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THERMODYNAMIC DATA BASES FOR MULTIVALENT ELEMENTS: AN EXAMPLE FOR RUTHENIUM

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A careful consideration and understanding of fundamental chemistry, thermodynamics, and kinetics is absolutely essential when modeling predominance regions and solubility behavior of elements that exhibit a wide range of valence states. Examples of this are given using the ruthenium-water system at 298.15 K, for which a critically assessed thermochemical data base is available. Ruthenium exhibits the widest range of known aqueous solution valence states.

Known solid anhydrous binary oxides of ruthenium are crystalline RuO_2, RuO_4, and possibly RuO_3 (thin film), and known hydroxides/hydrated oxides (all amorphous) are $Ru(OH)_3 \cdot H_2O$, $RuO_2 \cdot 2H_2O$, $RuO_2 \cdot H_2O$, and a poorly characterized Ru(V) hydrous oxide. Although the other oxides, hydroxides, and hydrous oxides are generally obtained as precipitates from aqueous solutions, they are thermodynamically unstable with regard to $RuO_2(cr)$ formation. Characterized aqueous species of ruthenium include RuO_4 (which slowly oxidizes water and which dissociates as a weak acid), RuO_4^- and RuO_4^{2-} (which probably contain lesser amounts of $RuO_3(OH)_2^-$ and $RuO_3(OH)_2^{2-}$, respectively, and other species), $Ru(OH)_2^{2+}$, $Ru_4(OH)_{12}^{4+}$, $Ru(OH)_4$, Ru^{3+}, $Ru(OH)^{2+}$, $Ru(OH)_2^+$, Ru^{2+}, and some hydroxytetramers with formal ruthenium valences of $3.75 \geq Z \geq 2.0$. Potential-pH diagrams of the predominance regions change significantly with concentration due to polymerization/depolymerization reactions. Failure to consider the known chemistry of ruthenium can yield large differences in predicted solubilities.

1. INTRODUCTION

Potential-pH diagrams ("Pourbaix diagrams") are an important way of visualizing predominance regions for the various valence states and different ionic and neutral forms of an element in aqueous solution under a variety of Eh-pH conditions. They will, in turn, provide information about solubilities, chemical properties, and absorption behavior.

Potential-pH and solubility calculations are frequently made using thermodynamic data taken from critically assessed data bases such as CODATA, JANAF, or NBS-270 series. These tabulated thermodynamic data are generally reliable. However, these data bases are limited to some thermodynamically well characterized pure compounds and aqueous ions, and for none of these is a detailed discussion provided for the chemistry. Thus, in most cases, it is not clear if these data bases are complete enough for detailed thermodynamic calculations for an element, or even whether the most important compounds and aqueous ions have been included.

One example should suffice to illustrate problems that arise from using an incomplete data base. Elsewhere, we have assessed chemical and thermodynamic data for technetium (1). We noted that most previous potential-pH calculations for aqueous solutions of this element included only TcO_4^- and Tc^{2+}, and the value for Tc^{2+} is estimated. Reduction of higher valence aqueous species or dissolution of oxides in non-complexing media never gives Tc^{2+}; instead many workers have found TcO^{2+} $TcO(OH)^+$, $TcO(OH)_2$, $[TcO(OH)_2]_2$, and Tc^{3+}. Clearly calculations that ignore Tc(III) and Tc(IV) species but include Tc(II) will not reproduce the basic chemistry, and thus cannot be trusted for solubility calculations. Some who did earlier potential-pH calculations seemed unaware of the incorrectly predicted chemistry.

The waste package performance assessment of NNWSI will require geochemical modeling to predict wasteform degradation and rock-water interactions. This geochemical modeling will, in turn, require a detailed thermodynamic data base for the aqueous species and solid compounds involved, and to utilize these data will require understanding of the relevant chemistry and kinetics. This paper gives an example of a proper use of a data base for modeling calculations.

In the following sections we illustrate the use of a thermochemical data base for aqueous solubility calculations. Ruthenium and osmium show the widest range of known valence states of any element. Ruthenium was chosen here since a critically assessed and nearly complete thermochemical data base is available for it (2).

Because of the very complicated behavior of ruthenium-O_2-H_2O, its chemistry, electrochemistry, thermodynamics, and reaction kinetics will first be discussed in detail. We will consider oxides and hydroxides; then solubility constant data; the nature of aqueous Ru(VIII) species; the nature of Ru(VIII), Ru(VII), and Ru(VI) in alkaline solutions; the nature of Ru(VIII) to Ru(III) in acidic solutions; and finally Ru(III) and Ru(II) in acidic solutions. Once this is done, we will present potential-pH and solubility calculations, and discuss which solid phases should be used to constrain the calculations under various conditions.

2. *PROPERTIES OF OXIDES, HYDRATED OXIDES, AND HYDROXIDES*

When ruthenium metal is exposed to air from room temperature to about 475 K, a thin film of "native oxides" forms with a composition approaching RuO (2). Evidence for RuO in surface films is somewhat equivocal, since it is based on electron binding energies that could possible represent interference between surface layers of RuO_2 and Ru in the bulk phase. Heating the metal in air or oxygen gives a surface film that is undoubtedly RuO_2 (2,3), but RuO_3 is present in the surface defect structure (2). Similarly, bulk RuO_2 also contains RuO_3 in the surface (2,4,5). Mass spectra from atom probes and SIMS (3,6,7) of ruthenium surfaces oxidized to 900 K have shown the presence of Ru^+, Ru^{2+}, RuO^+, RuO^{2+}, RuO_2^+, RuO_2^{2+}, RuO_3^+, RuO_3^{2+}, RuO_4^+, Ru_2^+, Ru_2O^+, Ru_2O^{2+}, and $Ru_2O_3^{2+}$. Only solid RuO_2 can be produced as a bulk phase oxide by direct reaction of metal with oxygen (2), but surface oxides are obviously much more complicated.

$RuO_2(s)$ heated in a vacuum decomposes to the elements, but when heated in air or O_2 it volatilizes by $RuO_3(g)$ and $RuO_4(g)$ formation. Since heating the metal in air produces a surface film of RuO_2, these volatile oxides can also form above the metal. Above $RuO_2(s)$ heated in one atm O_2, the $RuO_4(g)$ partial pressure exceeds that of $RuO_3(g)$ below 1290 ± 50 K (2), but RuO_3 dominates at higher temperatures. Above 1850 K, ruthenium metal is the stable solid phase, and $RuO_3(g)$ forms by direct reaction of Ru with O_2; around 1900 K and higher, $RuO_2(g)$ and $RuO(g)$ are also observed. All of the gas phase oxides of ruthenium decompose to $RuO_2(cr)$ and $O_2(g)$ or $Ru(cr)$, $RuO_2(cr)$, and $O_2(g)$ upon condensing (2).

Metastable $RuO_4(cr)$, $RuO_4(l)$, and $RuO_4(aq)$ can easily be prepared by chemical or electrolytic oxidation of lower valence ruthenium compounds (2). RuO_4 melts at 298.5 ± 0.5 K, it has a vapor pressure of 0.013 atm at 298.15 K, and it usually decomposes to $RuO_2(s)$ and $O_2(g)$ (sometimes violently) when heated to around 380 K. RuO_4 is a very strong oxidizing agent and will oxidize most solvents except CCl_4.

RuO_4 is tetrahedral in the vapor phase as indicated by electron diffraction measurements (2), but it probably has significant angular distortion in the crystal, like OsO_4 which is isostructural (8,9). RuO_4 is soluble in water to 0.10-0.14 mol kg^{-1} from 273-348 K, it dissociates as a weak acid with a first dissociation constant of $K_A = 3 \times 10^{-12}$ mol kg^{-1}, and it oxidizes water at a rate that increases with temperature (2). Its aqueous solution at 298.15 K has a vapor pressure of RuO_4 given by $P/atm = 0.098\ m$ where m is the RuO_4 molality.

Precipitation of Ru(IV) with OH^- from chloride containing aqueous solutions can give significant amounts of chloride in the "hydroxide" precipitate; e.g., $Ru(OH)_{3.7}Cl_{0.3}$ from $K_4[Ru_2OCl_{10}]$ solutions (10). Precipitation of Ru(IV) from solutions free of complexing anions yields a black amorphous material generally described as $RuO_2 \cdot nH_2O$ or $Ru(OH)_4$. Since this material shows variable water content, loses water over a reasonably wide temperature interval, and has no IR bands for the hydroxyl group (2), it is probably not a hydroxide. Consequently, we consider it to be a hydrated dioxide. A commercial sample of $RuO_2 \cdot nH_2O(s)$ was also reported (11) to contain ≈ 0.34 mole CO_2 per mole Ru.

