estimates its value at 64.4° to be 4×10^{-3} M. (This estimate ignores ionic strength effects, since in this case both acid and conjugate base are positive ions and variation of K_a with μ should be relatively small.) One thus derives values for k_1 and k_2 at 64.4° and $\mu = 12$ of 1.3×10^{-3} min.$^{-1}$ and 2×10^{-1} min.$^{-1}$. The observed k_2/k_1 ratio of 160 is of the expected order of magnitude for the labilizing effect of OH^- on displacement reactions of an adjacent ligand.[26]

A few experiments were done at 64.4° in 2 M HClO$_4$ in which the ionic strength of the solution was reduced by decreasing the $\text{Rh}(\text{ClO}_4)_3$ and/or $\text{Al}(\text{ClO}_4)_3$ concentrations. The results were:

μ, M	5.8	7.4	9.8	10.4	11.9
$R/[\text{Rh}_{aq}{}^{+3}]$, hr.$^{-1}$	0.042	0.069	0.081	0.103	0.100

The rate of reaction decreases below $\mu = 10$ according to an approximate log R vs. μ relation. The same data exhibit an almost equally satisfactory linear form if the plot is made of R vs. μ. While no simple theory is fully applicable here, it is of interest that both types of linear relation have been observed previously in hydrolysis processes involving charge separation.[27] A similar acceleration of the rate by ionic strength increase has also been noted in $\text{Cr}_{aq}{}^{+3}$ ion–water exchange.[2]

The temperature effect on the $\text{Rh}_{aq}{}^{+3}$ exchange was studied in runs made in 2.12 M HClO$_4$ and $\mu = 12$ at 64.4, 70.5, and 79.0°. The corresponding R values (M hr.$^{-1}$) were 0.095, 0.198, and 0.712, respectively. Since in 2.12 M acid nearly all the exchange ($\sim 80\%$) is *via* the acidity-independent mechanism, one deduces that the activation energy of this process is 33 ± 3 kcal./mole, and that $k_1 = 2.8 \times 10^{18} \exp(-33,000/RT)$ min.$^{-1}$. The rate constant for exchange of the $\text{Cr}_{aq}{}^{+3}$ ion, extrapolated from the published data[2] to give an estimate at $\mu = 10$, is $k_1 = 1.3 \times 10^{17} \exp(-27,000/$

(23) Independence of water concentration has been assumed, in keeping with the type of dissociative mechanism proposed. In fact, inclusion of water concentration terms in the calculation of R for the experiments at $\mu = 12$ leads to a less consistent set of data than otherwise, but the variation is practically within experimental error and cannot be taken as unequivocal evidence for a purely dissociative mechanism.

(24) An alternative mechanism involving a second-order OH$^-$–complex reaction may be ruled out on the usual basis of the unrealistically large frequency factor ($>10^{30}$) for k calculated for such a reaction. Also, direct exchange of H$_2$O or of "free" OH$^-$ for complexed OH$^-$ is unlikely, in view of the observed negligibly slow exchange of Co(NH$_3$)$_5$OH^{+2} with water (ref. 5).

(25) L. H. Sutcliffe and J. R. Weber, *Trans. Faraday Soc.*, **52**, 1225 (1956).

(26) D. R. Stranks in "Modern Co-ordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p. 129; see also ref. 4 and 5.

(27) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 2nd Ed., 1961, p. 150 *et seq.*

TABLE I

Reaction	—Cr, 35°— 10³k_1, min.$^{-1}$	Ref.	—Rh, 80°— 10³k_1, min.$^{-1}$	Ref.
$\text{M}(\text{H}_2\text{O})_6{}^{+3} + \text{H}_2\text{O}^{18} \rightarrow$ $\text{MH}_2\text{O}^{18}(\text{H}_2\text{O})_5{}^{+3} + \text{H}_2\text{O}$	9	2^a	10	This work
$\text{M}(\text{C}_2\text{O}_4)_3{}^{-3} + \text{H}_3\text{O}^+ + \text{H}_2\text{O} \rightarrow$ $\text{M}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2{}^- + \text{HC}_2\text{O}_4{}^-$	2	10^b	9	12^b
$\text{M}(\text{NH}_3)_5\text{Cl}^{+2} + \text{H}_2\text{O} \rightarrow$ $\text{M}(\text{NH}_3)_5\text{H}_2\text{O}^{+3} + \text{Cl}^-$	2	c	3	d
trans-$\text{M}(\text{en})_2\text{Cl}_2{}^+ + \text{H}_2\text{O} \rightarrow$ *trans*-$\text{M}(\text{en})_2\text{ClH}_2\text{O}^{+2} + \text{Cl}^-$	4	e	3	d

