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Chemistry and Thermodynamics of Ruthenium and Some of Its Inorganic Compounds and Aqueous Species

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I. Introduction

In 1826, Gottfreid Wilhelm Osann reported the isolation of three elements from a platinum extract from the Ural Mountains of Russia, and he named one of these ruthenium. His claim for discovery is not generally accepted owing to the impure nature of his material. In 1844, Carl Carlovich Claus (sometimes spelled with K's) repeated these experiments and prepared several grams of a fairly pure metallic form of element 44. He named this element ruthenium (Ru) after the Latin name for Russia, Ruthenia. He thereby honored his native country and also Osann's pioneering work. Actually, in 1804, Fourcroy and Vauquelin prepared what was probably a ruthenium blue. They mistakenly attributed the color to an osmium compound since Ru had not yet been discovered. See Griffith's book[1] and Mellor's treatise[2] for more details.

Ruthenium is a rather rare element, comprising about $10^{-8}\%$ of the earth's crust.[1] However, it is present in much greater amounts in chondrite and, especially, iron meteorites ($(1–6) \times 10^{-4}\%$).[3]

Ruthenium is usually found in association with other platinum group metals, usually as intermetallic solid solutions that may also contain Au, Ag, Fe, Cu, Ni, and Co. Platinum-rich ores are generally low in Ru owing to crystal structure differences. Most Ru is obtained from osmiridium that can contain up to several percent Ru or from the more common platinum ores that contain a smaller fraction of Ru. Ruthenium–systerkite and ruthenium–neujanskite contain even higher percentages of Ru. Only in the rare mineral laurite $(Ru,Os)S_2$ is Ru the dominant metal.[1-3] Platinum group metals also are occasionally found as Bi, Sn, As, or Te compounds.[3]

Ruthenium and osmium are generally extracted together by oxidizing them to the volatile tetraoxides. Extraction of Ru from its ores is described by Amundsen and Stern.[4] The separation of Ru from other elements and the analytical determination of its concentration have been reviewed in detail.[3,5,6]

Natural Ru is a mixture of stable isotopes with mass numbers of 96, 98, 99, 100, 101, 102, and 104. Their abundances range from 1.9% for ^{98}Ru to 31.6% for ^{102}Ru. Known radioisotopes have mass numbers 92, 93, 94, 95, 97, 103, 105, 106, 107, and 108. Their half-lives are relatively short, ranging from 50 s for ^{93}Ru to 1 year for ^{106}Ru.

Elemental Ru has a $4d^75s^1$ electronic structure. Consequently, it can form compounds with valences up +8. Ru^{2-} can occur in some solid compounds with electron-donating ligands.[7] Ruthenium forms dinuclear, trinuclear, and tetranuclear inorganic cluster compounds, resulting in mixed-valence polymers with average formal valences of 4.25, 3.75, 10/3, 11/3, 8/3, etc. Carbonyl compound clusters with three to six Ru atoms have recently been reviewed.[8] Clearly Ru, like most of the second-row transition metals, has very complicated chemistry both in the solid state and in aqueous solution. Owing to these complexities, much of its chemistry and thermodynamics are still poorly understood. Ru chemistry resembles that of Os in many, but not all, respects.

Most Ru compounds and complexes contain regular or distorted six-coordinated octahedra or, to a lesser extent, four-coordinated tetrahedra (e.g., RuO_4). Some five- or seven-coordinated compounds are known, but they are relatively uncommon.[7,9]

Ru has a number of commercial applications and other uses. The most important is a coating of RuO_2 on Ti to form dimensionally stable electrodes used in the chlor–alkali process. Under proper conditions, electrolysis with these electrodes can be nearly 100% current efficient, and overpotentials are lower than for previously used anode materials. RuO_2-coated electrodes have been reviewed in detail.[10,11]

Ru is also used as a hardener for some Pt and Pd alloys used in electrical circuits, and RuO_2 is a major constituent of resistive glaze/thick film resistors in electrical circuits.[4,11] A 5% alloy of Ru in Pt is commonly used in jewelry in USA. Ru is also used in various forms as a catalyst, but to a lesser extent than most other platinum group metals. Chemisorbed Ru^{3+} on *n*-GaAs considerably enhances its solar energy to electrical energy conversion efficiency.[12]

Large amounts of short-lived ruthenium isotopes are produced in nuclear reactors during the fission of ^{235}U and ^{239}Pu.[13] According to Fleishman et al.,[14] thermal neutron fission of ^{235}U yields 11% stable and 4.3% radioactive Ru isotopes. The formation of intermetallic compounds of Ru and other platinum group metals with U and Pu is so favorable that reduction of U and Pu oxide and carbide fuels occurs in reactors by reaction with fission products.[15]

Ru is also produced by nuclear explosions. Most of the resulting Ru from underground testing is absorbed onto bedrock, but a small percentage of ^{106}Ru was found to migrate as fast as tritium.[16] The underlying chemistry that explains this phenomenon is not understood.

