I. Ionization and hydration equilibria of periodic acid; II. Solubility and complex ion formation of the rare earth oxalates

Carl E. Crouthamel
Iowa State College

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UMI
I. IONIZATION AND HYDRATION EQUILIBRIA OF PERIODIC ACID
II. SOLUBILITY AND COMPLEX ION FORMATION OF THE RARE EARTH OXALATES

by
Carl E. Crouthamel

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Inorganic Chemistry

Iowa State College
1950
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IONIZATION AND HYDRATION EQUILIBRIA OF PERIODIC ACID

Apparent Ionization Constants of Periodic Acid at 25°

Introduction

Attempts to understand the solubility data of various insoluble periodates in aqueous solution failed. The main difficulty appeared to be the inability to specify the ionic species of periodate present in aqueous solution. A review of the literature revealed that little was known about periodic acid in solution. Latimer\(^1\) has summarized most of the known facts on the ionization constants and Hill\(^2\) has studied the ternary systems KOH - KIO\(_4\) - H\(_2\)O and NaOH - NaIO\(_4\) - H\(_2\)O. These two sources and the papers of Partington and Bahl\(^3\) contain the main portion of the work which pertains to the solution chemistry of the periodates.

The ionization constants reported\(^4\) to date are

1. \(H_5IO_6 \rightleftharpoons H^+ + H_4IO_6^-; K_1' = 2.3 \times 10^{-2}\)

2. \(H_4IO_6^- \rightleftharpoons H^+ + H_3IO_6^-; K_2' = 9 \times 10^{-8}\).


Latimer\(^1\) stated that the second ionization constant was complicated by the formation of the dimesoperiodate:

\[(3) \quad 2 \text{H}_3\text{IO}_6^{-} \underset{\text{I}_2\text{O}_9^\text{3-}}{\longrightarrow} + 3 \text{H}_2\text{O} \]  

From the work of Hill\(^2\) the solid phases which could exist in equilibrium with water appeared to be the sodium metaperiodate trihydrate, disodium paraperiodate, and trisodium paraperiodate. Above 35\(^\circ\), the trihydrate became unstable and the anhydrous sodium metaperiodate precipitated directly from solution. The stable potassium salts were the anhydrous metaperiodate and in alkali, potassium dimesoperiodate. The latter salt precipitated in the anhydrous condition above 78\(^\circ\) and as the ennea hydrated potassium dimesoperiodate, K\(_4\)I\(_2\)O\(_9\)•9 H\(_2\)O, at lower temperatures. However, the latter may be the para salt, K\(_2\)H\(_3\)I\(_6\)•3 H\(_2\)O. Paraperiodic acid, H\(_5\)I\(_6\), was the only acid which existed in equilibrium with aqueous solutions. The metaperiodic acid and the dimesoperiodic acid have been prepared\(^3\) by heating the para acid in a vacuum to 100\(^\circ\) and to 80\(^\circ\), respectively. The only other acid for which there was evidence was the mesoperiodic acid. Several mesoperiodate salts have been prepared\(^3\), as follows:

\[(4) \quad \text{Na}_2\text{H}_3\text{IO}_6 + 3 \text{AgNO}_3 \underset{\text{Ag}_3\text{I}_5\text{O}_5 + 2 \text{NaNO}_3 + \text{H}_2\text{O} + \text{HNO}_3}{\longrightarrow} \]  

black

\[(5) \quad \text{Ag}_2\text{H}_3\text{IO}_6 \underset{\text{Ag}_2\text{H}_5\text{I}_5 + \text{H}_2\text{O}}{\longrightarrow} \]  

reddish-brown

The structure of diammonium paraperiodic acid, (NH\(_4\))\(_2\)H\(_3\)I\(_6\), has been revealed by the x-ray analyses of Helmholtz\(^5\). The iodine atom is surrounded by a very nearly regular octahedron of oxygen

\(^{5}\text{Helmholtz, J. Am. Chem. Soc., 59, 2036 (1937).}\)
atoms, each 1.93±0.03 Å units distant from the central iodine. The metaperiodate structure has been investigated by Hazlewood. The crystal contains the tetrahedral, \( \text{IO}_4^- \), ion similar to the perchlorates. The oxygen atoms are each 1.79 Å units from the central iodine atom. The apparent pentabasic character of para-periodic acid with some metallic ions would appear surprising. The existence of an \( \text{IO}_6^- \) ion in aqueous solution seemed highly improbable. Nevertheless, the direct precipitation from periodate solutions of compounds such as \( \text{Ag}_5\text{IO}_6 \) and \( \text{Hg}_5(\text{IO}_6)_2 \) cannot be ignored.

The chemistry of periodic acid seemed to indicate the following equilibria in aqueous solution as the most consistent with the phenomena observed.

\[
\begin{align*}
(1) \quad & \text{H}_5\text{IO}_6 \rightleftharpoons \text{H}^+ + \text{H}_4\text{IO}_6^- \\
(2) \quad & \text{H}_4\text{IO}_6^- \rightleftharpoons \text{H}^+ + \text{H}_3\text{IO}_6^= \\
(3) \quad & \text{H}_3\text{IO}_6^= \rightleftharpoons \text{H}^+ + \text{H}_2\text{IO}_6^= \\
(4) \quad & \text{H}_2\text{IO}_6^= \rightleftharpoons \text{H}^+ + \text{H}_1\text{IO}_6^= \\
(5) \quad & \text{H}_1\text{IO}_6^= \rightleftharpoons \text{H}^+ + \text{IO}_4^- \\
(6) \quad & \text{H}_1\text{IO}_6^= \rightleftharpoons \text{H}_2\text{IO}_6^- + \text{H}_2\text{O} \\
(7) \quad & \text{H}_2\text{IO}_6^- \rightleftharpoons \text{H}_2\text{O} + \text{H}_1\text{IO}_6^- \\
(8) \quad & \text{H}_3\text{IO}_6^= \rightleftharpoons \text{H}_2\text{O} + \text{HIO}_5^- \\
(9) \quad & \text{H}_5\text{IO}_6^- \rightleftharpoons 2\text{H}_2\text{O} + \text{H}^+ + \text{IO}_4^- \\

\text{The meso- and dimesoperiodate species whose equilibria are enclosed by the dotted lines were shown to account for not more than one per cent of the total periodate in solution. The precipitation under favorable conditions of } \text{Ag}_3\text{IO}_5, \text{Ag}_2\text{HIO}_5, \text{and K}_4\text{I}_2\text{O}_9. \\
\text{Hazlewood, Z. Krist.}, 98, 439 (1938).
\]
in the anhydrous form would suggest the existence of small quantities of the meso- and dimesoperiodate ions.

The ionization of periodic acid in aqueous solutions has been studied previously by various authors. Giolitti and Partington and Bahl found evidence of the dibasicity of periodic acid. Dubrisay found somewhat doubtful evidence of a third replaceable hydrogen. Rothmund and Drucker from conductance data reported the dissociation constant $K_1' = 2.3 \times 10^{-2}$ for paraperiodic acid, $\text{H}_5\text{IO}_6$. Rae ran a conductometric titration of paraperiodic acid with sodium hydroxide and obtained two breaks. The first was in accord with the $K_1'$ value reported by Rothmund and Drucker, and from the second break he estimated that $K_2'$ may be of the order of $10^{-6}$.

Price and Kroll made a crude attempt to determine the first and second ionization constants during the course of a study of the kinetics of the periodate oxidation of 1,2 glycols. From a single titration of 0.1 N periodic acid with 1.0 N sodium hydroxide, they calculated $K_1' = 0.11$ and $K_2' = 2.5 \times 10^{-8}$. Their method of calculating $K_1'$ from the initial pH of a 0.1 N solution was very poor, and calculation of $K_2'$ without consideration of the activity coefficients would also introduce a large error. Kossiagi...
koff and Harker\textsuperscript{11} and later Ricci\textsuperscript{12} from theoretical considerations developed an empirical formula for calculating the ionization constants of the oxygen acids. Their calculated values have been compared with our observed values in a later section.

The method used in this study to evaluate the ionization constants was based on the variations of the ultraviolet absorption peak of periodate solutions found at 222.5 m\(\mu\) with the pH. Since the start of this investigation, MacDonald, Thompsett, and Mead\textsuperscript{13} reported the absorption maximum of periodate at 222 m\(\mu\) and indicated that Beer's law was obeyed. However, they did not study the critical nature of pH on the absorption peak.

**Experimental**

In these spectrophotometric studies, a Beckman Quartz Spectrophotometer (model DU) and a Cary Recording Spectrophotometer (Model 12) were employed. A Beckman Glass Electrode pH Meter (Model H-2) was used in carrying out the potentiometric titrations. Sources of periodate were paraperiodic acid manufactured by the G. Frederick Smith Chemical Company, Columbus, Ohio, and Baker and Adamson reagent grade potassium metaperiodate. The spectra obtained were found to be independent of the starting material in the absence of interfering substances. Ions which exhibited no interference were perchlorate, sodium, and potassium. Ammonium...
nium ion exhibited no interference in concentrations attained by adjusting $10^{-4}$ M potassium metaperiodate up to pH of ca. 10.2 with filtered reagent grade ammonia solutions. Nitrate, sulfate, and carbonate ions and carboxylate groups definitely interfered.