^{a} k_1 calculated from the equation derived for it above, at $\mu \sim 10$. ^{b} k_1 calculated as pseudo-first-order constant at unit [H$^+$]. ^{c} M. A. Levine, T. P. Jones, W. E. Harris, and W. J. Wallace, *J. Am. Chem. Soc.*, **83**, 2453 (1961). Independent of [H$^+$] at pH 1–10 (HClO$_4$). ^{d} S. A. Johnson, F. Basolo, and R. G. Pearson, *ibid.*, **85**, 1741 (1963). Acid concentration 0.1 N in HNO$_3$. ^{e} D. J. MacDonald and C. S. Garner, *ibid.*, **83**, 4152 (1961); D. C. Olson and C. S. Garner, *Inorg. Chem.*, **2**, 414 (1963). Acid concentration 0.1 N in HNO$_3$ or HClO$_4$.

RT) min.$^{-1}$. It is seen that nearly all the difference in rate between the two is ascribable to the activation energy term. The ionic radii of the two species concerned, $\text{Rh}_{aq}{}^{+3}$ and $\text{Cr}_{aq}{}^{+3}$, probably do not differ greatly in magnitude.[28] It is tempting therefore to attribute the relatively large activation energy difference to a fundamental mechanistic contrast, as was previously done for the oxalate exchange and aquation reactions of the trisoxalato complexes of the two metal ions.[11] The suggestion is consequently made that the d^6 rhodium(III) aquo ion exchanges water through a mainly dissociative separation of "primary sphere" water, while for the d^3 chromium(III) species, the distinction may be considerably less clear-cut, with bimolecular "secondary-sphere" ligand participation much more prominent. This interpretation also enables a justification of the apparent lack of dependence of the $\text{Cr}(\text{H}_2\text{O})_6{}^{+3}$ water exchange[2b,c] on acid concentration down to as low as [H$^+$] = 0.01, which is only partly explainable by the lower acidity of this ion[29] as compared to the rhodium analog. A considerably smaller k_2/k_1 ratio for the former is reasonable in any case, if its reaction mechanism is not primarily dissociative.

Finally, it is instructive to compare the rates of reaction of the aquo ions so far discussed with rates of aquation reactions of other types of complexes of these two metals. The data presented in Table I are for first-order rate constants of the specified ligand substitutions. The constants have been extrapolated where necessary to the specified temperature (35° for the Cr(III) series, 80° for the Rh(III) series) by use of the published temperature dependence data.

One notes that, while the rates of aquation of the two chloro–rhodium complexes are identical, those for the corresponding chloro–chromium species differ by a factor of 2. Similarly, the water exchange and oxalato aquation reactions, both of which involve

(28) Landolt–Börnstein Tables, Springer-Verlag, Berlin-Göttingen-Heidelberg, 6th Ed., 1955, Band I, Teil 4, p. 522 *et seq.*

(29) K. Emerson and W. M. Graven [*J. Inorg. Nucl. Chem.*, **11**, 309 (1959)] find $pK = 4.1$ for Cr(H$_2$O)$_6{}^{+3}$ at 25°.

reactions at or adjacent to a metal–oxygen bond, have nearly identical rates under the separately specified conditions in the Rh(III) case, but differ by a factor of 4.5 for Cr(III) under similarly specified conditions. Finally, the contrast in rates between the M–O and M–Cl types of complexes is somewhat more clear-cut for the Rh(III) series than for the Cr(III) series. These facts are quite understandable in terms of the contrasting mechanism assumption made earlier. Thus, the Cr(III) reactions, being largely associative with participation of a seven-coordinate activated state, require that bond-making to the entering water molecule be very significant and M–Cl or M–O bond stretching of less importance. One therefore would expect the mono- and dichloro complexes to differ in rate at least by the statistical factor of two as observed.