Samples of $RuO_2 \cdot nH_2O(am)$ can be prepared by reduction of aqueous RuO_4 by H_2O_2 in acidic media, adding alkali to acidic Ru(IV) solutions to cause precipitation, and are also commercially available. Various workers have analyzed their water compositions to be n = 2, 1.8, 2.3, 1.7, 2.5, 2.7, and 3.6 (11-18). The detailed study of Shorikov et al. (18) indicates that water in excess of the dihydrate is removed by heating between 343-373 K, and most is reabsorbed upon cooling. This implies that absorbed water is involved, and that the "true hydrate" is $RuO_2 \cdot 2H_2O$.

Reduction of RuO_4 by H_2 (19), by H_2O_2 in CCl_4 (20), by drying $RuO_2 \cdot nH_2O$ in a desiccator (21) or at 383 K (10,22), or heating $RuO_2 \cdot 2H_2O$ to 423 K (18) yields material with n = 0.9, 1.0, 1.1, and 1.3. We consider them all to be the monohydrate $RuO_2 \cdot H_2O$ with a slight water deficiency or excess. Complete dehydration of the monohydrate and dihydrate occurs above 600 K (10,15,16,18,20). IR evidence is available for water molecules bound by weak hydrogen bonds in $RuO_2 \cdot H_2O$ (22); i.e., it is not a hydroxide.

Precipitation of Ru(III) from aqueous solutions yields a solid that can be yellow, brown, greenish-yellow, greenish-brown, green, or black. The pure material is probably yellow, but Ru(III) solutions are very sensitive to oxidation by traces of O_2 so that contamination by $RuO_2 \cdot nH_2O$ causes the color to vary. Stretching and bending vibrations of bound water have been detected by IR spectroscopy (15), as have Ru-OH bands (15,23). Another study reported no specific Ru-OH IR bands were observed (24). Two thermal decomposition studies (15,24) indicate that 0.8-1.0 waters are present, so we consider the solid compound to be $Ru(OH)_3 \cdot H_2O$.

Early evidence for "Ru_2O_5" is of questionable reliability, but more recent results indicate its probable existence (2). Aqueous solutions of both ruthenate RuO_4^{2-} and perruthenate RuO_4^- disproportionate to form it when acidified (25):

$$3\ RuO_4^{2-}(aq) + 6H^+(aq) = RuO_4(aq) + Ru_2O_5(s) + 3H_2O(l) \qquad (1)$$

$$3\ RuO_4^-(aq) + 3H^+(aq) = 2RuO_4(aq) + 1/2Ru_2O_5(s) + 3/2H_2O(l) \qquad (2)$$

Similar reactions also occur for the corresponding osmium analogues (26).

The degree of hydration of "Ru_2O_5" is uncertain, so we treat it formally as unhydrated (2). It can be prepared by electrolytic reduction of RuO_4 in H_2SO_4 solutions at 1.12 V (27). Changing the reduction potential slightly causes the Ru_2O_5 to be reduced to $RuO_2 \cdot nH_2O$. Reduction of alkaline solutions of RuO_4^{2-} also produces Ru_2O_5, but it rapidly disproportionates to other valence states (28).

We earlier noted that RuO_3 can form in the gas phase when Ru(cr) or RuO_2(cr) are heated in the presence of O_2(g), and that RuO_3 is present in the surface defect structure of polycrystalline RuO_2. It has been claimed that RuO_3 forms as an unstable intermediate during the aniodic evolution of O_2 on a RuO_2 electrode (2). The first direct evidence for a thin film of solid RuO_3 comes from the photodecomposition of RuO_4(s) with 436 nm light (29). At 405 nm "$RuO_{2.7}$" was obtained instead, but at shorter wavelengths irradiation always produced RuO_2(s) and O_2(g). RuO_3 is undoubtedly metastable with regard to RuO_2(s) formation, and probably can exist only in thin films and as surface oxides.

All of the various oxides (except RuO_2(cr)), hydrated oxides, and hydroxides are thermodynamically metastable with regard to decomposition to two or more of Ru(cr), RuO_2(cr), O_2(g), and H_2O(l). The spontaneous decomposition reactions and their corresponding standard Gibbs energy changes per ruthenium atom in kJ mol^{-1} are:

$RuO_4(g,l,cr,\text{or } aq) = RuO_2(cr) + O_2(g)$ [-105,g;-94,l;-94,cr;-99,aq] (3)

$RuO_3(g,s) = RuO_2(cr) + 1/2O_2(g)$ [-197,g;?,s] (4)

$RuO_2(g) = RuO_2(cr)$ [-363] (5)

$RuO(g) = 1/2RuO_2(cr) + 1/2Ru(cr)$ [-466] (6)

$RuO_2\cdot 2H_2O(s) = RuO_2(cr) + 2H_2O(l)$ [-36] (7)

$Ru(OH)_3\cdot H_2O(s) = 3/4\ RuO_2(cr) + 1/4Ru(cr) + 5/2H_2O(l)$ [-17] (8)

$1/2Ru_2O_5(s) = RuO_2(cr) + 1/4O_2(g)$ [-31] (9)

Thermodynamic data are from the review article (2). Equations 7 and 8 are observed (equation 8 in the absence of O_2) only when samples are heated. Samples that are precipitated from aqueous solutions are Ru_2O_5, $RuO_2\cdot 2H_2O$, or $Ru(OH)_3\cdot H_2O$ rather than the thermodynamically stable $RuO_2(cr)$.

3. $RuO_2(s)$ ELECTRODES

Dimensionally stable RuO_2 electrodes are used extensively in the chlor-alkali process because of low overvoltages and high current efficiencies. They are prepared by thermal decomposition of so called "$RuCl_3\cdot 3H_2O$", usually on a titanium substrate with or without added TiO_2. Potential cycling of these electrodes in solution should give gradual hydration of this RuO_2. "Rest" or open circuit potentials have the reversible Nernstian slope of 0.059 V $(pH)^{-1}$ from pH=1 to 12 (2), and can be interpreted as corresponding to

$$RuO_2(hyd) + H^+(aq) + 2H_2O(l) + e^- = Ru(OH)_3\cdot H_2O(s) \qquad (10)$$

Another study of RuO_2 mounted on conducting graphite (30) gave a slope of 0.062 ± 0.002 V $(pH)^{-1}$, but with a slight hysteresis of 0.009 V $(pH)^{-1}$ for pH = 2 → 12 → 2. They suggested that formation of non-stoichiometric oxides is involved (30)

$$RuO_2(hyd) + 2\delta\ H^+(aq) + 2\delta\ e^- = RuO_{2-\delta}(hyd) + \delta\ H_2O(l) \qquad (11)$$

4. SOLUBILITIES OF HYDRATED OXIDES AND HYDROXIDES

Freshly precipitated Ru(IV) solutions that were initially $\gtrsim 10^{-4}$ mol kg^{-1} contain $Ru_4(OH)_{12}{}^{4+}(aq)$ as the dominant aqueous species at pH values of about 0-4 (2). Thus, the solubility reaction for dissolution of $RuO_2\cdot 2H_2O(s)$ is

$$4\ RuO_2\cdot 2H_2O(s) = Ru_4(OH)_{12}{}^{4+}(aq) + 4OH^-(aq) \qquad (12)$$

where $K_s^\circ = 7 \times 10^{-46}$ $mol^5\ kg^{-5}$ at infinite dilution. Monomeric $Ru(OH)_2{}^{2+}(aq)$ has been studied in the pH range 0.8-2.8; for it

$$RuO_2\cdot 2H_2O(s) = Ru(OH)_2{}^{2+}(aq) + 2OH^-(aq) \qquad (13)$$

has $K_s^\circ = 8.5\times10^{-28}$ mol^3 kg^{-3}. The polymerization/depolymerization reaction between $Ru(OH)_2^{2+}(aq)$ and $Ru_4(OH)_{12}^{4+}(aq)$ at 298 K takes at least several months to years to reach equilibrium (2). In well aged solutions (≈3-4 months), another solubility equilibrium is observed

$$RuO_2\cdot 2H_2O(s) = Ru(OH)_4(aq) \qquad (14)$$

for which the solubility is constant at about $(7\pm4)\times10^{-7}$ mol kg^{-1} from pH = 5-7 (22). Although we write these aqueous species as hydroxides, they may possibly be hydrated oxy-species; eg., $Ru_4(OH)_{12}^{4+}$ could be $Ru_4O_6\cdot nH_2O^{4+}$.