After originally establishing the nature of the absorption, solutions of both potassium metaperiodate and paraperiodic acid were scanned on the Cary instrument using 1.000 cm. silica cells at various pH values as adjusted with perchloric acid. Figure 1 shows the nature of the variation of the absorption spectra of solutions $1.01 \times 10^{-4}$ M potassium metaperiodate at various pH values, as adjusted with perchloric acid and using the Cary instrument. Figure 2 similarly shows the variation in the alkaline region of $1.05 \times 10^{-4}$ M potassium metaperiodate at various pH values, as adjusted by potassium hydroxide. Unlike Figure 1, these solutions are $10^{-2}$ M in sodium perchlorate. Isobestic points are apparent at approximately 213 m\(\mu\) and 244 m\(\mu\). Solutions of paraperiodic acid gave absorption curves identical within experimental error when similarly adjusted in pH. Figure 3 is a plot of the optical densities at 222.5 m\(\mu\) for solutions $1.009 \times 10^{-4}$ M in potassium metaperiodate at various pH values as adjusted with perchloric acid or sodium hydroxide. The Beckman instrument (0.998 cm. silica cells) was used up to pH 12, but at higher pH the Cary instrument was used because it appears to be better suited to the measurement of very high optical densities. High optical densities at pH values above 12.0 were due to the fact that sodium hydroxide solutions of very high pH, even though they contain only relatively small amounts of carbonate, nevertheless absorb considerably at
Fig. 1 - Absorption spectra of $1.01 \times 10^{-4}$ M KI$_4$ solutions at the following pH values: 1, 6.92; 2, 4.78; 3, 3.43; 4, 3.04; 5, 2.80; 6, 2.35; 7, 1.80; 8, 1.35; 9, 1.10
Fig. 2 - Absorption spectra of $1.05 \times 10^{-4}$ M KIO$_4$ solutions at the following pH values: 1, 6.50; 2, 7.50; 3, 8.50; 4, 9.30; 5, 10.15; 6, 10.75
FIG. 3 - VARIATION OF OPTICAL DENSITY AT 222.5 M\(^{-1}\) OF SOLUTIONS 1.000 \(\times\) 10\(^{-3}\) M IN KIO\(_4\) AT VARIOUS pH VALUES AS ADJUSTED WITH HClO\(_4\) OR NaOH USING THE Beckman INSTRUMENT: CURVE 1 - O, EXPERIMENTAL (BECKMAN); \(\circ\), EXPERIMENTAL (CARY) CONVERTED TO BECKMAN; \(\Box\), CALCULATED; CURVE 2 - \(\oplus\), EXPERIMENTAL (BECKMAN); \(\circ\), CALCULATED.
The experimental values plotted in Curve 1, Figure 3, above pH 12.0 represent the difference between optical densities of the periodate solutions at the pH values indicated and distilled water of the same pH values as adjusted by the same sodium hydroxide solution. As indicated on Figure 3, the series of experimental optical density values above pH 12.0 represent Cary instrument readings converted to equivalent Beckman instrument readings. This conversion was necessitated by the fact that different average molecular extinction coefficients, $\overline{C}_2$, were found for the $\text{H}_3\text{IO}_6^-$ ion on the two instruments. This was explainable because the average molecular extinction coefficient for the divalent species was determined not at an absorption maximum, but at a wavelength where the optical density was changing rapidly with wavelength. Therefore, minor discrepancies in the wavelength scales of the two instruments would be reflected quite sensitively in the molecular extinction coefficients obtained for this ion. In the case of the $\text{H}_4\text{IO}_6^-$ ion, no such discrepancy would be expected because the molecular extinction coefficient for this ion was determined at an absorption maximum where optical density was rather insensitive to wavelength. Experimental values were in agreement with this explanation. In Curve 1, Figure 3, the ionic strength, $\mu$, varied only as a consequence of the addition of perchloric acid or sodium hydroxide required in adjusting pH. The solutions for Curve 2, Figure 3, differ from those of Curve 1 only in that the former were all 0.0625 M in sodium perchlorate. Differences between Curves 1 and 2 were due only to differences in ionic strength and experimental error. Table I lists observed and cal-
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<td>0.001</td>
<td>0.000</td>
<td>0.012</td>
<td>0.583</td>
<td>0.595</td>
</tr>
<tr>
<td>11.0</td>
<td>0.25</td>
<td>0.805</td>
<td>0.428</td>
<td>0.350</td>
<td>0.000</td>
<td>0.125</td>
<td>100.8</td>
<td>0.013</td>
<td>0.000</td>
<td>0.001</td>
<td>0.590</td>
<td>0.591</td>
</tr>
</tbody>
</table>

*Curve 1  **Curve 2
culated data corresponding to Figure 3.

Figure 4 is a plot of the data obtained in the potentiometric titrations of two samples of paraperiodic acid with 0.2232 N potassium hydroxide using the Beckman pH Meter.

Discussion and calculations

Aqueous solutions of periodate were found to follow Beer’s law at given pH values from 1.0 to 10.5 at all wave lengths in the range where appreciable absorption occurs.

\[
\begin{align*}
(1) & \quad H_5IO_6 & \rightarrow H_4IO_6^- + H^+ : K_1' = \frac{a_{H^+} \sum a_{1i}}{\sum a_{0i}} \\
(2) & \quad H_4IO_6^- & \rightarrow H_3IO_6^{2-} + H^+ : K_2' = \frac{a_{H^+} \sum a_{2i}}{\sum a_{1i}} \\
(3) & \quad H_3IO_6^{2-} & \rightarrow H_2IO_6^{3-} + H^+ : K_3' = \frac{a_{H^+} \sum a_{3i}}{\sum a_{2i}}
\end{align*}
\]

where \( a_{ni} \) is the activity of the \( i^{th} \) species with a charge (-n), and \( \sum a_i \) is the sum of all species with the charge (-n).

The above equilibria predicted that the ratios of the activities of the various species would remain constant at constant pH. Yet deviation from Beer’s law might be caused by the variation of the activity coefficients in the solutions studied. In these solutions, however, either the ionic strength was so low that all activity coefficients were nearly 1.0, or the ionic strength was maintained constant by the addition of an electrolyte. In this work, the pH value indicated by the glass electrode instrument, calibrated by means of three standard buffers of pH 4, 7, and 10, was taken as
FIG. 4 - POTENTIOMETRIC TITRATION CURVES OF PARAPERIODIC ACID.
-log $a_{\text{H}^+}$. For values less than 1.0 or greater than 12.0, the pH was calculated from the molar concentration of $\text{H}^+$ or $\text{OH}^-$ and estimated values of activity coefficients.

However, an equilibrium such as

$$2 \text{H}_3\text{IO}_6^- \rightleftharpoons \text{I}_2\text{O}_9^- + 3 \text{H}_2\text{O}; \quad K_4 = \frac{a_{\text{I}_2\text{O}_9^-}}{a_{\text{H}_3\text{IO}_6^-}^2} \frac{a_{\text{H}_2\text{O}}^3}{a_{\text{H}_3\text{IO}_6^-}}$$

did predict a departure from Beer's law at any pH value at which this equilibrium was important, because the activities of the $\text{I}_2\text{O}_9^-$ and $\text{H}_3\text{IO}_6^-$ ions were raised to different powers in the expression for $K_4$. Therefore, this equilibrium was of no importance up to a pH of 10.5 and was probably never appreciably involved in the dilute aqueous solutions of periodates employed. The formulation $K_4\text{I}_2\text{O}_9\cdot 9 \text{H}_2\text{O}$ frequently encountered in the literature might well be represented as $K_2\text{H}_3\text{IO}_6\cdot 3 \text{H}_2\text{O}$. Reactions of simple hydration or dehydration of the various periodate species involved in Equations 1, 2, and 3 predicted no departure from Beer's law and were not considered in this initial study of periodate solutions. Treatment of the data obtained, using only $K_1'$, $K_2'$, and $K_3'$, accounted completely for the variation of the optical densities of the solutions with pH.

An average molecular extinction coefficient was estimated for the undissociated species, using a solution of known periodate concentration and 1.4 M in perchloric acid. Average molecular extinction coefficients for the univalent and divalent species were estimated from the wide plateaus obtained in dilute acid and dilute alkali solutions, respectively, in the plot of optical densities vs. pH for known concentrations of periodate.
Table II lists the average molecular extinction coefficients estimated for the various species of periodate, using both the Cary and Beckman instruments.

Table II

<table>
<thead>
<tr>
<th>Instrument</th>
<th>$\bar{\varepsilon}_0 \times 10^{-3}$</th>
<th>$\bar{\varepsilon}_1 \times 10^{-3}$</th>
<th>$\bar{\varepsilon}_2 \times 10^{-3}$</th>
<th>$\bar{\varepsilon}_3 \times 10^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beckman</td>
<td>2.18</td>
<td>10.08</td>
<td>5.24</td>
<td>0.00</td>
</tr>
<tr>
<td>Cary</td>
<td>2.18</td>
<td>9.97</td>
<td>5.86</td>
<td>0.00</td>
</tr>
</tbody>
</table>

*At any one temperature the molecular extinction coefficient of a species cannot be determined. However, an average molecular extinction coefficient of all periodate species having the same charge could be found. Such a quantity $\bar{\varepsilon}_n$ for a charge (-n) would be defined as

$$\bar{\varepsilon}_n = \frac{\sum \varepsilon_{n_i}}{\sum M_{n_i}}$$

where (-n) is the negative charge of an ion and i is an index. $\varepsilon_{n_i}$ is the molecular extinction coefficient of the i-th species with a charge (-n). $M_{n_i}$ is the molar concentration of the i-th species with a charge (-n). And $\sum$ is the sum of all species with the charge (-n).

Good agreement was obtained except in the case of the divalent species, and the probable reason for this has already been cited (see Experimental). This was not unexpected, since Ewing and Parsons have shown relative discrepancies of half this magnitude among ten Beckman instruments themselves at constant band width.

By substituting $y_0 \left( \sum M_{0i} \right)$, $y_1 \left( \sum M_{1i} \right)$, and $y_3 \left( \sum M_{3i} \right)$ for the activities of the undissociated, univalent, divalent, and trivalent species, respectively, in Equations 1, 2, and 6, and solving

these equations for the molar concentrations of the various periodate species, the following equation may be written for the total periodate concentration, assuming that $Y_0 = 1$:

(11) $M_{\text{total}} = \sum_i M_{0i} + \frac{K_1 \sum M_{0i}}{Y_1^{a_{H^+}}} + \frac{K_2 \sum M_{0i}}{Y_2^{a_{H^+}}} + \frac{K_3 \sum M_{0i}}{Y_3^{a_{H^+}}}$

The activity coefficients as functions of the ionic strength were estimated in the following manner for all points except for pH 14. For $Y_1$, values of $Y_\pm$ for aqueous potassium chloride solutions were used. Values for $Y_2$ were calculated from values of $Y_{C_2O_4^{2-}}/(Y_{Cl^-})(Y_{HC_2O_4^-})$ indicated in the potentiometric evaluation of the second ionization constant of oxalic acid together with the values of $Y_1$. The activity coefficient, $Y_3$, was calculated in the conventional manner from values of $Y_\pm$ reported for various rare earth chlorides. For pH of 14, $Y_1$ was taken from values of $Y_\pm$ for sodium hydroxide, and $Y_2$ was calculated from values of $Y_\pm$ for alkaline earth halides tabulated by Harned and Owen. The values of $K_1'$, $K_2'$, and $K_3'$ were estimated quite easily from Equation 10 and the following relation for the optical density:

(12) $D = 1\left[\frac{\bar{\varepsilon}_0 \left(\sum M_{0i}\right)}{Y_1^{a_{H^+}}} + \frac{\bar{\varepsilon}_1 \sum M_{0i}}{Y_2^{a_{H^+}}} + \frac{\bar{\varepsilon}_2 \sum M_{0i}}{Y_3^{a_{H^+}}} \right]$

---


The $a_{H^+}$ is known from pH measurements, $M_{total}$ is known from chemical analysis, $l$ is the cell thickness in cm. and $\bar{\varepsilon}$ is very nearly zero. In this way, the values for $K_1'$, $K_2'$, and $K_3'$ which, in combination with consistent activity coefficients, gave the best agreement between experimental and calculated optical density values at low ionic strength were found to be the following:

$$K_1' = 2.30 \times 10^{-2};$$
$$K_2' = 4.35 \times 10^{-9};$$
$$K_3' = 1.05 \times 10^{-15}.$$ 

The value of $K_1'$ thus determined agreed exactly with previously reported conductometric values. The value of $K_2'$, a new constant, was substantiated from the potentiometric titration data shown in Figure 4 in the following manner.