Several reviews are available regarding various aspects of Ru chemistry. References have already been given for analytical chemistry and separation methods.[3-6] Several good reviews are also available for the chemical properties of ruthenium. Mellor's treatise[2] gives an excellent guide to the early literature, but many early claims have proven to be in error. Griffith's book[1] is probably the best on the subject, but it is somewhat dated. Gulliver and Levason's[9] review is up to date but is limited to chemistry of the upper valence states. Ru halides and oxyhalides have also been reviewed.[17]

A good thermodynamic review has appeared,[18] but it is restricted mainly to solid compounds, and much new data have been published since then. Llopis and Tordesillas[19] have reviewed aqueous electrochemistry and corrosion behavior of the metal.

The present review provides an up-to-date critical review (1910 through mid 1984) of the inorganic chemistry of some Ru compounds and aqueous species, with special emphasis on thermodynamic properties. Much of these data have not been reviewed previously. Systems considered here are Ru metal, hydrides, phase diagrams, intermetallic compounds, chalcogenides, oxides, hydroxides, halides, oxyhalides (except for fluorides), complex sulfates, sulfites, nitrates, nitrites, aquo ions, aqueous oxyanions and hydrolyzed species, and aqueous halide and sulfate complexes. The chemistry of halides, oxyhalides, oxides, hydrous oxides, hydroxides, and aqueous solutions are described in considerable detail. This is because of their great complexity and because of the large number of unsubstantiated and contradictory claims about them in the published literature.

Auxiliary thermodynamic data were taken from the 1977 CODATA values when available there. Data not available from CODATA were taken from other sources as noted in the text. The most commonly required quantities are $\Delta G^\circ_{298,f}(H_2O(l)) = -237.19$, $\Delta H^\circ_{298,f}(H_2O(l)) = -285.83$, $\Delta G^\circ_{298,f}(OH^-(aq)) = -157.33$, and $\Delta H^\circ_{298,f}(OH^-(aq)) = -230.03$ kJ mol^{-1}. Thermodynamic data were converted to current values of molecular weights and fundamental constants in those rare cases when the accuracy warranted it. All potentials reported are reduction potentials relative to the normal hydrogen electrode; conversions of data relative to the saturated calomel electrode were made by assuming a difference of 0.242 V. In most cases the recommended thermodynamic values are reported to one or two more figures than the accuracy of the data warrant. This is to avoid round off error in calculations because some values are very accurately known *relative* to other species (e.g., $RuO_4(aq)$, $RuO_4^-(aq)$, and $RuO_4^{2-}(aq)$). Also, 298 K is used to denote 298.15 K in this report.

II. Metallic Ru, Phase Diagrams, and Intermetallic Compounds

A. Ru(g,l,c)

Ru, like most platinum group metals, is fairly resistant to chemical attack. At moderate temperatures Ru is unaffected by aqua regia, H_2SO_4, HCl, HF, or H_3PO_4 solutions. Aqueous Cl_2 and Br_2 solutions attack Ru slowly, whereas aqueous cyanides and $HgCl_2$ corrode Ru more rapidly. Fusion with oxidizing alkali (e.g., KOH–KNO_3, NaOH–Na_2O_2) oxidizes Ru rapidly and completely. Cl_2 and Br_2 oxidize Ru at high temperatures, as does O_2 above 700 K.[2,4]

Most Ru compounds decompose to metallic Ru when heated sufficiently or when reduced with H_2. A common method of preparing the metal is to heat $(NH_4)_2RuCl_6$ in alcohol to form an oxychloride, which is then reduced by H_2 under pressure.[4] H_2 reduction of ruthenocene vapor (bis(cyclopentadienyl)ruthenium) at 868 K gave a very pure Ru film.[20] Ru is nearly insoluble in Hg ($<10^{-5}$ wt % at 773 K[21]).

Ru metal has a Mg-type hexagonal close-packed (hcp) structure. In 1931, Jaeger and Rosenbohm[22] did drop calorimetry measurements for Ru up to 1877 K relative to 298 K. Their data showed several large breaks that seemed to indicate structural changes with large enthalpies of transformation. The implied structural changes were $\alpha \rightarrow \beta$ at 1308 K, $\beta \rightarrow \gamma$ at 1473 K, and $\gamma \rightarrow \delta$ at 1770 K. The γ form had a specific heat that was consistent with the α form, but the β and δ forms had much different behavior. Mellor[2] gives a phase diagram based on these measurements.