The solubility of $Ru(OH)_3\cdot H_2O$ is given by the reaction

$$Ru(OH)_3\cdot H_2O(s) = Ru(OH)_2^+(aq) + OH^-(aq) + H_2O(l) \qquad (15)$$

in the pH range 1.5-4.2, which has $K_s^\circ = 1.4\times10^{-16}$ mol^2 kg^{-2} at infinite dilution. Note that $[H_2O]=1$ at infinite dilution since solvent activities are defined on the mole fraction scale.

Ru_2O_5 does not dissolve in water or 0.5 mol dm^{-3} H_2SO_4 (27). However, it does dissolve in Ru(IV) solutions to form aqueous Ru(4.25), which is an oxidized form of $Ru_4(OH)_{12}^{4+}$. The failure of Ru_2O_5 to dissolve in water or 0.5 mol dm^{-3} H_2SO_4 may be due to the fact that no Ru(V) solution species are known, even as unstable transients. It is possible to dissolve Ru_2O_5 to form higher or lower valence aqueous species. For example,

$$2Ru_2O_5(s) + 4H_2O(l) + 4H^+(aq) = Ru_4(OH)_{12}^{4+}(aq) + O_2(g) \qquad (16)$$

has $\Delta G^\circ_{rxn} = -38$ kJ mol^{-1} so it should be spontaneous. However, it could be kinetically inhibited.

5. AQUEOUS SOLUTIONS AND REACTIONS

This section is concerned with the aqueous chemistry and thermodynamics of ruthenium in non-complexing media. Several comments are in order. Studies in acidic media generally involve $HClO_4$ or HCl, but other acids have been used (2). However, 1) HCl reduces upper valence solutions of ruthenium to Ru(IV) or Ru(III). In addition, chloride and sulfate complexes of Ru(II), Ru(III), and Ru(IV) are moderately strong, so HCl or H_2SO_4 will cause the chemistry to differ from the non-complexed case. The same may possibly be true for CF_3COOH. 2) CF_3SO_3H, CH_3SO_3H, and p-toluene sulfonic acid form virtually no complexes and are ideal for many applications. However, they cannot be used for RuO_4, RuO_2^{2+}, etc., solutions because of the likelihood of oxidation. 3) Solutions of HNO_3 have little complex formation, and can be used to study valence states from Ru(III) to Ru(VIII), although nitrosyl formation can be a problem for Ru(III). 4) Solutions of $HClO_4$ work fine in most cases, but they oxidize Ru(II) rapidly and Ru(III) in about a day (much slower oxidation at 273 K). Not only does this make the chemistry more complicated, but reduction of $HClO_4$ yields Cl^- to form ruthenium chloride complexes. Also, $HClO_4$ concentrations of ≈6 mol dm^{-3} will even oxidize Ru(IV) solutions to Ru(4.25) tetramers. 5) Solutions of RuO_4 are reduced to RuO_4^- or RuO_4^{2-} by OH^-. Most commercial NaOH and KOH (especially from polyethylene bottles) contains sufficient oxidizable impurities to cause further reduction to $RuO_2 \cdot 2H_2O(s)$.

5.1 Ru(VIII) in Aqueous Solutions

We noted earlier that RuO_4 exists as a regular tetrahedron in the gas phase. RuO_4 in the liquid state or dissolved in CCl_4 should likewise have a tetrahedral structure. The number of vibrational fundamentals of RuO_4 depend on its structure in its environment, so a regular tetrahedral structure is distinguishable from a distorted one. Consequently, a comparison of the vibrational frequencies of RuO_4 in water and in aqueous solutions of acids and bases should give information about RuO_4 symmetry.

For molecules with tetrahedral symmetry in the ground state there are four fundamental vibration modes: $\Gamma = A_1(\nu_1) + E(\nu_2) + 2F_2(\nu_3,\nu_4)$. All four modes are Raman active, but only ν_3 and ν_4 are IR active. Only the A_1 mode (ν_1) is polarized. The ν_2 and ν_4 frequencies are very close for RuO_4, and some authors give inconsistent assignments. However, of this pair, only ν_4 is IR active and IR data indicates the higher energy vibration is ν_4. A combinational band $\nu_1 + \nu_3$ is also observed by IR, so ν_1 can be derived.

IR and/or Raman vibrational frequencies of RuO_4 are available for pure gas, liquid, and for CCl_4 and aqueous solutions (31-36). The more accurate values were averaged and are reported in Table 1. They are for normal isotopic abundances; data are also available for various oxygen and ruthenium isotopes (35-37). RuO_4 is assumed to show angular distortion in the solid state which would lower its symmetry; consequently ν_2, ν_3, and ν_4 are split for both crystalline and amorphous samples (33, 34, 38).

The vibrational frequencies in Table 1 are nearly identical for RuO_4 for each case. Since RuO_4 is tetrahedral in the gas phase, this indicates that tetrahedral molecules of unsolvated RuO_4 must also be the dominant species in liquid and solution.

Absorption spectra have been measured for RuO_4 in the gas phase, and for aqueous and CCl_4 solutions (13, 39-46). These UV measurements yield frequencies for the electronic absorption bands and, in some cases, their vibrational and rotational fine structure. The positions and frequencies of the vibrational components of the electronic band centered around 26,000 cm^{-1} are identical in water, in 1-12 mol dm^{-3} HNO_3 (42, 45), and in 10^{-4}-10^{-3} mol dm^{-3} NaOH (45). The ground state vibrational frequencies discussed above show that unhydrated tetrahedral RuO_4 is the dominant aqueous species, and electronic absorption band vibrational components were interpreted (42, 45) to indicate that this is also true from pH $\approx$ -1 to 11. If so, then acidic or basic forms of RuO_4 do not form to a significant degree in this pH range. Higher pH values were not studied because the rate of reduction of RuO_4 by $OH^-(aq)$ becomes significant.

Electromigration experiments for RuO_4 in 1-11 mol dm^{-3} HNO_3 show no preferential migration to anode or cathode, and thus confirm that species such as $HRuO_4^+$ do not form in significant amounts (42). However, there is evidence that the basic form of RuO_4, which we will

TABLE 1. Ground State Vibrational Energies of RuO_4, RuO_4^-, and RuO_4^{2-} in cm^{-1}

State	$\nu_1(A_1)$	$\nu_2(E)$	$\nu_3(F_2)$	$\nu_4(F_2)$
		RuO_4		
gas	883±3	319	920±1	332.5±3
liquid	882±1	326±4	915±2	335±3
CCl_4 solution	881±1	-	915±1	333.4
aqueous solution	883	318	921	332
		RuO_4^-		
aqueous solution	827	-	846	-
		RuO_4^{2-}		
aqueous solution	838±2	331±1	807±3	333±3

write as $RuO_4(OH)^-(aq)$, and its reduction products can be present in significant amounts without major changes in the electronic absorption band around 26,000 cm^{-1}.

The 26,000 cm^{-1} absorption band of RuO_4 has 5-6 peaks or shoulders for aqueous solutions (42,43,45) and for HNO_3 and NaOH solutions (42,45). This structure is due to the vibrational fundamentals and combinational bands or overtones. The UV electronic spectra for $RuO_4^-(aq)$ and $RuO_4^{2-}(aq)$ in this region are smooth and nearly featureless and are centered at nearly the same frequency as for $RuO_4(aq)$ (13,39,45,47-50). Obviously, significant amounts of $RuO_4^-(aq)$ and $RuO_4^{2-}(aq)$ could also be present in alkaline solutions, but their presence would only change the height of this $RuO_4(aq)$ UV band and not its essential features ($RuO_4^{2-}(aq)$ absorbs strongly at 21,500 cm^{-1} where $RuO_4(aq)$ and $RuO_4^-(aq)$ absorb little). The acidic dissociation for "H_2RuO_5" noted above indicates that significant $RuO_4(OH)^-(aq)$ should be present by pH = 11, about 20% for an initial $RuO_4(aq)$ concentration of 10^{-3} mol dm^{-3}. If the corresponding UV absorption band for $RuO_4(OH)^-(aq)$ is also nearly featureless or weak, then it also would have no obvious effect on the 26,000 cm^{-1} $RuO_4(aq)$ band. The ν_2 and ν_4 vibrations of $RuO_4^{2-}(aq)$ are close to those for $RuO_4(aq)$, whereas ν_1 and ν_3 are shifted by 40-115 cm^{-1} (Table 1). Thus, a Raman spectroscopic investigation of alkaline $RuO_4(aq)$ could possibly detect other species.