From Equation 2, it follows that

$$(13) \quad K_2' = a_{H^+} \text{ when } \frac{a_{H^+}I_0_{65}}{a_{H^+}I_{0,6}} = \frac{\gamma_2\left(\sum \frac{M_{2i}}{1}\right)}{\gamma_1\left(\sum \frac{M_{1i}}{1}\right)} = 1.$$ 

Knowing the total quantity of periodate, the volume of solution, how the assumed values for $\gamma_1$ and $\gamma_2$ vary with ionic strength, and how the ratio of $M_2 / M_1$ varies with ml. of base added, the condition where Equation 13 is satisfied was evaluated by a series of successive approximations. This condition was found to occur where $\sqrt{\mu}$ was ca. 0.25 and

$$\frac{\sum \frac{M_{2i}}{1}}{\sum \frac{M_{1i}}{1}} = \frac{\gamma_1}{\gamma_2} = \frac{0.805}{0.428} = 1.88.$$
This molar ratio corresponded to pH values of 8.24 and 8.26 on curves 1 and 2, respectively, in Figure 4. This gave a value of $K'_2 = 5.6 \times 10^{-9}$ which, in view of the uncertainties involved in $Y_1$ and $Y_2$ was in good agreement with the value of $K'_2 = 4.35 \times 10^{-9}$ obtained from the spectrophotometric studies.

The value of $K'_3$, also a new constant, agreed, within experimental error, with the value of $K'_3$ obtained from $K'_1$ and $K'_2$, using the method of Kossiakoff and Harker.

**Analytical significance**

From these studies it was quite obvious that for the analytical determination of periodate (in the absence of interfering substances) spectrophotometrically, pH was a very important factor. Inspection of the plot of optical density at 222.5 μm versus pH showed clearly that a pH of ca. 5.0 was the optimum pH to use in acid solutions for this determination. For solutions of low ionic strength, pH values of 5.0±1.5 were quite satisfactory, the optical density not varying appreciably in this region. Concentrations as low as $10^{-7}$ molar in periodate should be detectable using 5.00-cm. silica cells. In the event that it is desirable to determine periodate spectrophotometrically in alkaline solutions, pH values between ca. 10.5 and 12.5 are desirable. Such analysis led to a sacrifice in sensitivity of the method at 222.5 μm because of the lower average molecular extinction coefficient of the divalent species, as compared to that of the univalent species used in the lower pH range. This disadvantage may be eliminated by simply carrying out the analysis at a somewhat lower wave length, i.e., at a wave length nearer to or at which the divalent species shows an absorption maximum.
The Hydration Equilibria and Ionization Constants of Paraperiodic Acid

Introduction

It has been pointed out in the first section that the hydration equilibria involving dimerization was ruled out, since the periodate solutions obeyed Beer's law at any given pH and temperature. However, no differentiation could be made from the data of the first section in the cases of simple dehydration such as would be involved in the following reactions:

\[(7a) \quad H_\text{4}^\text{IO}_6^- \rightarrow H_\text{2}^\text{IO}_5^- + H_2O\]
\[(7b) \quad H_\text{4}^\text{IO}_6^- \rightarrow I_\text{4}^- + 2 H_2O\]
\[(8) \quad H_\text{3}^\text{IO}_6^- \rightarrow H\text{I}_\text{O}_5^- + H_2O\]

Thus the apparent ionization constants written in more general form would be

\[(14) \quad \frac{(a_{H^+}) \sum_i a_{li}}{\sum_i a_{0i}} = K_1'\]
\[(15) \quad \frac{(a_{H^+}) \sum_i a_{2i}}{\sum_i a_{li}} = K_2'\]

where \(a_{H^+}\) is the activity of the hydrogen ion, and \(\sum_i a_{0i}\), \(\sum_i a_{li}\), \(\sum_i a_{2i}\) are respectively the sums of the activities of the undissociated forms, singly charged, and doubly charged ionic species. Since the ionization of three hydrogen ions was observed, the acid was designated as the hydrated species, \(H_\text{3}^\text{IO}_6^-\).
In the first section it was established that the absorption maximum at 222.5 m\(\mu\) was caused by univalent ions. From the known chemistry of periodic acid the most probable terms in the summations of the activities are as follows:

\[
\sum_1 a_{01} = \left( a_{\text{H}_5\text{IO}_6} \cdot a_{\text{H}_3\text{IO}_5} \cdot a_{\text{HIO}_4} \right).
\]

Since the metaperiodic acid is probably a very strong acid (comparable to perchloric acid) the activity of undissociated metaperiodic acid would be very small.

\[
\sum_1 a_{11} = \left( a_{\text{H}_4\text{IO}_6^-} \cdot a_{\text{H}_2\text{IO}_5^-} \cdot a_{\text{IO}_4^-} \right)
\]

\[
\sum_1 a_{21} = \left( a_{\text{H}_3\text{IO}_6^-} \cdot a_{\text{HIO}_5^-} \right)
\]

The extinction coefficients which have been associated with the undissociated, univalent, and divalent species probably are average values for the species in Equations 16, 17, and 18. Fortunately, it can be shown that the mesoperiodate concentration in solution is very small and at 222.5 m\(\mu\) with favorable temperature and pH values, extinction coefficients of the \(\text{H}_5\text{IO}_6^-\) and \(\text{IO}_4^-\) can be calculated. The absorption maximum at 222.5 m\(\mu\) was studied with variable temperatures and activities of water.

This data indicates that the univalent species, \(\text{IO}_4^-\), is responsible for this absorption. It was therefore possible to determine the concentration of this ion which permitted a detailed analysis of the dehydration phenomena. The behavior in acid and neutral solutions was adequately described by the following three equilibria:
It is important to note that Equations 19 and 21 do not have the same meaning as Equations 1 and 2 in the first section. We are now distinguishing between the simple hydrated species as defined in (16), (17), and (18). When no such distinction was made in an equilibrium expression, the constant has been primed, as in (14) and (15), and referred to as an apparent constant. The constants for reactions (19), (20), and (21) have been evaluated over a temperature range of 0-70° C., as have the apparent constants, \( K_1' \) and \( K_2' \).

**Experimental**

**Materials and instruments.** In the spectrophotometric studies a Cary Recording Spectrophotometer (Model 12) was employed. A Beckman Glass Electrode pH Meter (Model G) calibrated with standard buffer solutions was used for pH measurements. Solutions used in the ultraviolet absorption measurements were prepared from reagent grade samples of potassium metaperiodate manufactured by the G. F. Smith Chemical Co., and the General Chemical Co. No appreciable iodate was detectable by titration with standard thiosulfate in acid and in neutral buffered solutions. The oxidizing capacity of a weighed sample
corresponded to a purity of better than 99.9%. Standard stock solutions of periodate were prepared by dissolving 0.1150 gms of pure potassium metaperiodate in 500 ml. of solution. For the greatest accuracy, standard solutions were prepared each day. Double distilled water from alkaline permanganate, specific conductance of $0.9 \times 10^{-6}$ mhos cm$^{-1}$ was used throughout. Methanol when used was purified by refluxing in alkali and iodine and redistilling. Dilute periodate solutions ($2 \times 10^{-4}$ M) in methanol were stable for a day as measured by the spectrophotometer.

Temperature control. Absorption measurements with the Cary instrument at 32.5° and below were made by suitably controlling the room temperature and allowing sufficient time for the solutions and instrument to attain thermal equilibrium. Copper tanks, constructed so that they would fit into the sample chamber next to the silica cell, were filled with water at the proper temperature to act as a thermal ballast. At higher temperatures the cell containing the sample was immersed in a water bath at the correct temperature until thermal equilibrium was attained. The cell was then dried and placed in the sample chamber as quickly as possible. The time needed was from ten to fifteen seconds to transfer the cell, dry, and make a measurement. Cooling rates were found to be less than 0.5-1°/min. in the temperature range of the measurements. Temperature fluctuations in these measurements made a negligible contribution to the errors.
**Spectrophotometric measurements.** Potassium metaperiodate solutions at various pH values were scanned at different temperatures with the Cary instrument, using 1.000 cm silica cells. The pH adjustments were made with perchloric acid or with carbonate free sodium hydroxide. Figures 5 and 6 are plots of the optical densities of various periodate solutions (Ca, $2 \times 10^{-4}$ M) at several pH values and temperatures. When necessary, corrections were made for volume changes by using density temperature information for pure water. The optical densities of pure potassium metaperiodate solutions in methanol-water mixtures were measured at 0°. These solutions were diluted to volume at this temperature to avoid differences in the coefficient of expansion caused by the varying solvent composition.

**Potentiometric measurements.** Potentiometric titrations of paraperiodic acid with 0.1795 N sodium hydroxide were made at temperatures of 0.5° C., 25.0° C., and 45.0° C. For these measurements a Beckman Model 1190 glass electrode, and a Beckman Model 1170 calomel electrode, recommended for use over this temperature range, were used with the Model "G" pH meter.

Calibration was made at the proper temperature with standard buffer solutions after thermal equilibrium was attained. These curves are given in Figure 7. Additional potentiometric titrations of paraperiodic acid with potassium hydroxide in various methanol-
Fig. 5 Optical density of $2.35 \times 10^{-4}$ M periodate solutions at various temperatures and hydrogen ion activities.
Fig. 6 Optical density of $2.33 \times 10^{-4}$ M periodate solutions at various temperatures and hydrogen ion activities.
Fig. 7 Potentiometric titration of periodic acid at various temperatures in aqueous solns.
Discussion and Results

Spectrophotometric studies. Consideration of the plots of optical density at 222.5 m\(\mu\) (Figures 5 and 6) led to the following observations:

1. The optical density of solutions at a pH value of 6, where essentially all the periodate would be present as monovalent ions, varied considerably with temperature and approached an upper limiting value at higher temperatures.

2. The optical density approached a lower limiting value at low pH values and low temperatures.

3. The optical density of solutions in the pH range 10.5 - 12.0 did not change appreciably with temperatures from 0\(^\circ\) to 50\(^\circ\) when the volume changes of pure water were used to correct the concentrations.

4. Beer's law was obeyed at a given pH and temperature.

To interpret these observed facts, it was first necessary to assume that absorptions of light at a wavelength of 222.5 m\(\mu\) corresponds to an electron transition and should be characteristic of a given ionic or molecular species. The energy involved in the absorption of light of this wavelength was so large that moderate temperature changes (i.e., 0-100\(^\circ\) C.) should have had virtually no effect upon the population statistics of this process, i.e., the extinction coefficient of a species should not have been a function of temperature in the range observed. In
Fig. 8 Potentiometric titration of periodic acid in methanol-water solvents at 25° C.
such a case, changes in optical density with temperature would be caused by a change of species. Subsequent experiments confirmed the validity of this assumption. The original choice of species was governed by the known chemistry of periodic acid and its salts. The known polybasicity of the acid and the fact that vacuum drying at 100°C was necessary to prepare the meta-acid led to the choice of H₅IO₆ as the undissociated acid. The well known para- and metaperiodate salts suggested the forms H₄IO₆⁻ and IO₄⁻ for the monovalent ions, and this was later substantiated by the equilibrium behavior.

At a pH of 10.5 there was very little change in the optical density at 222.5 m\(\mu\) with temperature from 0°C to 45°C and Beer's law was obeyed in this region. These facts seemed to indicate that dehydration involving dimerization (i.e., as in the formation of I₂O₉ species) was of no importance. However, a simple dehydration of the H₅IO₆⁻ to form HIO₅⁻ could have occurred and not have caused apparent discrepancies in Beer's law at a given temperature. Also, if the extinction coefficient of the H₅IO₆⁻ and HIO₅⁻ ions were not appreciably different at 222.5 m\(\mu\) temperature variations of optical density would have been very small. However, the variations of \(K_2\)' with temperature were quantitatively explained by the dehydration equilibria of H₄IO₆⁻ alone. Therefore, the mesoperiodate species was probably only a small fraction of the total periodate in solution.