Most handbooks and standard reference texts still mention these structural allotropes and present thermodynamic data based on them. They are still occasionally invoked to explain experimental observations such as an endotherm found in the thermal decomposition of RuO_2.[23] However, there is a significant body of evidence indicating that these discontinuities[22] are probably experimental artifacts and are not due to bona fide structural polymorphs of Ru.

Jaeger and Rosenbohm[24] later measured the thermoelectric effect for a Ru–Pt thermocouple junction and again found evidence for structural transformations; in contrast negative results were obtained by Rudnitskii and Polyakova[25] up to 1470 K. Also, McCaldin and Duwez[26] detected no transformation enthalpies in their thermal analysis study to over 1870 K. Moreover, the spectral emissivity of Ru between 1200 and 2470 K showed no abrupt changes.[27]

Even more important evidence for the absence of allotropes comes from crystal structure measurements between 291 and 2453 K.[25,28-33] These combined results show only a regular lattice expansion with increasing temperature; thus Ru does not undergo any allotropic transformations in this temperature range.

Lattice parameters for hcp Ru at room temperature are mostly in good agreement,[25,29,30,32,33] but Owen and Roberts[28] reported slightly smaller values and a higher c/a ratio. Best values at 298 K of $a = 2.704 \pm 0.003$ Å and $c = 4.281 \pm 0.003$ Å were obtained by averaging results from the other five studies.[25,29,30,32,33] The linear expansion coefficients vary slightly with temperature;[28] best values are $\alpha_a = 7.0 \times 10^{-6}$ and $\alpha_c = 11.1 \times 10^{-6}$ K^{-1} for 298–1773 K.[31]

Published melting points for Ru are 2523 ± 10,[27] 2523,[31] 2593 ± 30,[33] 2583 ± 20,[34] 2523,[35] 2500,[36] 2607 ± 1,[37] 2527,[38] and 2553 K.[39] Hultgren et al.[40] cited two other values of 2523 and 2723 K. The recommended value is the average of all but the last: 2546 ± 36 K.

Estimated boiling points for Ru metal are 4000,[41] 4350 ± 100,[42] 4350 ± 100,[43] and 4150 ± 100 K.[44] The last three values are based on vapor pressure measurements. While these estimated values are in reasonable agreement with each other, they are based on long (1600–1800 K) extrapolations of sublimation pressure (not vaporization pressure) data. A boiling point of around 4400 K is more consistent with vapor pressure data.[40] Enthalpies of sublimation are in good agreement.[42-45]

Heat capacity measurements have been reported for Ru(c) by several different groups of workers for temperatures of 1.2–20,[46] 11.4–272.5,[47] 0.27–1.2,[48] 1.5–4,[49] and 2–11.5 K.[50] Hultgren et al.[40] gave 0.48 ± 0.01 K as the superconducting transition temperature from five independent determinations. Relative enthalpies are also available up to 1173 and 1877 K.[22,51] A heat capacity of 51.9 J K^{-1} mol^{-1} was reported for molten Ru from relative enthalpy measurements.[52]

Clusius and Piesbergen's heat capacities[47] are the only set between low temperatures and room temperature. Reese and Johnson's measurements[50] connect up very smoothly with Clusius and Piesbergen's and are confirmed at the lower temperatures by Ho and Viswanathan.[49] Wolcott's[46] results are in reasonable agreement with these other studies up to about 12 K but shows significant deviations at 20 K; Batt's results[48] are slightly low.

Furukawa et al.'s critical review[53] from 0 to 300 K agrees with these three data sets[47,49,50] and is accepted here. Their results at 298 K are heat capacity C_p = 24.06 J K^{-1} mol^{-1}, entropy S^0 = 28.61 J K^{-1} mol^{-1}, relative enthalpy $H°_{298} - H°_0$ = 4601 J mol^{-1}, and relative free energy $G°_{298} - H°_0$ = −3930 J mol^{-1}.

Furukawa et al.[53] gave best values of the Debye temperature Θ_D = 530 ± 30 K at 0 K and electronic heat capacity coefficient γ = 2.95 ± 0.15 mJ mol^{-1} K^{-2}. Acoustical measurements[54] yield a Debye temperature of Θ_D = 554 K at 4 K, which agrees with the heat capacity value. These authors also studied elastic moduli from 4 to 923 K.[54]

Relative enthalpy measurements[22,51] at high temperatures are not in very good agreement with each other. Jaeger and Rosenbohm's values[22] seem to be more nearly consistent with the heat capacity data, but our confidence in them is reduced by the presence of the claimed but probably nonexistent phase transitions. Hultgren et al.'s[40] estimated data above 300 K are accepted provisionally until higher quality experimental values become available. Hultgren et al.'s[40] relative enthalpies of Ru(c) are accurately represented (in kJ mol^{-1}) by

$$H°_T - H°_0 = -2.218 + 0.02197T + 3.03 \times 10^{-6}T^2 \quad (1)$$

for 200 < T < 1400 K.