Two obvious mechanisms can be given for the formation of basic forms of $RuO_4(aq)$. Mechanism A has three steps

$$RuO_4(aq,unhyd) + H_2O(l) = RuO_3(OH)_2(aq) \tag{17}$$

$$RuO_3(OH)_2(aq) = RuO_4(OH)^-(aq) + H^+(aq) \tag{18}$$

$$RuO_4(OH)^-(aq) = RuO_5{}^{2-}(aq) + H^+(aq) \tag{19}$$

Mechanism B has two steps

$$RuO_4(aq,unhyd) + OH^-(aq) = RuO_4(OH)^-(aq) \tag{20}$$

$$RuO_4(OH)^-(aq) + OH^-(aq) = RuO_4(OH)_2{}^{2-}(aq) \tag{21}$$

Thus, the predicted singly charged anion is identical for both mechanisms, but the doubly charged anions are different and, in principle, chemically distinguishable. Solid salts of the osmium analogues (51-53) contain $OsO_4(OH)_2{}^{2-}$. When the pH is high enough to form the doubly charged anion, reduction of $RuO_4(aq)$ to $RuO_4{}^-(aq)$ or $RuO_4{}^{2-}(aq)$ occurs instead, so the difference between mechanisms A and B may seem academic for ruthenium. However, similar hydroxy species may be present in $RuO_4{}^-(aq)$ and $RuO_4{}^{2-}(aq)$ solutions, so we will discuss their chemistry.

5.2 Ru(VIII), Ru(VII), and Ru(VI) in Alkaline Solutions

There are a number of types of evidence, both chemical and electrochemical, that have some bearing on the state of Ru(VIII), Ru(VII), and Ru(VI) in alkaline solutions.

Reduction potentials for one electron reductions of Ru(VIII) to Ru(VII) and for Ru(VII) to Ru(VI) (39,54,55) from pH = 9-12.1 are independent of pH. In addition, the redox equilibrium constant between Ru(VII), Mn(VI), Ru(VI), and Mn(VII) for pH≈13.3-13.6 was measured (56). Also, the following equilibrium was investigated (13) from pH = 10.3-10.9

$$3RuO_4{}^{2-}(aq) + 4H_2O(l) = 2RuO_4{}^-(aq) + RuO_2 \cdot 2H_2O(s) + 4OH^-(aq) \tag{22}$$

where the equilibrium constant is $K^\circ = (6 \pm 3) \times 10^{-9}\ mol^3\ kg^{-3}$. These equilibrium constant data (13,56) give a consistent value for the $RuO_4{}^{2-}(aq)/RuO_4{}^-(aq)$ potential (2).

Since redox potentials for Ru(VIII)/Ru(VII) and Ru(VII)/Ru(VI) are independent of pH from ≈9 to 13.6, and since $RuO_4(aq)$ is the dominant species at pH = 9-11.5 for Ru(VIII), we assume (2) the reactions correspond to

$$RuO_4(aq) + e^- = RuO_4{}^-(aq), \qquad E^\circ = 0.996 \pm 0.005\ V \tag{23}$$

$$RuO_4{}^-(aq) + e^- = RuO_4{}^{2-}(aq), \qquad E^\circ = 0.586 \pm 0.011\ V \tag{24}$$

The lack of a pH dependence for E° of equation 23 implies that $RuO_4(OH)^-(aq)$ is not electroactive under these conditions.

Isolation and characterization of salts that precipitate from aqueous solutions sometimes give an indication of the nature of the corresponding solution species. Although several perruthenate salts have been prepared (2), only $KRuO_4$ is structurally characterized (39). It is prepared by reaction of RuO_4(aq) with 0.1-1.0 mol dm^{-3} KOH followed immediately by chilling the solution (2). It has the scheelite structure with nearly tetrahedral RuO_4^-; this suggests that RuO_4^-(aq) ions may be present in aqueous alkaline solutions. The osmium analogues offer little insight since they are unstable at all pH values (57).

Both IR and Raman spectra have been reported for solid $KRuO_4$ (33, 58, 59). Vibration fundamentals occur at $\nu_1(A_1) = 827 \pm 2$, $\nu_2(E) = 339$, $\nu_3(F_2) = 845 \pm 3$ and 835, and $\nu_4(F_2) = 316 \pm 1$ and 308 ± 4 cm^{-1}; ν_3 and ν_4 are split into doublets. The IR spectrum of $KRuO_4$ in aqueous alkali has vibrational bands at 827, 846, and 1656 cm^{-1} (48); the first two are undoubtedly ν_1 and ν_3, and the latter probably an overtone. Values of both ν_1 and ν_3 in solution and in solid $KRuO_4$ are identical; this is at least consistent with the predominant aqueous species being unhydrated tetrahedral RuO_4^-(aq). Both potassium persulfate (48) and potassium hypochlorite (60) stabilize perruthenate solutions.

When RuO_4 is added to aqueous alkali it can be reduced to the orange-red ruthenate ion, which is usually written as RuO_4^{2-}(aq). Formation of ruthenates rather than perruthenates is favored by longer reaction times, warmer temperatures, and higher OH^-(aq) concentrations (2). A number of ruthenate salts have been prepared (2), but only "$BaRuO_4 \cdot H_2O$" has been structurally characterized (61). It actually contains layers of trigonal-bipyramidal $RuO_3(OH)_2^{2-}$ ions. "$BaRuO_4 \cdot H_2O$" loses water when heated to 563 K, presumably to form anhydrous $BaRuO_4$, but the anhydrous form begins to lose oxygen immediately (62).

More "osmate" salts have been characterized than ruthenate salts. "$K_2OsO_4 \cdot 2H_2O$" is actually $K_2[OsO_2(OH)_4]$ (63, 64). The rubidium and cesium salts are isostructural (65). Addition of Ba^{2+}, Sr^{2+}, or Ca^{2+} to basic Os(VI) solutions gave (66) crystalline salts of the type $MOsO_3(OH)_2 \cdot nH_2O$, and also $CaOsO_2(OH)_4$. Since ruthenium and osmium have similar chemistry in the upper valence states, this suggests that ruthenate solutions may be mixtures of RuO_4^{2-}(aq), $RuO_3(OH)_2^{2-}$(aq), and $RuO_2(OH)_4^{2-}$(aq). Solid complexes only with even numbers of hydroxides have been isolated for ruthenium and osmium. Griffith (58) reported that the IR spectra of "RuO_4^{2-}" in D_2O and alkaline D_2O were identical, so no major change in structure is occurring with pH.

Griffith (33) and Gonzalez-Vilchez and Griffith (59) reported Raman vibrational frequencies for aqueous alkaline "RuO_4^{2-}". Their assignments of ν_1 and ν_3 are reversed; the later assignment will be assumed reliable. These values are given in Table 1. Results for both solid K_2RuO_4 with its presumed RuO_4^{2-} ion (33) and "$BaRuO_4 \cdot H_2O$" with its $RuO_3(OH)_2^{2-}$ ion (58, 59) are similar to the solution values (except ν_3 is split in the solids), so they cannot be used to uniquely characterize solution species. However, the absence of splittings in the aqueous solution peaks is certainly consistent with tetrahedral symmetry.

Reduction of $RuO_4(aq)$ by $OH^-(aq)$ was found to obey the following rate law at constant ionic strength (45)

$$\frac{d[RuO_4,aq]}{dt} = -k[RuO_4,aq][OH^-,aq] \tag{25}$$

where $k=(1.9\pm0.4)\times10^{-3}$ mol^{-1} dm^3 s^{-1} at 283 K and I = 0.264 mol dm^{-3}. Assuming the same mechanism applies at 298.15 K and I = 0.1 mol dm^{-3}, then $k = 9.7\times10^{-3}$ mol^{-1} dm^3 s^{-1} at that temperature (45). We will use this result to calculate whether reduction by $OH^-(aq)$ could have affected the measurements of the first acidic constant of $RuO_4(aq)$ using liquid-liquid extraction of RuO_4 between H_2O and CCl_4 at various pH values (39, 67).

Silverman and Levy (39) used one minute reaction/extraction times and Martin (67) ten minutes so 0.6-2.5% and 0.6-5.5%, respectively, of the aqueous RuO_4 could have been reduced. Reduction of $RuO_4(aq)$ would make the apparent distribution ratio of RuO_4 in CCl_4 to water too low and the calculated first acidic dissociation constant too high. This error should have been greater for Martin's study and, indeed, his K_A values are about a factor of five greater than for Silverman and Levy, although this difference is greater than expected.