The equilibria necessary to describe the observed data have been given as 19, 20, and 21. It was also necessary to determine which species absorbed at 222.5 m\(\mu\). It was known from
the work of the first section that the undissociated acid and the divalent ion did absorb at this wavelength; however, the absorption by these species could be kept to less than 1% by proper pH adjustment. Analysis of the absorption curves for a potassium metaperiodate solution (at a pH of 5.80) at two temperatures (Figure 9) showed that at wavelengths of 222.5 m\(\mu\) and greater, only one species was absorbing within the accuracy of measurement. (Under these conditions at least 99.9% of the periodate present existed as some singly charged ion.) At wavelengths below this value, two species were absorbing, as shown by the isobestic point at 205.0 m\(\mu\). This was demonstrable since the ratio (optical density, 25\(^\circ\)/optical density, 0\(^\circ\)) remained constant for wavelengths of 222.5 m\(\mu\) and greater to within the accuracy possible, ca. 5%. The absorption was greatest at the higher temperature; hence this was associated with a dehydration process and the metaperiodate ion, IO\(4^-\), was assigned to this absorption.

By plotting the optical densities of potassium metaperiodate solutions versus temperature (at a pH 6), the extinction coefficient of the metaperiodate ion, IO\(4^-\), could be estimated. With this information, together with the total periodate in solution and the assumption that the activity coefficients of the two forms of monovalent ions were equal, the dehydration constant

\[
(22) \quad K_D = \left( \frac{M_{\text{IO}_4^-}}{M_{\text{H}_4\text{IO}_6^-}} \right) a_{\text{H}_2\text{O}}^2
\]

could be computed. Figure 10 is a plot of the optical density versus temperature of these solutions. The limiting value at
Fig. 9 Optical densities of a potassium metaperiodate solution at two temperatures.
Fig. 10. Optical densities of a potassium metaperiodate solution at pH of 6.0 and at various temperatures.
high temperatures was used for the calculation of the value 10,700 as the molar extinction coefficient of IO₄⁻. The test for the validity of reaction (20) was afforded by measurements of the variation of optical density, and hence of the \( \left( \frac{MIO₄^-}{MH₄IO₆^-} \right) \) ratio with changes of the \( a_H₂O \) in water-methanol solutions. For the reaction considered, this ratio should satisfy the following:

\[
\log(MIO₄^-/MH₄IO₆^-) = \log(aIO₄^-/aH₄IO₆^-) = \log K_D - 2 \log a_H₂O.
\]

This was an equation of a straight line with a slope of -2 and an intercept, \( \log K_D \), when \( \log (MIO₄^-/MH₄IO₆^-) \) was plotted versus \( \log a_H₂O \). Methanol was employed to vary the activity of water, since it neither reacts with periodate nor absorbs appreciably at this wavelength, and \( pH \) measurements showed that in methanol-water mixtures, appreciable amounts of the undissociated acid were not formed. The activity of water in aqueous methanol mixtures was computed from known vapor composition information at 25°C. Solutions containing the same amount of potassium meta-periodate in various methanol-water mixtures at 0°C were measured on the spectrophotometer, and the resulting information is given in Figure 11. The ratio \( MIO₄^-/MH₄IO₆^- \) was calculated, using the value for the extinction coefficient obtained by extrapolating the optical density curve versus mole fraction of water to zero.

This extrapolation was necessary, since at mol fractions of methanol greater than 0.8 it was apparent that interaction of the periodate with methanol became important. This extinction coefficient checked, within experimental error, the value obtained at high temperatures in aqueous solutions. Plotting of this data

\[ \text{Ferguson and Funnell, J. Phys. Chem., 33, 1 (1929).} \]
Fig. 11 Experimental verification of Equation (23).
yielded a straight line with a slope of -2.0, and the intercept value checked the value obtained for log K_D at this temperature.

Values of the apparent first ionization constant, K_1', were computed from the optical density-pH curves shown in Figure 5 using the method of the first section. The log K_1' was plotted versus the reciprocal of the absolute temperature in Figure 12. Log K_D and log (K_D + 1) were also plotted on this figure. If the constants K_1', K_D, and K_1 are taken as

\[
(a_{H^+}) \frac{[a_{IO_4^-} + (a_{H_2IO_6^-})]}{a_{H_5IO_6}} = K_1'
\]

\[
\frac{(a_{H^+}) (a_{H_2IO_6^-})}{a_{H_5IO_6}} = K_1
\]

\[
\left(\frac{a_{IO_4^-}}{a_{H_2IO_6^-}}\right) a_{H_2O}^2 = K_D
\]

it follows that

\[
K_1' = K_1 (K_D + 1)
\]

or

\[
\log K_1' = \log K_1 + \log (K_D + 1),
\]

hence the log K_1 may be obtained by subtraction of log (K_D + 1) from log K_1'. The resulting values for log K_1 have been plotted in Figure 12.

The slopes of these curves made possible the evaluation of the heat of reaction for the following:

\[
H_4IO_6^- \rightarrow 2 H_2O + IO_4^- : \Delta H_{O-700} = 10.9 \text{ Kcal}
\]
Fig. 12 Plots of the logarithm of the various constants versus the reciprocal of the absolute temperature.
Potentiometric titrations. The determination of a true second ionization constant for $H_5IO_6$ from spectrophotometric data would require further analyses of the spectra in the alkaline region. However, by a treatment similar to the above where

$$K_2 = \frac{a_{H^+} a_{H_3IO_6}}{a_{H_4IO_6^-}} , \quad \text{and}$$

$$K_2' = \frac{a_{H^+} a_{H_3IO_6}}{(a_{H_4IO_6^-} + a_{IO_4^-})} ,$$

the following expression can be obtained which corrects for the dehydration of the univalent ion:

$$K_2 = K_2' (K_D + 1).$$

Values of $K_2'$ were calculated from the series of potentiometric titrations with solutions thermostated at 0.5° C., 25.0° C., and 45.0° C. (Figure 7) by the methods used in the first section. Values of $K_2'$ and $K_2$ from these experiments have been included in Table III. It should be noted that the apparent constant, $K_2'$, at 25° agreed closely with the constant obtained from the spectrophotometric data in the first section.
Table III
(Values of $K_2'$ and $K_2$)

<table>
<thead>
<tr>
<th>$-\log K_2'$</th>
<th>$^\circ$ C.</th>
<th>$\log (K_D + 1)$</th>
<th>$-\log K_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.40</td>
<td>0.5</td>
<td>0.95</td>
<td>6.45</td>
</tr>
<tr>
<td>8.40</td>
<td>25.0</td>
<td>1.61</td>
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<tr>
<td>8.65</td>
<td>45.0</td>
<td>2.15</td>
<td>6.50</td>
</tr>
</tbody>
</table>

The value of $\Delta H$ obtained from plotting $\log K_2'$ versus $1/T$ was approximately -11 Kilocalories at room temperature. This corresponded to the heat effect of the dehydration reaction of the monovalent ion, and indicated that at near room temperatures the major portion of the divalent ion could be described as $\text{H}_3\text{IO}_6^\text{--}$. The values of $K_2$ remained essentially constant over the temperature range within the accuracy of measurement, again agreeing with the characteristics of other oxy-acids.

Figure 8 shows potentiometric titrations made in methanol-water mixtures. An unusual effect was observed here since the pH values in methanol-water mixtures were lower than in water. The dehydrating effect of methanol apparently overcame the usual effect of depression of the ionization of the acid when methanol is used. In this regard it is also well to point out that meta-periodic acid, $\text{HIO}_4$, would be expected to be a very strong acid similar to perchloric.

Theoretical treatments$^{11, 12}$ have indicated that two properties appear to classify the inorganic oxygen acids with respect to ionization constants into distinct groups. First,
the formal charge on the central atom and, second, the number of non-hydroxyl oxygen atoms in the molecule. Iodine in periodic acid has a formal charge of m = 1, and the non-hydroxyl oxygen atoms are n = 1, 2, 3 for H₅IO₆, H₄IO₆⁻, and H₃IO₆²⁻ species, respectively. Using the semi-empirical expression derived by Ricci⁵, \( \text{pK} = 8.0 - m(9.0) + n(4.0) \), an improved correlation was obtained between calculated and observed values when the true ionization constants were used. In Table IV a summary of the ionization constants is given.

Table IV

Comparison of Observed and Calculated Values of the Ionization Constants of Periodic Acid

<table>
<thead>
<tr>
<th>Temperature, 25°</th>
<th>Apparent pK</th>
<th>True pK</th>
<th>Calculated pK¹²</th>
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<td>6.7</td>
<td>7.0</td>
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<tr>
<td>pK₃</td>
<td>14.3</td>
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<td>11.0</td>
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</table>

It is interesting to note that the first apparent ionization constant of carbonic acid has a very small value because of a hydration equilibria between CO₂ and the undissociated acid as first reported by McBain²⁰ and later investigators²¹, ²².

Solubility of potassium metaperiodate. Inconsistencies exist in the solubility values reported for KIO₄ in the literature. The early values of Barker²³, ²⁴ were apparently too high when compared with the later values of Hill² and Jones²⁵. From the equilibria (19) and (20) it could be seen that the solubility of potassium metaperiodate should have increased by both excess acid and alkali. Thus it was not surprising to find that potassium hydroxide did not depress the solubility of potassium metaperiodate salt according to the common ion effect². Also it was known that strong acids dissolved potassium metaperiodate quite readily. Using the data of Hill² and Jones²⁵ for the solubility of potassium metaperiodate, the solubility product at various temperatures was calculated. The following equations should apply to solutions of potassium metaperiodate with no excess acid or alkali (pH = 5 - 6.8):

\[
\begin{align*}
(35) \quad MIO_4^-/M_H_4IO_6^- &= K_D \\
(36) \quad K_D/(K_D + l) M_T &= M_{IO_4^-} \\
(37) \quad (a_{K^+})(a_{IO_4^-}) &= K_{sp} \\
(38) \quad \sqrt{2} (M_{K^+})(M_T) [K_D/(K_D + l)] &= K_{sp} \\
(39) \quad KIO_4 (S) \rightleftharpoons K^+ + IO_4^-; \Delta H = 15.1 \text{ Kcal.}
\end{align*}
\]

²⁴"International Critical Tables", Vol. 4, 239 (1928).
Where \( M_T \) is the total periodate concentration, moles/liter, in solution and \( \gamma^+ \) is the mean activity coefficient calculated by Jones\(^{25}\). Using the solubility data of Jones\(^{25}\) for potassium metaperiodate at 25° where

\[
\gamma^+ = 0.866, \quad M_{K^+} = M_T^{25\circ} = 0.02248, \quad \text{and} \quad K_D = 40
\]

\[
(3.77 \times 10^{-4}) \left[ \frac{K_D}{K_D + 1} \right] = 3.70 \times 10^{-4} = K_{sp}^{25\circ}.
\]