Similarly, since the reactive intermediate for the oxalato complex is the proton-pre-equilibrated form[10] $Cr(C_2O_4)_2OC_2O_3H \cdot OH_2^{-2}$, with aquation taking place at the $Cr-OC_2O_3H$ bond, one would expect a statistical factor between this and the $Cr(H_2O)_6^{+3}$ species of not less than 2 and not more than 6, again as observed. The Rh(III) complexes, on the other hand, reacting largely in a dissociative fashion with formation of a distorted octahedral activated state by stretching of the M–O or M–Cl bond to be broken, should show a distinct contrast in rate for the two types of bond stretch, as observed.

Preparation and Properties of Sodium and Potassium Molybdenum Bronze Crystals

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Pure MoO_2 crystals were grown by electrolytic reduction of $MoO_3-Na_2MoO_4$ mixtures at 675°. In addition both sodium molybdenum bronze and potassium molybdenum bronze crystals were grown from molybdenum(VI) oxide–alkali molybdate melts under carefully controlled conditions.

Introduction

There have been conflicting reports in the literature concerning the existence of alkali metal molybdenum bronzes. Stavenhagen and Engels[2] prepared sodium molybdenum bronze by electrolytic reduction of fused sodium molybdate and Cannert[3] prepared the lithium, sodium, and potassium molybdenum bronzes by electrolytic reduction. Burgers and Van Liempt[4] as well as Hägg[5] obtained only molybdenum oxides in similar experiments. Straumanis and Irani[6] have reported that molybdenum(VI) oxide could not be dissolved by a tungsten bronze and that solid solutions of the type $NaW^VO_3(Mo^{VI}O_3)_x$ were impossible to prepare. In addition, they attempted to prepare alkali metal molybdenum bronzes by heating dry sodium molybdate, molybdenum(VI) oxide, and molybdenum powder under vacuum at 510 and 450°, respectively The insoluble product that remained was identified as MoO_2.

The purpose of this paper is to describe the preparation, by electrolytic reduction, of sodium and potassium molybdenum bronze single crystals in addition to molybdenum(IV) oxide single crystals. The successful preparation of alkali metal molybdenum bronzes is dependent upon both the reduction temperature and the molar ratio of alkali metal molybdate to molybdenum(VI) oxide.

Experimental

Electrolytic Reduction Apparatus.—Molybdenum bronze crystals were grown by electrolytic reduction of alkali metal molybdate–molybdenum(VI) oxide mixtures. A detailed drawing of the apparatus used in the growth of these crystals is shown in Fig. 1, with an insert showing its position in a vertically mounted split tube furnace. It can be seen that the crucible support assembly centers the crucible in the hot zone of the furnace. In addition the support assembly positions the temperature control thermocouple and provides external electrical connections between the cell and its power supply. The bottom of the ceramic (Lava) support column is mounted in a brass plate and the crucible support plate (Lava) is fitted to the upper end of the column. The cell power leads and the thermocouple leads are brought up through the hollow center of the column and out through the support plate. The furnace control thermocouple is inserted through the support plate to a fixed position midway between the radiation shield and the cell wall. The external anode lead wire is connected to a platinum washer seated on the recessed edge of the crucible support plate, and the external cathode lead wire is connected to a platinum disk seated in the center of the support

(1) Operated with support from the U. S. Army, Navy, and Air Force.
(2) A. Stavenhagen and E. Engels, *Ber.*, **28**, 2281 (1895).
(3) C. Cannert, *Gazz. chim. ital.*, **60**, 113 (1930).
(4) W. G. Burgers and J. A. M. Van Liempt, *Z. anorg. allgem. Chem.*, **202**, 325 (1931).
(5) G. Hägg, *Z. physik. Chem.*, **B29**, 192 (1935).
(6) M. E. Straumanis and K. K. Irani, *J. Am. Chem. Soc.*, **74**, 2114 (1952).