Nikitina et al. (45) proposed the following two-step mechanism to account for the kinetic rate law

$$RuO_4(aq) + OH^-(aq) \underset{k_{-1}}{\overset{k_1}{=}} RuO_4^-(aq) + OH(aq) \tag{26}$$

$$OH(aq) + OH(aq) \overset{k_2}{=} H_2O(l) + 1/2O_2(g) \tag{27}$$

This yields the rate expression

$$\frac{d[RuO_4(aq)]}{dt} = -k_1[RuO_4,aq][OH^-,aq] + k_{-1}[RuO_4^-.aq][OH,aq]$$

$$= -k_1[RuO_4,aq][OH^-,aq] \tag{28}$$

provided [OH,aq] remains very small.

Other mechanisms could also account for this rate law. For example,

$$RuO_4(aq) + OH^-(aq) \underset{k_{-1}}{\overset{k_1}{=}} RuO_4(OH)^-(aq) \tag{29}$$

$$2RuO_4(OH)^-(aq) \underset{k_{-2}}{\overset{k_2}{=}} 2RuO_4^-(aq) + H_2O_2(l) \tag{30}$$

The H_2O_2 then catalytically decomposes to H_2O and 1/2 O_2. This yields the rate expression

$$\frac{d[RuO_4,aq]}{dt} = -k_1\ [RuO_4,aq][OH^-,aq] + k_{-1}[RuO_4(OH)^-,aq] \tag{31}$$

If the rate of reduction of $RuO_4(aq)$ is slow compared to establishment of acid/base equilibrium, then

$$[RuO_4(OH)^-,aq] = \frac{K_A[RuO_4,aq]}{[H^+,aq]} = \frac{K_A}{K_w}\ [RuO_4,aq][OH^-,aq] \tag{32}$$

and thus

$$\frac{d[RuO_4,aq]}{dt} = \{-k_1 + k_{-1}(\frac{K_A}{K_w})\ \}[RuO_4,aq][OH^-,aq] \tag{33}$$

which is the observed rate law. We could also have

$$RuO_4(aq) + H_2O(l) = RuO_3(OH)_2(aq) \tag{34}$$

followed by

$$RuO_3(OH)_2(aq) + OH^-(aq) = RuO_4(OH)^-(aq) + H_2O(l) \tag{35}$$

etc.

It should thus be clear that there are several reduction mechanisms compatible with the rate equation. The overall reaction for reduction of $RuO_4(aq)$ by $OH^-(aq)$ is

$$RuO_4(aq) + OH^-(aq) = RuO_4^-(aq) + 1/4O_2(g) + 1/2H_2O(l) \tag{36}$$

Larsen and Ross (47) found that H_2O_2 was the likely product when ruthenium tetroxide or perruthenate solutions were reduced by aqueous base. Thus, equations 29 and 30 can explain this, and they are also compatible with the known acidic properties of $RuO_4(aq)$.

Reduction of aqueous perruthenate by $OH^-(aq)$ involves H_2O_2 formation (47), followed by decomposition of H_2O_2 to O_2. Above about pH = 10.65 the overall reaction appears to be

$$RuO_4^-(aq) + OH^-(aq) = RuO_4^{2-}(aq) + 1/4O_2(g) + 1/2H_2O(l) \tag{37}$$

and $O_2(g)$ bubbles were observed (39). At constant ionic strength and 10^{-4} - 10^{-5} mol dm^{-3} $RuO_4^-(aq)$, the reaction kinetics are given by (45)

$$\frac{d[RuO_4^-,aq]}{dt} = -k_1[RuO_4^-,aq]^2[OH^-,aq] - k_2[RuO_4^-,aq] \tag{38}$$

In contrast, at somewhat higher $RuO_4^-(aq)$ concentrations (49, 68)

$$\frac{d[RuO_4^-,aq]}{dt} = -k_1[RuO_4^-,aq]^2[OH^-,aq]^3 \qquad (39)$$

A somewhat complicated reaction sequence is required to account for the latter equation (68). It is obvious that both equations 38 and 39 will require a hydroxy intermediate such as $RuO_4(OH)^{2-}(aq)$ or $RuO_4(OH)_2^{3-}(aq)$.

One thing should be clear from the above discussion: neither mechanism A or B alone can account for all of the experimental facts. That is, a mixed mode involving equations 17-21 may be in operation. Thus, $RuO_4(aq)$ may also contain $RuO_3(OH)_2(aq)$, $RuO_4(OH)^-(aq)$, $RuO_4(OH)_2^{2-}(aq)$ and $RuO_5^{2-}(aq)$; $RuO_4^-(aq)$ may also contain $RuO_3(OH)_2^-(aq)$, $RuO_4(OH)^{2-}(aq)$, $RuO_4(OH)_2^{3-}(aq)$, and $RuO_5^{3-}(aq)$; and $RuO_4^{2-}(aq)$ may also contain $RuO_3(OH)_2^{2-}(aq)$, $RuO_4(OH)^{3-}(aq)$, $RuO_4(OH)_2^{4-}(aq)$, $RuO_2(OH)_4^{2-}(aq)$, and $RuO_5^{4-}(aq)$.

Table 2 summarizes the redox and chemical equilibrium behavior of ruthenium in alkaline aqueous solutions at 298.15 K. Several additional reactions were taken from the review (2). Direct experimental values of $\Delta G°$, $E°$, or $K°$ are given when available. Values in square brackets are for known reactions but for which the thermodynamic data or redox potentials are unknown or for which more accurate values can be obtained from the self-consistent $\Delta G_f°$ data (2). The value in parentheses is for a reaction not observed at room temperature. The reaction of $RuO_4^-(aq)$ with $H_2O(l)$ was claimed to occur by Silverman and Levy (39).

5.3 Ru(VI), Ru(IV), and Ru(3.75) to Ru(III) in Acidic Solutions

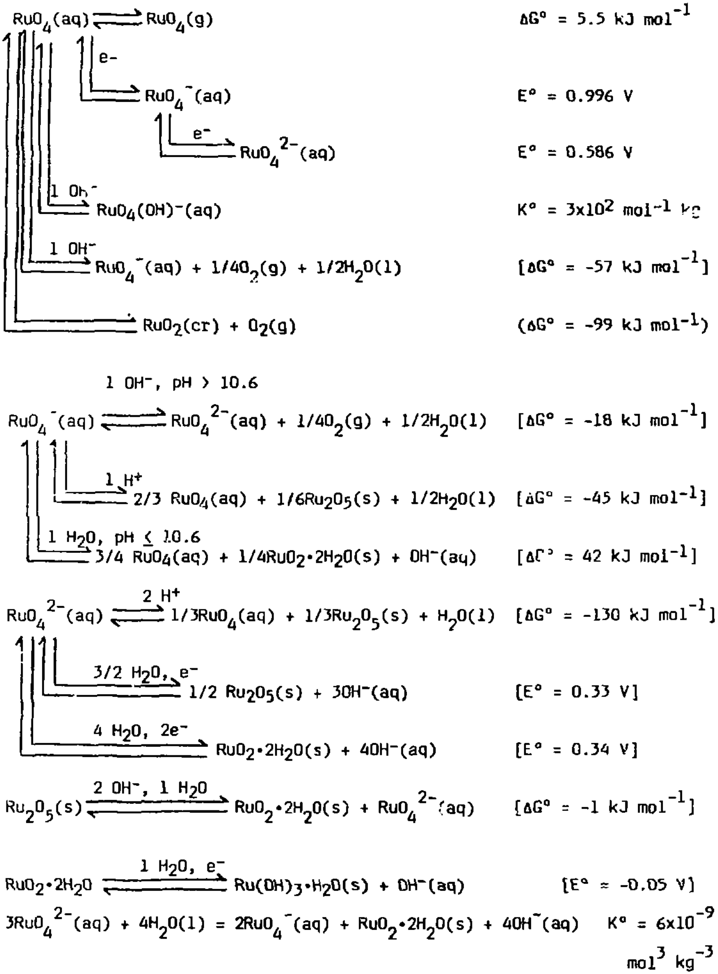
We now consider aqueous acidic non-complexing media. Although $RuO_4(aq)$ slowly oxidizes water, a few milligrams of chlorine stabilize its solutions (69).

Reduction of RuO_4 in aqueous H_2SO_4 either electrolytically around 1.3 V or chemically yields a green ion of Ru(VI) that is usually assumed to be $RuO_2^{2+}(aq)$ or a sulfate complex (27,70-72). Solutions of $RuO_2^{2+}(aq)$ disproportionate in a few hours to $RuO_4(aq)$ and Ru(IV) (27,70,71). Reaction of freshly prepared (but not aged) Ru(IV) with RuO_4 gives RuO_2^{2+} also (70), as does anodic oxidation of Ru(III) sulfates at about 1.4 V (73).