At lower temperatures, 0°, the value of \( K_D \) became less than 10 and the effect of the hydration equilibria on \( K_{sp} \) was more pronounced. In Figure 13 is plotted the log \( K_{sp} \) versus 1/T. These values were calculated using the solubility data of Hill\(^{2}\) and the solubility product equation (38). The heat of reaction (39) was calculated from the slope of this curve.
Fig. 13 Solubility product data of potassium metaperiodate at various temperatures.
Summary

In solution, periodic acid apparently exists mainly as a mixture of two acids. The two acids are the metaperiodic acid, HIO₄, which is a very strong acid comparable to perchloric acid, and the paraperiodic acid, which is a weak acid. The precipitation of meso- and dimeso- salts under special conditions was most probably due to the much greater insolubility of the particular salts, since no evidence for the formation of these acids in more than small fractions (1-2% under the most favorable conditions) was obtained. The equilibrium between the meta- and para-acids was found to be too fast to observe with fairly rapid rates of heating and cooling of small 2-3 cm. samples. The apparent pentabasic salts of paraperiodic acid are surprising. The following equilibria have been evaluated for periodic acid from 0° - 70°:

\[
\begin{align*}
\text{H}_4\text{IO}_6^- & \rightleftharpoons \text{I}_4\text{O}_4^- + 2 \text{H}_2\text{O} : K_D \\
\text{H}_5\text{IO}_6 & \rightleftharpoons \text{H}_4\text{IO}_6^- + \text{H}^+ : K_1 \\
\text{H}_4\text{IO}_6^- & \rightleftharpoons \text{H}_3\text{IO}_6^2^- + \text{H}^+ : K_2 \\
\text{HIO}_4^- & \rightleftharpoons \text{H}^+ + \text{I}_4\text{O}_4^- : K_0 > 1
\end{align*}
\]

\[
K_1' = K_1 (K_D + 1) \\
K_2 = K_2' (K_D + 1)
\]

where \( K_1' \) and \( K_2' \) are the apparent ionization constants of the mixture of para- and metaperiodic acid in aqueous solutions.
LITERATURE CITED

Dubrisay, Compt. rend., 157, 1150 (1913).


SOLUBILITY AND COMPLEX ION FORMATION OF THE RARE EARTH OXALATES

Introduction

One of the most widely used methods for analysis and separation of the rare earths is the oxalate precipitation from dilute acid solutions. In working with radioactive rare earths in this laboratory, it became necessary to precipitate rare earths from solutions containing approximately $10^{-3}$ molar concentration of the rare earth ion. The formation of an insoluble precipitate under these conditions occurred only within a definite range of total oxalate and acid concentrations. Thus, it was felt that because of the wide use of the oxalate precipitation in analytical and in recovery processes, a better understanding of the equilibria involved in such systems was definitely needed. The solubility of rare earth oxalates in excess oxalate has been noted previously by workers in this field\(^1\).

In general, the ability of rare earth ions to form complexes increases with atomic number. It was especially important to use the optimum conditions for the heavy rare earth oxalate precipitations, since the maximum insolubility ($3.2 \times 10^{-5}$ mole/liter for ytterbium) was not too great. The use of radioactivity greatly facilitated these studies, since the necessary determination of the very low rare earth concentrations could be conveniently performed with adequate accuracy by radioassays. For such work, an isotope was required with a moderately long

\[^1\text{Yost, Russell, and Garner, "The Rare Earth Elements and Their Compounds", New York, N. Y., John Wiley, 1947, p. 59.}\]
half-life and which could be prepared with a sufficiently high specific activity. Yb^{169}, Na^{147}, and Ce^{141} were the radioactive isotopes used in these studies.

Experimental

Materials

The water used was prepared by redistilling distilled water from alkali permanganate solutions in a tin still. The specific conductance was less than $1.0 \times 10^{-6}$ mho $\cdot$ cm$^{-1}$. A primary standard of Sorensen's sodium oxalate was used to standardize the permanganate solutions. Recrystallized reagent grade oxalic acid and the primary standard sodium oxalate were used in preparing the oxalate-buffered solutions for the solubility studies. Standard HCl or HClO$_4$ was used when necessary to adjust the hydrogen ion activity of the solutions with very low divalent oxalate ion activities.

The very pure rare earth samples were prepared by Dr. Spedding and his co-workers. The ytterbium was prepared by removal of the cerium fraction, including samarium and europium, by ion exchange columns using amberlite IR-100 cation exchange resin. The ytterbium was then further purified by removal of the other heavy rare earths by repeated sodium-amalgam reduction and extractions. The experimental conditions for sodium-amalgam extractions of ytterbium have been described by Moeller and Kremers$^2$.

The sample had finally been precipitated as the oxalate and ignited to the oxide. Following this, it was irradiated for 30 days in the Argonne National Laboratory pile to produce the Yb\textsuperscript{175} with a 100 hour half-life and Yb\textsuperscript{169} with a 32 day half-life. About 99\% of the activity was carried in three extractions with sodium amalgam. Absorption curves for the radiation of the residue from these extractions indicated that any activity of significantly different character was probably less than 0.1\% of the original. In particular, no evidence was noted for the 105 day half-life Tm\textsuperscript{170} activity.

The neodymium starting material was a sample of Lindsay Light Co. neodymium carbonate. Two separations in IR-100 columns gave a sample which was reported as "spectroscopically pure". The neodymium oxide was irradiated with slow neutrons for 30 days in the Argonne National Laboratory pile to form Nd\textsuperscript{147} which decays with an 11 day half-life. The half-life estimated in this laboratory was 11.6 days. The lead absorption curve of the radiation gave a half-thickness of 5.4 gm./cm.\textsuperscript{2} (corresponding to 0.57 mev), and the estimated end point for the range of the electrons in Al was 400 mg./cm.\textsuperscript{2} (corresponding to about 1.0 mev). No evidence to indicate any short-lived activity was discovered, and it was therefore concluded that the sample of neodymium oxide had been exceptionally pure.

The source material for the cerium was G. F. Smith's ammonium nitrato-cerate, standard of reference purity. Spectrographic analysis indicated that this material was free from other rare earths. Trivalent cerium was formed by adding 30\%
hydrogen peroxide solution to a dilute acid solution of the tetravalent nitrato-cerate. The oxalate was precipitated after boiling off the excess peroxide. The washed oxalate precipitate was then ignited to CeO₂. The cerium oxide was irradiated with slow neutrons for 30 days in the Argonne National Laboratory pile to form Ce¹⁴⁺, which decays with a 28 day half-life. The half-life estimated in this laboratory was also 28 days, and no evidence for any foreign radiation was found on material from the same source.

Procedures

A Beckman Model "G" pH Meter was used throughout this work. Standardization of the pH meter was made on buffer solutions, pH 7.0 and 4.0, prepared by the National Technical Laboratories and based on 0.1 N calomel electrode, Eₒ = 0.3358 volt at 25°. This gave pH on the activity scale and the aH⁺ was evaluated directly from the pH measurements.

Radioactive assays were made by means of Geiger-Mueller counters with an end mica window of 2.5 mg./cm.², model VG, manufactured by the Victoreen Instrument Co. The counter tube was operated with a conventional scale of 64 circuit. Counting was standardized by use of a commercial plastic counter mount with five shelves for supporting samples. Assay samples were prepared by the evaporation of known volumes of the solution on copper plates or aluminum dishes. A brass plate was placed behind the samples to keep the back scattering constant and at a maximum. The aliquots used for counting were 10-10⁶ μl portions
evaporated under infrared lamps to very thin deposits. For the most acid solutions the aliquots were neutralized with dilute NaOH before evaporation. It was also found helpful to place a very thin layer of silicone grease over the aluminum or copper plate. The acid solutions could then be evaporated on this without attacking the metal surface. At least 10,000 counts were obtained for each sample. A number of radioactive standards were prepared with various amounts of inert electrolyte. The counting rate above background of each sample was then compared with that of the standard containing a comparable amount of inert electrolyte, and prepared simultaneously by the evaporation of an aliquot of the standard solution which most nearly matched the ionic strength of the equilibrium solution. From the ratio of the counting rates and the known rare earth content of the standard in the solution, a value for the concentration of total rare earth could be calculated for which errors due to decay, self-absorption, and scattering were minimized. Radioassays of the same solution agreed in general to within ±2% and did not vary if the aliquots were withdrawn from near the surface or from the center of the solution.

The specific activity of the three radioactive rare earths was determined essentially in the same manner. Several 0.05–0.1 gm. samples of the oxide were weighed into flasks and dissolved in diluted perchloric acid. In the case of CeO₂, a little 30% hydrogen peroxide was added slowly to reduce the cerium to the trivalent state. The excess of acid was then boiled off, and the sample diluted to volume in a volumetric flask. In the
case just described, the perchlorate ion concentration needed for the subsequent calculation of ionic strength was estimated by means of a careful measurement of pH and the known rare earth concentration. Since for these solutions

\[ M_{\text{ClO}_4^-} = M_{H^+} + 3 M_{\text{Nd}^{+++}} \]

where M's represent molar concentrations (moles/liter). The concentration of ClO$_4^-$ was computed from these data by the use of a unicharged ion activity coefficient which was consistent with the finally calculated ionic strength for converting the activity of H$^+$ to molar concentration. Since the ionic strength was increased in some of the standard rare earth solutions by adding sodium perchlorate, approximate corrections of the specific activity with ionic strength could then be made by using the proper standard solution in obtaining the specific activities during the course of the work. The specific activities obtained on the second shelf were originally of the order of $7.0 \times 10^4$, $2 \times 10^6$, and $3 \times 10^6$ cts./mg rare earth x min. for ytterbium, neodymium, and cerium, respectively. The neodymium activity was the only one of the three activities whose half-life was short enough to necessitate collecting the data as quickly as possible. The low solubility of the neodymium oxalate also was a contributing factor. In addition, the Nd$^{147}$, which decays by the emission of a 0.9 mev/β$^-$ or a 0.4 mev/β$^-$ and 0.58 mev γ, forms a daughter isotope, Pm$^{147}$, which is also radioactive, decaying by the emission of a 0.2 mev/β$^-$ with a half-life of 3.7 years. The mass of this element formed would
be of "tracer" magnitude, and would not be expected to influence the equilibrium. However, the activity, defined as disintegrations per unit time, would become appreciable. The ratio of Pm/Nd disintegration rate was computed to be 0.007 at the end of the 30 day irradiation, and 0.07 30 days later. Consequently, in the counting measurements performed a month after the end of the irradiation, a 30 mg./cm.$^2$ Al absorber was employed which was estimated to reduce the Pm/Nd counting ratio by a further factor of at least $1/20 - 1/40$. Any effects of this daughter were believed to have been effectively removed from the measurements.

The equilibrium solutions were always prepared so that the was less than 0.7, where $\mu$ is the ionic strength. In the majority of the solutions the value of $\sqrt{\mu}$ was approximately 0.1. The following simple hypothesis has been stated by Lewis and Randall$^3$ which can be applied to solutions of moderate concentration: "In dilute solution the activity coefficient of any ion depends solely upon the total ionic strength of the solution and the charge." Thus, by accepting this hypothesis, the activity coefficient of a salt can be calculated from the known activities of other salts at the same ionic strength. This method has been used in evaluating activity coefficients in this work when necessary. If the $\sqrt{\mu}$ is greater than 0.3, there may be serious deviation. However, wherever possible, activity data of the same, or very similar, salts have been

---

employed and only a few solutions with $\sqrt{\mu}$ appreciably greater than 0.3 were analyzed.