Addition of RuO_4 to concentrated aqueous HCl containing CsCl or RbCl yields salts of the type $M_2[RuO_2Cl_4]$ (2). Bromide and oxalate analogues are also known (2). $M_2[RuO_2Cl_4]$ can be dissolved in and recovered from dilute HCl, but in water it instantly hydrolyzes to form RuO_4 and $RuO_2 \cdot nH_2O(s)$ (74). These $M_2[RuO_2Cl_4]$ are undoubtedly salts of RuO_2^{2+}.

Many workers doubt the existence of hydrated Ru_2O_5, and instead believe that reduction of higher valence compounds always gives $RuO_2 \cdot 2H_2O(s)$. However, acidification of alkaline $RuO_4^-(aq)$ and $RuO_4^{2-}(aq)$ gave "Ru_2O_5" quantitatively (25). Some reasons for the confusion are: 1) Electrolytic reduction of alkaline

TABLE 2. Reactions of Ruthenium in Alkaline Solution



$RuO_4(aq) \rightleftharpoons RuO_4(g)$ — $\Delta G° = 5.5\ kJ\ mol^{-1}$

$\xrightarrow{e^-} RuO_4^-(aq)$ — $E° = 0.996\ V$

$\xrightarrow{e^-} RuO_4^{2-}(aq)$ — $E° = 0.586\ V$

$\xrightarrow{1\ OH^-} RuO_4(OH)^-(aq)$ — $K° = 3x10^2\ mol^{-1}\ kg$

$\xrightarrow{1\ OH^-} RuO_4^-(aq) + 1/4O_2(g) + 1/2H_2O(l)$ — $[\Delta G° = -57\ kJ\ mol^{-1}]$

$\rightarrow RuO_2(cr) + O_2(g)$ — $(\Delta G° = -99\ kJ\ mol^{-1})$

$RuO_4^-(aq) \xrightleftharpoons{1\ OH^-,\ pH > 10.6} RuO_4^{2-}(aq) + 1/4O_2(g) + 1/2H_2O(l)$ — $[\Delta G° = -18\ kJ\ mol^{-1}]$

$\xrightarrow{1\ H^+} 2/3\ RuO_4(aq) + 1/6Ru_2O_5(s) + 1/2H_2O(l)$ — $[\Delta G° = -45\ kJ\ mol^{-1}]$

$\xrightarrow{1\ H_2O,\ pH \leq 10.6} 3/4\ RuO_4(aq) + 1/4RuO_2 \cdot 2H_2O(s) + OH^-(aq)$ — $[\Delta G° = 42\ kJ\ mol^{-1}]$

$RuO_4^{2-}(aq) \xrightleftharpoons{2\ H^+} 1/3RuO_4(aq) + 1/3Ru_2O_5(s) + H_2O(l)$ — $[\Delta G° = -130\ kJ\ mol^{-1}]$

$\xrightarrow{3/2\ H_2O,\ e^-} 1/2\ Ru_2O_5(s) + 3OH^-(aq)$ — $[E° = 0.33\ V]$

$\xrightarrow{4\ H_2O,\ 2e^-} RuO_2 \cdot 2H_2O(s) + 4OH^-(aq)$ — $[E° = 0.34\ V]$

$Ru_2O_5(s) \xrightleftharpoons{2\ OH^-,\ 1\ H_2O} RuO_2 \cdot 2H_2O(s) + RuO_4^{2-}(aq)$ — $[\Delta G° = -1\ kJ\ mol^{-1}]$

$RuO_2 \cdot 2H_2O \xrightleftharpoons{1\ H_2O,\ e^-} Ru(OH)_3 \cdot H_2O(s) + OH^-(aq)$ — $[E° = -0.05\ V]$

$3RuO_4^{2-}(aq) + 4H_2O(l) = 2RuO_4^-(aq) + RuO_2 \cdot 2H_2O(s) + 4OH^-(aq)$ — $K° = 6x10^{-9}\ mol^3\ kg^{-3}$

$RuO_4{}^{2-}(aq)$ solutions yields two 1e⁻ reductions (75), the first to "Ru_2O_5" which then goes to $RuO_2 \cdot 2H_2O(s)$. However, "Ru_2O_5" is unstable in the 2-10 mol dm^{-3} NaOH used and rapidly disproportionates to $RuO_2 \cdot 2H_2O(s)$. 2) Reduction of $RuO_4(aq)$ in H_2SO_4 produces "Ru_2O_5", but the yield decreases with H_2SO_4 concentration (27), and by 5 mol dm^{-3} no Ru_2O_5 formation is observed. 3) Good yields of "Ru_2O_5" could be obtained by reduction of RuO_4 in 0.5 mol dm^{-3} H_2SO_4 at 1.12 V (27). However, slight departures from this potential gives rapid reduction to $RuO_2 \cdot 2H_2O$ (27). It thus appears that the stability field of "Ru_2O_5" extends only slightly below the oxidation limit for water for moderately acidic to alkaline pH values, and outside its stability field "Ru_2O_5" readily disproportionates or is reduced to $RuO_2 \cdot 2H_2O(s)$.

Connick and Hurley (76) studied the reaction

$$4RuO_4{}^-(aq) + 4\ H^+(aq) = 3RuO_4(aq) + RuO_2 \cdot 2H_2O(s) \qquad (40)$$

from pH = 5.01-5.72 for which $K° = (2.5 \pm 2.9) \times 10^{27}$ mol^{-5} kg^5. A powdered ruthenium catalyst was used.

Reduction of $\geq 10^{-4}$ mol kg^{-1} $RuO_4(aq)$ by H_2O_2 in aqueous $HClO_4$ yields the hydroxy tetramer $Ru_4(OH)_{12}{}^{4+}(aq)$, as does potentiometric pH titration of $5 \times 10^{-3} - 2 \times 10^{-4}$ mol kg^{-1} Ru(IV) in acidic nitrate or methanesulfonate solutions (2,77).

It is possible to isolate monomeric $Ru(OH)_2{}^{2+}(aq)$ by ion-exchange from solutions prepared by reduction of RuO_4 with H_2O_2 (14,78). Other workers (22,79) suggested that various monomeric Ru(IV) species are more important than polymers in aged systems. However, solubility experiments and spectroscopic measurements indicate that it takes several months or longer for the monomer/polymer reaction to reach equilibrium (2,22,80). Chloro complexes of these same monomeric cations form in HCl solutions (81).

Charge per ion and charge per ruthenium determinations confirm the existence of $Ru(OH)_2{}^{2+}(aq)$ and $Ru_4(OH)_{12}{}^{4+}(aq)$, as do solubility measurements as a function of the Ru(IV) concentration and pH for fresh precipitates (2). Using solubility data and Gibbs energies of formation we calculate the polymerization constant of

$$4Ru(OH)_2{}^{2+}(aq) + 4H_2O(l) = Ru_4(OH)_{12}{}^{4+}(aq) + 4H^+(aq) \qquad (41)$$

to be $K° = 1.5 \times 10^7$ mol kg^{-1}. For neutral $Ru(OH)_4(aq)$ we have

$$4Ru(OH)_4(aq) + 4H^+(aq) = Ru_4(OH)_{12}{}^{4+}(aq) + 4H_2O(l) \qquad (42)$$

for which $K° = 2.6 \times 10^{35}$ mol^{-7} kg^7. The experimental $\Delta G_f°$ for $RuO_2 \cdot 2H_2O(s)$ is based on three studies with fresh precipitates (2).
However, it was necessary to assume the same value for aged precipitates (22) to calculate $\Delta G_f°$ for $Ru(OH)_4(aq)$ from equation 14 since there are no $\Delta G_f°$ data for aged precipitates. This value, $\Delta G_f°(Ru(OH)_4,aq) = \Delta G_f°(RuO_2 \cdot 2H_2O,s) - RT\ln K_s° = -655.9 \pm 14$ kJ mol^{-1}, was not reported previously.

Electrolytic reduction of $Ru_4(OH)_{12}{}^{4+}(aq)$ occurs in four one electron steps (2)

$$Ru_4(OH)_{12-2n}^{4+n}(aq) + e^- + 2H^+(aq) = Ru_4(OH)_{10-2n}^{5+n}(aq) + 2H_2O(l) \quad (43)$$

where n = 0 to 3. These reduction potentials are listed in Table 3 and are uncertain by 0.02-0.05 V, mainly because most studies were done in $HClO_4$ which slowly oxidizes Ru(III) and lower valence tetramers.