Solutions were brought to equilibrium in various ways.

(1) The radioactive rare earths were precipitated directly from solutions of their chlorides or perchlorates with oxalate buffers. Both hot and cold solutions were used. Precipitation from hot solutions definitely gave the most crystalline precipitates. However, the final equilibrium solubilities did not vary with the method employed. (2) Wet washed radioactive rare earth oxalate crystals were added to oxalate buffers and shaken. Many of these solutions were heated after equilibrium was attained and brought back to equilibrium again at 25°. The checks obtained in all cases were very good.

In all three studies with ytterbium, neodymium, and cerium, the solutions were analyzed periodically for at least 30 days, although in many cases with good shaking, equilibrium values were reached in a few days. No ageing effects were noted in this period. The neodymium and cerium were shaken continuously in a thermostat at 25° with a Burrell wrist action shaker. Ytterbium was shaken by hand periodically and some of the solutions required 30 days to reach equilibrium.

Analysis of a solution consisted of a careful pH measurement, a permanganate titration for total oxalate in solution, and a radioassay to determine the total rare earth solubility. The aliquots for radioassay were always taken by pipetting from the clear settled solutions. Filtering was not feasible, since with the very low rare earth concentrations ($10^{-6}$ - $10^{-4}$
mole-liter) appreciable quantities of the ions are adsorbed by the filtering media. Also by pipetting small samples, as many as 6 to 12 radioassays were made on each solution. The radioassays were always run in pairs. Thus if accidental pipetting of floating particles or unsettled particles was made, checks were not obtained and additional radioassays were made. In general, the radioassays of the same solution agreed to within ±2%, and did not vary if the aliquots were withdrawn from near the surface or from the center of the solution.

Discussion of Results

Results of the analyses of the equilibrium solutions for the three systems are contained in Tables I, II, and III. From the data collected, an estimate of the state of the oxalate-hydrogen ion equilibrium could be accomplished by means of the equation

\[ M = \frac{m_{H_2C_2O_4} + m_{HC_2O_4^-} + m_{C_2O_4^{2-}}}{\gamma_0 m_{H_2O}} \]

and the first and second dissociation constants:

\[ \gamma_1 \frac{m_{HC_2O_4^-}}{m_{H_2C_2O_4}} = a_{H^+} \]

\[ = K_1 = 5.32 \times 10^{-2} \]  

\[ \gamma_2 \frac{m_{C_2O_4^{2-}}}{m_{HC_2O_4^-}} = a_{H^+} \]

\[ = K_2 = 5.42 \times 10^{-5} \]  

\[ ^4 \text{Darken, J. Am. Chem. Soc., 63, 1007 (1941).} \]

\[ ^5 \text{Pinching and Bates, J. Research Natl. Bur. Standards, 40, 405 (1948).} \]
Table I
Data from Solubility Experiments of \( \text{Yb}_2(\text{C}_2\text{O}_4)_3 \cdot 10 \text{H}_2\text{O} \) at 25.0°C.

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<th>pH</th>
<th>(-\log M^*)</th>
<th>(-\log a_{\text{C}_2\text{O}_4}^=)</th>
<th>(-\log \text{Yb}^{**})</th>
<th>(-\log \text{Yb})</th>
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<td>2.81</td>
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* \( M \) is the total oxalate concentration, moles/liter.

** \( \text{Yb} \) is the total rare earth solubility, moles/liter.
Table II
Data from Solubility Experiments
of Ce₂(C₂O₄)₃·9H₂O at 25.0°C.

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<th>-log aC₂O₄⁻</th>
<th>-log Ce **</th>
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<td>3.71</td>
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<td>5.76</td>
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<td>4.90</td>
<td>5.43</td>
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<td>6.97</td>
<td>2.94</td>
<td>2.92</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*M is the total oxalate concentration, moles/liter.

**Ce is the total rare earth solubility, moles/liter.
Table III

Data from Solubility Experiments of Nd$_2$(C$_2$O$_4$)$_3$·10 H$_2$O at 25.0° C.

<table>
<thead>
<tr>
<th>pH</th>
<th>$\log M^*$</th>
<th>$\log a_{C_2O_4^-}$</th>
<th>$\log M$</th>
<th>$\log Nd^{**}$</th>
<th>$\log Nd$</th>
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<tbody>
<tr>
<td>0.252</td>
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<td>1.41</td>
<td>1.11</td>
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<td>1.41</td>
<td>2.07</td>
<td>5.08</td>
<td>4.96</td>
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<td>2.26</td>
<td>5.05</td>
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<td>5.12</td>
</tr>
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<td>0.154</td>
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<td>5.36</td>
</tr>
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</tr>
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<td>2.79</td>
<td>5.28</td>
<td>5.36</td>
</tr>
<tr>
<td>0.092</td>
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<td>2.90</td>
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<td>3.81</td>
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<tr>
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<td>4.07</td>
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<td>5.83</td>
</tr>
<tr>
<td>0.136</td>
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<td>4.14</td>
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<td>2.69</td>
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<td>4.18</td>
<td>5.71</td>
<td>5.36</td>
</tr>
<tr>
<td>0.135</td>
<td>2.05</td>
<td>1.87</td>
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<td>5.25</td>
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<td>1.77</td>
<td>4.28</td>
<td>5.75</td>
<td>5.34</td>
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<td>2.23</td>
<td>4.37</td>
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<td>5.86</td>
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<td>2.66</td>
<td>4.37</td>
<td>5.91</td>
<td>5.87</td>
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<tr>
<td>0.136</td>
<td>1.75</td>
<td>1.82</td>
<td>4.50</td>
<td>5.72</td>
<td>5.83</td>
</tr>
<tr>
<td>0.026</td>
<td>3.00</td>
<td>3.20</td>
<td>4.51</td>
<td>5.56</td>
<td>5.94</td>
</tr>
<tr>
<td>0.057</td>
<td>2.43</td>
<td>2.79</td>
<td>4.64</td>
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<td>5.63</td>
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<td>0.088</td>
<td>1.73</td>
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<td>5.00</td>
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<tr>
<td>0.500</td>
<td>0.60</td>
<td>2.68</td>
<td>7.12</td>
<td>3.56</td>
<td>3.67</td>
</tr>
<tr>
<td>0.543</td>
<td>0.52</td>
<td>2.73</td>
<td>7.32</td>
<td>3.38</td>
<td>3.33</td>
</tr>
</tbody>
</table>

* $M$ is the total oxalate concentration, moles/liter.

**$ Nd$ is the total rare earth solubility, moles/liter.
where "a" represents activities; "m" represents molar concentrations; \( \gamma_1 \) represents the activity coefficient of the singly charged ion, \( \text{HC}_2\text{O}_4^- \); \( \gamma_2 \) represents the activity coefficient of the doubly charged ion, \( \text{C}_2\text{O}_4^{2-} \) (the activity of \( \text{H}_2\text{C}_2\text{O}_4 \) was taken as 1.00); \( M \) represents the total molar oxalate concentration as determined from the permanganate titration.

The assumption that only a negligible fraction of the oxalate was associated in rare earth complexes, as is implied in Equation (1), was justified in later portions of the calculations. The simultaneous solution of Equations (2), (3), and (4) yields the following expression for the oxalate ion activity. Within the accuracy of the data, differences between molal and molar concentrations could be considered negligible for the concentrations employed.

\[
(5) \quad a_{\text{C}_2\text{O}_4^{2-}} = \frac{K_1 K_2 M}{a_{\text{H}^+}^2 + \frac{a_{\text{H}^+} K_1}{\gamma_1} + \frac{K_1 K_2}{\gamma_2}}
\]

\( \gamma_1 \) was estimated from values of \( \gamma_1 \) for HCl in KCl solutions of the same ionic strengths\(^6\).

Values of the quantity corresponding to \( \gamma_{\text{C}_2\text{O}_4^{2-}}/\gamma_{\text{HC}_2\text{O}_4^-} \) which were indicated in the potentiometric determination of \( K_2 \) for oxalic acid\(^5\) were plotted as a function of ionic strength. \( \gamma_2 \) for each equilibrium solution was computed from this graph by multiplying values taken from this curve by \( \gamma_1^2 \) which had been estimated as described above. The calculation of the oxala-

late ion activity was accomplished for each solution by means of successive approximations in which the ionic strength and hence the activity coefficients from each preceding computation were employed. Table IV contains the ionic activity coefficients used in this work.

Table IV

<table>
<thead>
<tr>
<th>$\sqrt{\mu}$</th>
<th>$\gamma_1$</th>
<th>$\gamma_2$</th>
<th>$\gamma_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.050</td>
<td>0.945</td>
<td>0.795</td>
<td>0.700</td>
</tr>
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<td>0.100</td>
<td>0.900</td>
<td>0.660</td>
<td>0.473</td>
</tr>
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<td>0.150</td>
<td>0.865</td>
<td>0.561</td>
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</tr>
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<td>0.835</td>
<td>0.488</td>
<td>0.231</td>
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<td>0.810</td>
<td>0.426</td>
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<td>0.300</td>
<td>0.790</td>
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</tr>
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<td>0.750</td>
<td>0.301</td>
<td>0.0795</td>
</tr>
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<td>0.500</td>
<td>0.735</td>
<td>0.278</td>
<td>0.0700</td>
</tr>
<tr>
<td>0.550</td>
<td>0.730</td>
<td>0.264</td>
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</tr>
<tr>
<td>0.600</td>
<td>0.720</td>
<td>0.249</td>
<td>0.0562</td>
</tr>
<tr>
<td>0.650</td>
<td>0.710</td>
<td>0.234</td>
<td>0.0515</td>
</tr>
<tr>
<td>0.700</td>
<td>0.705</td>
<td>0.224</td>
<td>---------</td>
</tr>
<tr>
<td>0.750</td>
<td>0.700</td>
<td>0.216</td>
<td>---------</td>
</tr>
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</table>

The total rare earth content of the equilibrium solutions was found to depend primarily upon the oxalate ion activity. Variations of the pH were only effective in controlling the
oxalate activity according to Equation (4). Various attempts to include the binoxalate activity in the explanation of the experimental values failed to reveal any primary effect in controlling the solubility of the rare earth oxalates within the ranges tested. $10^{-4} < a_{HC_{2}O_{4}}^{-} < 0.1$ molar. Experimental solubilities have therefore been shown in Figures 1, 2, and 3 as functions of the oxalate ion activity.