All of these mixed valence tetramers are unstable with regard to disproportionation to $Ru_4(OH)_{12}^{4+}(aq)$ and $Ru^{3+}(aq)$. Also, $Ru_4(OH)_4^{8+}(aq)$ spontaneously depolymerizes with first order kinetics and $k = 2.5 \times 10^{-3}$ s^{-1} at 25°C (82). Similarly, the unstable dimer of Ru(III) can be reduced irreversibly to $Ru^{2+}(aq)$.

The redox potential measurements for equation 43 were done in 0.01 to 2.0 mol dm^{-3} acid (pH = -0.3 to 2.0), but the majority were at 1.0 mol dm^{-3}. The reduction potentials E° show pH dependences at higher pH values, so additional hydrolysis may be occurring (83, 84).

Other redox reactions are observed to occur at acidic pH values

$$RuO_2 \cdot 2H_2O(s) + e^- + H_2O(l) = Ru(OH)_3 \cdot H_2O(s) + OH^-(aq) \quad (44)$$

$$Ru(OH)_3 \cdot H_2O(s) + 3e^- + 3H^+(aq) = Ru(cr) + 4H_2O(l) \quad (45)$$

$$RuO_2 \cdot 2H_2O(s) + e^- + H^+(aq) = Ru(OH)_3 \cdot H_2O(s) \quad (46)$$

Although experimental redox potentials are available for these reactions, they are fairly uncertain because $Ru(OH)_3 \cdot H_2O(s)$ is readily oxidized to $RuO_2 \cdot 2H_2O(s)$ by traces of oxygen (2). More accurate redox potentials were calculated from the self consistent thermodynamic data.

Table 3 summarizes the redox and chemical equilibrium behavior in acidic aqueous solutions.

5.4 Ru(III) and Ru(II) in Acidic Solutions

The reduction potential for

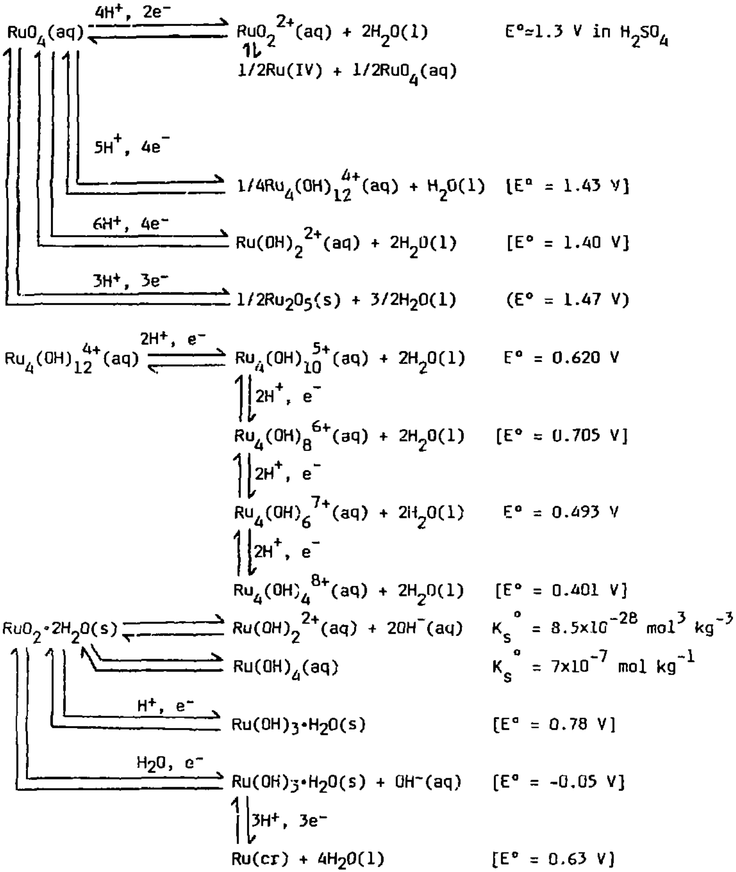
$$Ru^{3+}(aq) + e^- = Ru^{2+}(aq) \quad (47)$$

$E° = 0.239 \pm 0.007$ V is well characterized (2) and independent of pH for $pH \leq 2.9$. Salts of $Ru(H_2O)_6^{2+}$ and $Ru(H_2O)_6^{3+}$ have been isolated (2, 85), and leave little doubt that these same cations are present in acidic aqueous solutions. Above pH = 2.9 the reduction potential varies with pH, which indicates that hydrolysis is occurring. These reduction potentials and spectrophotometric pH titration yield $pK^o = 2.24 \pm 0.25$ (2) for

$$Ru^{3+}(aq) + H_2O(l) = Ru(OH)^{2+}(aq) + H^+(aq) \quad (48)$$

Unfortunately, these results for $Ru^{3+}(aq)$, $Ru(OH)^{2+}(aq)$, and $Ru^{2+}(aq)$ cannot be directly related to the thermodynamic results of Tables 2 and 3, but their ΔG_f^o values can be obtained within an additive constant ψ. Reduction potentials of $Ru^{3+}(aq)$ and $Ru^{2+}(aq)$ to Ru(cr) are unknown, and reduction of Ru(IV) aqueous species does not yield these species or yields irreversible couples (2). Using known

TABLE 3. Reactions of Ruthenium in Acidic Solutions



$4RuO_2{\cdot}2H_2O(s) = Ru_4(OH)_{12}^{4+}(aq) + 4OH^-(aq)$ $K_s° = 7\times10^{-46}$ mol^5 kg^{-5}

$Ru(OH)_3{\cdot}H_2O(s) = Ru(OH)_2^+(aq) + OH^-(aq) + H_2O(l)$ $K_s° = 1.4\times10^{-16}$ mol^2 kg^{-2}

$Ru_2O_5(s) + 3H_2O(l) + 2H^+(aq) + 2e^- = 2RuO_2{\cdot}2H_2O(s)$ $[E° = 1.17]$

$4RuO_4^-(aq) + 4H^+(aq) = 3RuO_4(aq) + RuO_2{\cdot}2H_2O(s)$ $K° = 2.5\times10^{27}$ mol^{-5} kg^5

chemical properties of ruthenium we estimated concordant values of ψ in three ways (2). However, there is some uncertainty, so calculated redox couples between $Ru^{3+}(aq)$, $Ru^{2+}(aq)$, or $Ru(OH)^{2+}(aq)$ with other species and compounds in Tables 2 and 3 will be uncertain by about 0.15 V for 1 e^- reactions (2).

Using the value of ψ we can estimate potentials for several additional reactions. They are given in Table 4.

TABLE 4. Reactions of Lower Valence Ruthenium Species

$Ru^{3+}(aq) + e^-$	=	$Ru^{2+}(aq)$	$E^\circ = 0.239$ V
$Ru^{3+}(aq)$	$\xrightarrow{H_2O}$	$Ru(OH)^{2+}(aq) + H^+(aq)$	$K^\circ = 5.8\times10^{-3}$ mol kg^{-1}
$Ru(OH)^{2+}(aq)$	$\xrightarrow{H_2O}$	$Ru(OH)_2^{+}(aq) + H^+(aq)$	[$K^\circ \approx 0.05$ mol kg^{-1}]
$Ru^{3+}(aq)$	$\xrightarrow{3e^-}$	$Ru(cr)$	($E^\circ \approx +0.60$ V)
$Ru^{2+}(aq) + 2e^-$	=	$Ru(cr)$	($E^\circ \approx +0.78$ V)
$RuO_2\cdot 2H_2O(s) + e^-$	=	$Ru(OH)_2^{+}(aq) + 2OH^-(aq)$	($E^\circ \approx -0.99$ V)

6. POTENTIAL-pH DIAGRAMS AND SOLUBILITY CALCULATIONS

Solubility and potential-pH calculations were performed for the Ru-H_2O system at 25°C using the available thermodynamic data base (2) together with $\Delta G_f^\circ(Ru(OH)_4,aq)$ given above. These calculations were done by W. L. Bourcier at LLNL using EQ3NR/soluplot (86).

Figure 1 shows the Ru-H_2O system at various concentrations of ruthenium of 10^{-3}, 10^{-6}, and 10^{-9} mol kg^{-1}. This illustrates predominance regions for the various aqueous forms of Ru only; solid phases were not allowed to form. It should be noted that within a stability field significant amounts of other aqueous forms can be present; e.g., within the $RuO_4^{2-}(aq)$ field, $RuO_4^-(aq)$ and $Ru(OH)_4(aq)$ can also occur.

The main feature to notice is that $Ru_4(OH)_{12}^{4+}(aq)$ has a large stability field at higher concentrations, but it gradually disappears by depolymerization as the total concentration decreases, and stability fields for $Ru(OH)_2^{2+}(aq)$ and $Ru(OH)_4(aq)$ "grow" to replace it. It should be recalled that various aqueous forms of Ru(IV) take months or longer to reach equilibrium. If an aqueous solution initially contained only one Ru(IV) species, then modeling for "short times" would involve only that species.

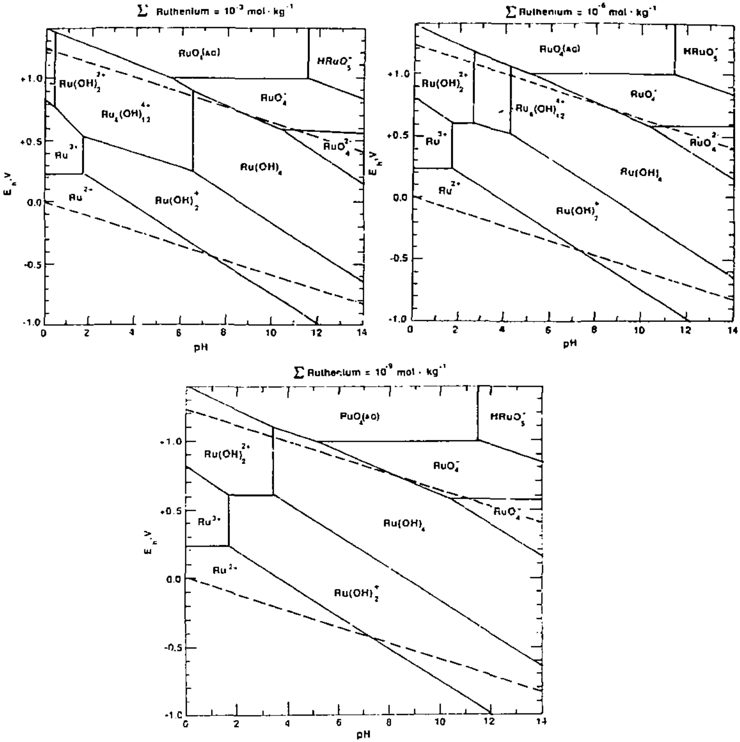


FIGURE 1. Pourbaix diagrams for 10^{-3}, 10^{-6}, and 10^{-9} mol kg^{-1} ruthenium, no solid phases allowed to form. Dashed lines indicate the water stability limits.

Figure 2 shows the 10^{-6} mol kg^{-1} calculations repeated with solid phases that precipitate. Two conditions are illustrated: 1) all possible solid phases were allowed to form, and 2) all but RuO_2(cr) were allowed to form. It was noted above that RuO_2(cr) is the only truely stable solid oxide, but $RuO_2 \cdot 2H_2O$, $Ru(OH)_3 \cdot H_2O$, Ru_2O_5, and RuO_4 form instead under normal laboratory and field conditions. Thus, "without RuO_2(cr)" corresponds to most experiments. However, if RuO_2(cr) forms, then it will remain. Isherwood (87) noted that RuO_2(cr) should be the solubility controlling phase for Ru produced in an underground nuclear explosion. Similar calculations at 10^{-3} and 10^{-9} mol kg^{-1} with RuO_2(cr) predict formation of solid phases virtually the same as the 10^{-6} mol kg^{-1} case, as does 10^{-3} mol kg^{-1} "without RuO_2(cr)". However, for 10^{-9} mol kg^{-1} ruthenium "without RuO_2(cr)", only Ru(cr) can form as a solid.

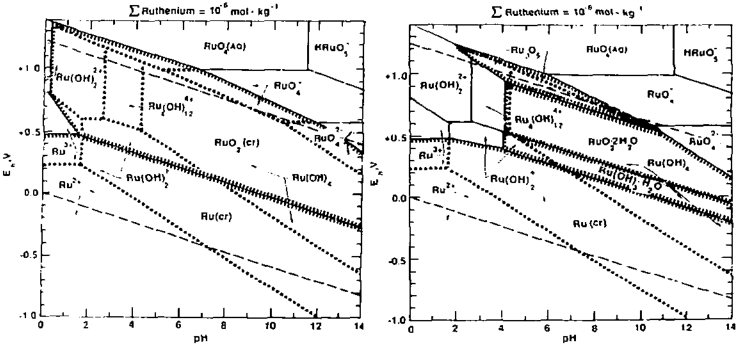


FIGURE 2. Pourbaix diagrams for 10^{-6} mol kg^{-1} ruthenium with and without RuO_2(cr). Dashed lines indicate the water stability limits. The hatched lines indicate solid-solid and solid-solution boundaries. For "with RuO_2(cr)" the only solid phases are RuO_2(cr) and Ru(cr); for "without RuO_2(cr)" the solid phases are Ru_2O_5(s), $RuO_2 \cdot 2H_2O$(s), $Ru(OH)_3 \cdot H_2O$(s), and Ru(cr).

Figure 3 shows the total ruthenium solubility corresponding to O_2 saturated H_2O (2.5 x 10^{-4} mol kg^{-1} O_2, O_2 fugacity = 0.2 atm) with and without RuO_2(cr). Solubility calculations with RuO_2(cr) predict much lower solubilities than without it. Knowing the chemical form of the solid phase initially present would allow a choice as to which of these solubility curves is appropriate for a particular application. Under reducing conditions corresponding to the hematite/magnetite buffer, Ru(cr) becomes the solid phase and solubilities are predicted to be $< 10^{-22}$ mol kg^{-1} which is negligible.

Varshal et al. (22) found that the solubility of Ru(IV) increased with pH for pH > 7, and attributed this to formation of $Ru(OH)_5^-$(aq). Figure 3 indicates that partial oxidation of $Ru(OH)_4$(aq) to RuO_4^-(aq) and RuO_4^{2-}(aq) probably caused their solubility increase rather than $Ru(OH)_5^-$(aq) since they did not exclude air. In fact, our predicted solubilities for O_2 saturated H_2O "without RuO_2(cr)" in Figure 3 agree quite well with the average of Varshal et al's (22) solubilities "from above" and "from below" for aged solutions in the pH range 4-10. In addition, the solubility increase beginning at pH ≈4 is close to the experimental pH value (22).

Our predicted solubilities for pH < 4 are based mainly on data for $Ru_4(OH)_{12}^{4+}$(aq). Experimental solubilities for monomeric species at pH < 4 differ from each other by 2-3 orders of magnitude (14,22) and are all lower than for the tetramer, and may reflect non-equilibrium speciation differences in the aqueous phase and real differences in the solid "hydrated RuO_2". The lower solubilities are for well aged solutions; this would be expected <u>if</u> partial dehydration of $RuO_2 \cdot 2H_2O$(s) is occurring at low pH values. Much higher

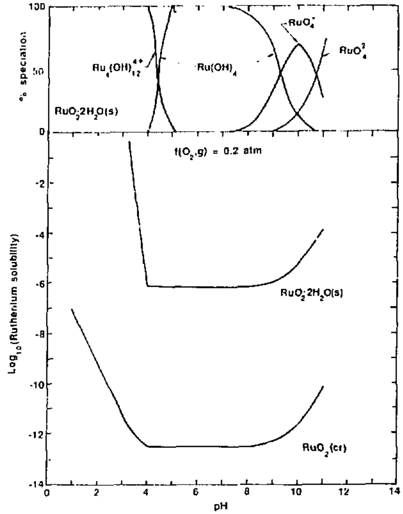


FIGURE 3. Predicted solubilities and speciation for ruthenium in air saturated water without $RuO_2(cr)$ and solubilities with $RuO_2(cr)$.

concentrations can be obtained for freshly prepared solutions: 10^{-2} mol dm^{-3} Ru(IV) in 1 mol dm^{-3} (84) or 3-4 mol dm^{-3} $HClO_4$(79), and 0.3 mol dm^{-3} Ru(IV) in 9 mol dm^{-3} $HClO_4$(40). It is possible that the OH^--to-Ru(IV) ratio may become <2 at these high acidities.

The solubility curve for "with $RuO_2(cr)$" is six orders of magnitude lower than for "without $RuO_2(cr)$". There are no directly measured solubilities for $RuO_2(cr)$ so they were estimated from ΔG_f° values; these estimated solubilities are uncertain by several orders of magnitude. Very low solubilities for $RuO_2(cr)$ are concordant with its use as dimensionally stable electrodes in the chlor-alkali process (2).

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