A striking feature of all three systems is the moderate variation of the total rare earth concentration (ca. 100) over oxalate ion activities varying by about $10^{6}$. Also, the points on all three systems clustered around a fairly definite smooth curve. These features, together with the increasing solubility at high oxalate activity, indicated that complex ions had formed in all three cases. The possibility of ions of the type $R(C_{2}O_{4})_{n}^{3-2n}$ was considered, where $R^{++}$ is the rare earth ion. The slope of the curves representative of the data in the region of high oxalate ion activity should indicate the complex species present in this region, since to a first approximation the formation of $R(C_{2}O_{4})_{3}^{3-}$ would lead to a slope of $\frac{3}{2}$, $R(C_{2}O_{4})_{2}^{-}$ to a slope of $\frac{1}{2}$, and $RC_{2}O_{4}^{+}$ to a slope of $\frac{1}{4}$. The following equilibria explained the experimental data of the three systems studied:

\begin{align*}
(6) & \quad R(C_{2}O_{4})_{3}^{3-} \rightleftharpoons R(C_{2}O_{4})_{2}^{-} + C_{2}O_{4}^{2-} ; K_{I} \\
(7) & \quad R(C_{2}O_{4})_{2}^{-} \rightleftharpoons R(C_{2}O_{4})^{+} + C_{2}O_{4}^{-} ; K_{II} \\
(8) & \quad R(C_{2}O_{4})^{+} \rightleftharpoons R^{+++} + C_{2}O_{4}^{2-} ; K_{III}
\end{align*}
Fig. 1 Yb(total) Concentration in Buffered Oxalate Solutions.

- Experimental concentrations after dissolving wet washed crystals.
- Experimental concentrations after precipitation.
- Concentrations calculated by means of equation 9.
Fig. 2 Nd (total) Concentration in buffered oxalate solutions.
- Equilibrium approached from super-saturated side by direct precipitation.
- Solution of wet washed crystals
- Calculated from Equation (15).
Fig. 3 Ce (total) Concentration in buffered oxalate solutions.

- Experimental values
- Calculated values
(9) \( \text{R}_2(C_2O_4)_3 \text{ (s)} \rightarrow \text{R}^{+++} + \text{R}(C_2O_4)_3^{-}; \text{K}_{sp1} \)

(10) \( \text{R}_2(C_2O_4)_3 \text{ (s)} \rightarrow \text{R}(C_2O_4)^{+} + \text{R}(C_2O_4)_2^{-}; \text{K}_{sp2} \)

(11) \( \text{R}_2(C_2O_4)_3 \text{ (s)} \rightarrow 2 \text{R}^{+++} + 3 \text{C}_2\text{O}_4^{-}; \text{K}_{sp3} \)

Only one solubility product is required, since performing the indicated multiplication of the various equilibrium expressions defined above will yield

\[
(12) \text{K}_{sp3} = \text{K}_{sp2} \text{K}_{II} \text{K}_{III}^2 \quad \text{and} \quad \text{K}_{sp1} = \text{K}_{sp2} \text{K}_{III}/\text{K}_{I}
\]

From the above six reactions and their corresponding equilibria equations, the molar concentrations of each species can be calculated as a function of the oxalate ion activity, the various equilibrium constants, and the appropriate activity coefficients. By summing these terms, an expression for the total rare earth concentration, \( M_{\text{total}} \), moles/liter, can be derived.

\[
(14) M_{\text{total}} = m_{\text{R}^{+++}} + m_{\text{R}(C_2O_4)^{+}} + m_{\text{R}(C_2O_4)_2^{-}} + m_{\text{R}(C_2O_4)_3^{-}}
\]

Substituting the equivalent expressions in (14) which have been derived as functions of \( a_{C_2O_4}^{-} \) and the various equilibrium constants, there was obtained:

\[
(15) M_{\text{total}} = \frac{\text{K}_{sp2} \text{K}_{II} \text{K}_{III}^{-3/2}}{\text{K}_{sp2} \text{K}_{III}/\text{K}_{I}} \times a_{C_2O_4}^{-3/2} + \frac{\text{K}_{sp2} \text{K}_{II}^{-1/2}}{\text{K}_{II} \text{K}_{III}} \times a_{C_2O_4}^{-1/2} + \frac{\text{K}_{sp2} \text{K}_{III}^{3/2}}{\text{K}_{I} \text{K}_{II}} \times a_{C_2O_4}^{-3/2}
\]
where the terms in (15) have been summed in the same order as in (14), and thus each of the four expressions can be identified with the molar concentration of the corresponding rare earth ionic species. The process of evaluating the various constants was simplified by rewriting (15) as follows:

\[
M_{\text{total}} = \frac{A}{\sqrt[3]{3}} \cdot aC_{2O_{4}}^{2-} + \frac{B}{\sqrt[1]{1}} \cdot \frac{1}{2} \cdot aC_{2O_{4}}^{2-} + \frac{C}{\sqrt[1]{1}} \cdot \frac{1}{2} \cdot aC_{2O_{4}}^{2-} + \frac{D}{\sqrt[3]{3}} \cdot \frac{3}{2} \cdot aC_{2O_{4}}^{2-}
\]

The constants A, B, C, and D in these studies could be directly evaluated to a first approximation in the regions where the particular species predominated. The nature of the equilibria was such that the co-existence of appreciable quantities of two rare earth species occurred over a fairly limited range (ca. 300) of oxalate ion activity. The solubility data for each of the rare earth systems covered a total range of about one million in divalent oxalate ion activity. Further minor adjustments of these constants gave in every case a function which fitted the experimental data very well, as can be seen in Figures 1, 2, and 3. Values of the activity coefficients for experimental points were used, and since the concentrations of the rare earth species were usually very low compared to the other ions in solution, successive approximations were not generally needed to obtain activities consistent with the data. Having obtained good values for the constants in (16), the equilibrium constants of reactions (6) to (11) could be evaluated, using (15).
The equilibrium constants, if varied by ±5%, caused maximum variations in the calculated values on the plots in Figures 1, 2, and 3, which were quite appreciable. The values of \( \gamma_1 \) and \( \gamma_2 \) used in the oxalate equation were also employed in (15). \( \gamma_3 \) was calculated from the values of \( \gamma_1 \) and the new mean activity coefficient of LaCl\(_3\). Since this work has been started, the new edition of Harned and Owen\(^7\) has pointed out that the original calculations for the activity coefficients of LaCl\(_3\) were in error. In this work, the corrected values of \( \gamma_1 \) for LaCl\(_3\) have been employed throughout, re-calculations having been made on the earlier work. Values of \( \gamma_3 \) are tabulated in Table IV.

The equilibrium constants obtained for the rare earth oxalates are tabulated in Table V.

**Table V**

**Solubility Product and Instability Constants of Three Rare Earth Oxalates**

<table>
<thead>
<tr>
<th>Constants at 25°</th>
<th>Ce</th>
<th>Nd</th>
<th>Yb</th>
</tr>
</thead>
<tbody>
<tr>
<td>( K_{sp1} )</td>
<td>1.2 x 10^-18</td>
<td>&lt;10^-22</td>
<td>&lt;10^-19</td>
</tr>
<tr>
<td>( K_{sp2} )</td>
<td>6.0 x 10^-13</td>
<td>4.0 x 10^-13</td>
<td>1.9 x 10^-10</td>
</tr>
<tr>
<td>( K_{sp3} )</td>
<td>5.9 x 10^-30</td>
<td>7.69 x 10^-32</td>
<td>1.24 x 10^-29</td>
</tr>
<tr>
<td>( K_I )</td>
<td>0.15</td>
<td>&gt; 90</td>
<td>&gt; 90</td>
</tr>
<tr>
<td>( K_{II} )</td>
<td>1.1 x 10^-4</td>
<td>5.0 x 10^-5</td>
<td>2.6 x 10^-5</td>
</tr>
<tr>
<td>( K_{III} )</td>
<td>3.0 x 10^-7</td>
<td>6.2 x 10^-8</td>
<td>5.0 x 10^-8</td>
</tr>
</tbody>
</table>

Since the limiting slopes at high divalent oxalate activities were one half within experimental error for both neodym-

---

ium and ytterbium, it was assumed that negligible quantities of the $\text{R(C_2O_4)_3}^{5-}$ species was formed. The data was quantitatively explained by using only the first three terms in the summation for the total rare earth solubility in (15). There is a change in the formula of the solid phase, beginning with cerium, i.e., both cerium and lanthanum oxalates are reported$^8, 9, 10$ to form the ennea-hydrated salt in equilibrium with aqueous solutions, whereas the heavier rare earth oxalates precipitate as the deca-hydrated salt. The decrease in hydration in the crystal is probably associated with the larger ionic radii of lanthanum and cerium. However, the relatively stable trivalent oxalate complex of cerium, reflected by the lower value of $K_I$, seems to indicate that the formation of a trioxalate complex in the heavier rare earths with smaller ionic radii may be prevented mainly by steric reasons. Table VI contains the standard free energy, $\Delta F^\circ_{25}$, calculated from the constants of Table V.

Estimations of the limits for $K_I$ and $K_{SP_1}$ for neodymium and ytterbium were made as follows:

$$(17) \quad m_{\text{R(C_2O_4)_3}^{5-}} = \frac{1}{3} \left( \frac{1}{K_I} \cdot \frac{K_{SP_2}}{K_{III}} \right), \text{ or}$$

Table VI

Standard Free Energy Changes of the Reactions Involving Cerium, Neodymium, and Ytterbium at 25°

<table>
<thead>
<tr>
<th></th>
<th>Ce Kcalories</th>
<th>Nd Kcalories</th>
<th>Yb Kcalories</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta F_{I}^{o}$</td>
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<td>$&lt;-2.67$</td>
<td>$&lt;-2.67$</td>
</tr>
<tr>
<td>$\Delta F_{II}^{o}$</td>
<td>+4.40</td>
<td>+5.87</td>
<td>+6.26</td>
</tr>
<tr>
<td>$\Delta F_{III}^{o}$</td>
<td>+8.90</td>
<td>+9.85</td>
<td>+9.96</td>
</tr>
<tr>
<td>$\Delta F_{sp1}^{o}$</td>
<td>+24.44</td>
<td>&gt;+30.51</td>
<td>&gt;+25.96</td>
</tr>
<tr>
<td>$\Delta F_{sp2}^{o}$</td>
<td>+16.67</td>
<td>+16.91</td>
<td>+13.26</td>
</tr>
<tr>
<td>$\Delta F_{sp3}^{o}$</td>
<td>+39.37</td>
<td>+42.43</td>
<td>+39.35</td>
</tr>
</tbody>
</table>

The values of $K_{sp3}^{o}$ and $\Delta F_{sp3}^{o}$ were obtained from (12).

Typical values for neodymium oxalate are $a_{C_{2}O_{4}}^{2-} = 3.16 \times 10^{-2}$, $\gamma_{3} = 0.2$, and $M_{T} = 1.78 \times 10^{-5}$. If the total solubility found was approximately $0.5 \times 10^{-5}$ moles/liter higher in this region, it would be considered an appreciable deviation from the $\gamma_{3}$ slope observed. This additional solubility would be mainly the $M_{R}(C_{2}O_{4})_{3}^{2-}$. Thus, substituting these values into (13), we obtained as an estimate of the lower limit, $K_{I} > 90$ for neodymium. A similar calculation for ytterbium gave approximately the same lower limit for $K_{I}$. It has been shown that

$$K_{sp1}/K_{sp2} = K_{III}/K_{I}$$
and by employing the limiting values for $K_1$ calculated above, maximum values were assigned in Table V to $K_{sp1}$ for neodymium and ytterbium.

The precision of the experimental results in Figures 1, 2, and 3 was tested by the quantity $\sqrt{(1/N)\sum_{i=1}^{N} \sigma_i^2}$, where $\sigma_1 = \log (R_{\text{obs}}) - \log (R_{\text{calc}})$. For 31 points in the ytterbium system shown in Figure 1, this quantity amounted to 0.123. For 27 points in the neodymium system, this quantity was 0.150. And for 21 points in the cerium system, it was 0.065. Contributions to this quantity were mainly from errors inherent in the micro-pipetting of solutions and the subsequent radioassays by counting techniques.

Additional evidence for the formation of the negative complexes was obtained. For ytterbium, the first rare earth oxalate system studied, several additional experiments were made to demonstrate qualitatively the existence of a negative ion containing ytterbium. Three electrolysis cells with anode and cathode chambers separated by a fine sintered glass disc were equipped with Ag-AgCl electrodes. In one chamber was placed a solution of pH 3.38 and a total oxalate concentration of $4.43 \times 10^{-2}$ molar containing radioactive ytterbium. Virtually 100% of the ytterbium in such a solution was predicted from the equilibria to be in the form of $\text{Yb(C}_2\text{O}_4)_2^-$. In the other chamber of the cell was placed an identical oxalate solution with no ytterbium. Three such cells were prepared. Cell 1 contained the ytterbium in the chamber with the negative electrode, cell 2 contained the ytterbium in the chamber with the positive
electrode; and cell 3 was maintained as a diffusion control with no applied voltage. A current of 1.0 ma. was passed through cells 1 and 2 for 10 hours and a radicassay performed to determine the activity present in the cell which originally had contained no ytterbium. It was found that in cell 1, the rate of migration of Yb activity was twice as great as in cell 3. However, no detectable quantity of Yb activity had passed through the sintered glass barrier of cell 2, verifying the original assumption that most of the ytterbium was present as a negative ion. When the voltage was reversed on cell 2, the rate of migration was in this case again twice as great as in the diffusion control.

Still more evidence was obtained by batch experiments with ion exchange resins. The cation exchange resin, "Amberlite IR-100", failed to adsorb a detectable amount of ytterbium activity in a pH range of 2.5 - 3.5 with sufficiently high oxalate concentrations that the major portion of the ytterbium was predicted to be in the form of $\text{Yb(C}_2\text{O}_4)_2^-$. However, from these solutions an anion exchanger resin, "Duolite A-2", adsorbed 75% of the activity. It would appear, therefore, that nearly all of the ytterbium in solutions of high oxalate activity must exist in the form of a negative ion.

The conductances of the three rare earth oxalates in pure water were calculated, using the above equilibria data and estimated ionic mobilities. These values have been tabulated in Tables VIIa, VIIb, and VIIc and compared with the values of Rimbach and Schubert and Sarvar and Brinton.

Table VIIa

Calculated Conductivity of a Saturated Solution of Yb$_2$(C$_2$O$_4$)$_3$·10 H$_2$O in Pure H$_2$O at 25.0° C.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Concentration (mole/liter)</th>
<th>Equivalent Conductance</th>
<th>$\frac{N_a \lambda_0}{1000}$ x 10$^6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yb$^{+++}$</td>
<td>1.41 x 10$^{-7}$</td>
<td>72*</td>
<td>0.031</td>
</tr>
<tr>
<td>Yb(C$_2$O$_4$)$^+$</td>
<td>2.40 x 10$^{-5}$</td>
<td>70**</td>
<td>1.68</td>
</tr>
<tr>
<td>Yb(C$_2$O$_4$)$_2$</td>
<td>7.88 x 10$^{-6}$</td>
<td>70***</td>
<td>0.55</td>
</tr>
<tr>
<td>C$_2$O$_4$$^-$</td>
<td>8.50 x 10$^{-6}$</td>
<td>71</td>
<td>1.21</td>
</tr>
</tbody>
</table>

Total Specific Conductance = 3.47 x 10$^{-6}$
(a) 4.85 x 10$^{-6}$

Table VIIb

Calculated Conductivity of a Saturated Solution of Nd$_2$(C$_2$O$_4$)$_3$·10 H$_2$O in Pure Water at 25.0° C.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Concentration (mole/liter)</th>
<th>Equivalent Conductance</th>
<th>$\frac{N_a \lambda_0}{1000}$ x 10$^6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd$^{+++}$</td>
<td>0.11 x 10$^{-6}$</td>
<td>72****</td>
<td>0.024</td>
</tr>
<tr>
<td>Nd(C$_2$O$_4$)$^+$</td>
<td>3.35 x 10$^{-6}$</td>
<td>70**</td>
<td>0.235</td>
</tr>
<tr>
<td>Nd(C$_2$O$_4$)$_2$</td>
<td>0.12 x 10$^{-6}$</td>
<td>70***</td>
<td>0.008</td>
</tr>
<tr>
<td>C$_2$O$_4$$^-$</td>
<td>1.80 x 10$^{-6}$</td>
<td>71</td>
<td>0.256</td>
</tr>
</tbody>
</table>

Total Specific Conductance = 0.523 x 10$^{-6}$
(a) 0.750 x 10$^{-6}$
(b) 3.690 x 10$^{-6}$
Table VIIc

Calculated Conductivity of a Saturated Solution of Ce₂(C₂O₄)₃·9 H₂O in Pure Water at 25.0°C.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Concentration mole/liter</th>
<th>Equivalent Conductance N₁ λ₀ x 10⁶</th>
<th>λ₀ ohm⁻¹ cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce⁺⁺⁺</td>
<td>0.471 x 10⁻⁶</td>
<td>72***</td>
<td>0.102</td>
</tr>
<tr>
<td>Ce(C₂O₄)⁺</td>
<td>4.67 x 10⁻⁶</td>
<td>70**</td>
<td>0.327</td>
</tr>
<tr>
<td>Ce(C₂O₄)₂⁻</td>
<td>0.13 x 10⁻⁶</td>
<td>70**</td>
<td>0.009</td>
</tr>
<tr>
<td>Ce(C₂O₄)₃⁻</td>
<td>2.58 x 10⁻¹²</td>
<td>--</td>
<td>---</td>
</tr>
<tr>
<td>C₂O₄⁻</td>
<td>2.95 x 10⁻⁶</td>
<td>71</td>
<td>0.418</td>
</tr>
</tbody>
</table>

Total Specific Conductance = 0.856 x 10⁻⁶
(a) 0.651 x 10⁻⁶
(b) 1.24 x 10⁻⁶

* Calculated from data of Rimbach and Schubert using the methods of Onsager.

** Estimated.


(a) = specific conductance values of Rimbach and Schubert.
(b) = specific conductance values of Sarvar and Brinton.

The method used in calculating the solubility and specific conductance of the saturated solutions of the rare earth oxalates at 25°C in pure water is illustrated with the specific case of cerium oxalate below, where A⁻ = C₂O₄⁻:

(19) \[ M_{total \ Ce} = \frac{2}{3} M_{oxalate \ total} \]
Expanding in terms of the various species:

\[(20) \ 3(M_{Ce}^{3+} + M_{Ce}^{4+} + M_{Ce}^{2+} + M_{Ce}^{3+} + M_{Ce}^{4+}) =
2(M_{Ce}^{3+} + 2M_{Ce}^{2+} + 3M_{Ce}^{3+} + M_{A}^{+})
\]

Simplifying the above equation, as follows:

\[(21) \ 3M_{Ce}^{3+} + M_{Ce}^{4+} + M_{Ce}^{2+} + 3M_{Ce}^{3+} + 2M_{A}^{+} = 0.
\]

The expressions derived previously in Equation (16) for the molar concentration of the rare earth species as functions of the activity of the oxalate ion were substituted in the above equation, and there resulted the following:

\[(22) \ 3A_{c}C_{2}O_{4}^{2-} + B_{c}C_{2}O_{4}^{2-} + C_{C_{2}O_{4}^{2-}} + 3D_{c}C_{2}O_{4}^{2-} + 2a_{C_{2}O_{4}^{2-}} = 0.
\]

\[(23) \ 3A_{c}C_{2}O_{4}^{2-} + B_{c}C_{2}O_{4}^{2-} + 3D_{c}C_{2}O_{4}^{2-} + 2a_{C_{2}O_{4}^{2-}} = 0.
\]

Substituting the values of A, B, C, and D found for the cerium oxalate system there was obtained:

\[(24) \ 7.14 \times 10^{-15} a^{-2} + 8.00 \times 10^{-9} a^{-1} + 1.53 \times 10^{-3} a + 2a^{1/2} =
7.5 \times 10^{-5}, \text{ where } a_{C_{2}O_{4}^{2-}} = 2.95 \times 10^{-6}.
\]

This was calculated value for the activity of the divalent oxalate ion in a saturated solution of pure water and cerium oxalate at 25° C. Using this value and the expressions for the various cerium oxalate species, the molar concentrations of Table VIIc were calculated.

The similarity between neodymium and ytterbium in forming complexes was somewhat surprising. Although \(\Delta F_{I}^{0}\) and \(\Delta F_{II}^{0}\) for neodymium were actually larger than for ytterbium as had
been expected, the difference between the two elements for these reactions must be considered negligible. Thus the rather large difference in ionic radii which must be approximately 0.2 Å has little overall effect on the free energy for the formation of oxalate complexes in aqueous solutions. A feature of these systems worthy of note would be the stability of the dioxalate complex as indicated by the values of $\Delta F_{II}^o$. These values seemed particularly large when compared with the corresponding $\Delta F_{III}^o$ values which would contain the contributions from the separation of a greater charge and the low entropy of the trivalent ion.

Summary

The determination of rare earth solubilities in various saturated solutions of oxalate buffers has been accomplished by means of radioactive assays. The experimental data have indicated the presence of monoxalate and dioxalate complex ions in the ytterbium and neodymium systems and an additional trioxalate complex in the cerium system. The equilibrium constants have been evaluated for the following six reactions:

(6) $\text{R(C}_2\text{O}_4\text{)}_3 \rightleftharpoons \text{R(C}_2\text{O}_4\text{)}_2^- + \text{C}_2\text{O}_4^-$; $K_I$

(7) $\text{R(C}_2\text{O}_4\text{)}_2^- \rightleftharpoons \text{R(C}_2\text{O}_4\text{)}^+ + \text{C}_2\text{O}_4^-$; $K_{II}$

(8) $\text{R(C}_2\text{O}_4\text{)}^+ \rightleftharpoons \text{R}^{+++} + \text{C}_2\text{O}_4^-$; $K_{III}$

(9) $\text{R}_2(\text{C}_2\text{O}_4\text{)}_3 (s) \rightleftharpoons \text{R}^{+++} + \text{R(}_{\text{C}_2\text{O}_4}^\text{(s)})^3$; $K_{sp_1}$

(10) $\text{R}_2(\text{C}_2\text{O}_4\text{)}_3 (s) \rightleftharpoons \text{R(}_{\text{C}_2\text{O}_4}^\text{(s)})^+ + \text{R(}_{\text{C}_2\text{O}_4}^\text{(s)})_2$; $K_{sp_2}$
(11) $\text{R}_2(\text{C}_2\text{O}_4)_3 \, (s) \rightleftharpoons 2 \text{R}^{+++} \, + \, 3 \text{C}_2\text{O}_4^{-} ; K_{sp3}$,

where $\text{R} = \text{Ce, Nd, and Yb.}$
LITERATURE CITED


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