Mass spectroscopic analysis of Ru vapor indicates only monatomic Ru(g).[42-45] Ideal gas thermodynamic data for Ru(g) were calculated by Hilsenrath et al.[55] up to 10 000 K. Results at 298 K are C_p = 29.84 J K^{-1} mol^{-1}, $S°_{298} - S°_0$ = 186.4 J K^{-1} mol^{-1}, $H°_{298} - H°_0$ = 6.234 kJ mol^{-1}, and $G°_{298} - H°_0$ = −49.34 kJ mol^{-1}. These properties except C_p are all relative to the vapor at 0 K. High-temperature vapor pressure data also exist and can be related to the standard state of Ru(c) at 298 K.

High-temperature vapor pressures of Ru(c) were measured by Knudsen effusion, Langmuir vaporization, and mass spectrometry[42-45,56] between about 1900 and 2600 K. Third-law extrapolation of high-temperature free energy data (including vapor pressures) is usually considered to be more accurate than a second-law extrapolation and will be used here.

For the sublimation of a pure metal, the third-law method yields

$$\Delta H°_{298,\mathrm{subl}} = T(\textstyle\sum/T) - RT \ln P \quad (2)$$

where R is the gas constant 8.3144 J K^{-1} mol^{-1} and P is the vapor pressure. The value of $\sum$ is given in this case by

$$\sum = (G°_T - H°_{298})_c - (G°_T - H°_{298})_g \quad (3)$$

The first three sets of data were reextrapolated by using our recommended high-temperature data and yield $\Delta H°_{298,\mathrm{subl}}$ values of 649.8 ± 6.7,[42] 634.7 ± 2.1,[43] and 653.1 ± 4.6 kJ mol^{-1}.[44] Krikorian et al.[56] did not report the actual pressure data but gave a third-law value relative to Mo of 668.2 ± 6.3 kJ mol^{-1}. Norman et al.[45] only reported $\Delta H°_{T,\mathrm{subl}}$; extrapolation to 298.15 K yields 642 ± 13 kJ mol^{-1}. The average of 649.6 ± 13 kJ mol^{-1} is accepted. The enthalpy of sublimation at 0 K, 648.0 ± 15 kJ mol^{-1}, was obtained from

$$\Delta H°_{298,\mathrm{subl}} = (H°_{298} - H°_0)_g - (H°_{298} - H°_0)_c + \Delta H°_{0,\mathrm{subl}} \quad (4)$$

Once $\Delta H°_{298,\mathrm{subl}}$ is known, eq 2 can be evaluated at 298 K to yield $RT \ln P$ at this temperature. For sublimation to the hypothetical ideal gas at 298 K, $\Delta G°_{298,\mathrm{subl}}$ = 602.5 ± 16 kJ mol^{-1} and $\Delta S°_{298,\mathrm{subl}}$ = 157.8 ± 5.4 J K^{-1} mol^{-1}. The vapor pressure of Ru(c) at 298 K is thus $\simeq 10^{-106}$ atm.

Kats et al.[57] reported relative enthalpy data for liquid Ru between 2613 and 2757 K that was represented by

$$H°_T - H°_{298} = 17.07 + 0.0514T \quad (5)$$

in kJ mol^{-1}. Enthalpy measurements with drop calorimetry give an enthalpy of fusion of $\Delta H°_{\mathrm{fus}}$ = 38.8 ± 1.8 kJ mol^{-1} and an entropy of fusion $\Delta S°_{\mathrm{fus}}$ = 15.2 ± 0.7 J K^{-1} mol^{-1}.[52]

A rough check on the enthalpy of fusion can be made from phase diagram data. Most phase diagrams are reported as small scale graphs or contain few points in the Ru-rich region, so only estimates can be made. Data for Ru–U yield ≃36 kJ mol^{-1},[58] Ru–Sc ≃23 kJ mol^{-1},[59] and Ru–Ti yield ≃49 kJ mol^{-1}.[60] They are at least in qualitative agreement with the direct determination.[52]

The surface tension of Ru at its melting point was measured by using static pendant-drop and dynamic drop weight methods.[61] Its value is 2.34 ± 0.03 J m^{-2}.

Table I summarizes these data for Ru.

B. Ru Hydrides

Müller and Schwabe[62] prepared Ru(c) by reduction of the oxide and studied H_2 absorption. They concluded that H_2 is irreversibly adsorbed (chemisorbed). In contrast Gutbier and Schieferdecker[63] studied H_2 adsorption as a function of temperature and concluded that only slight adsorption was involved. They found desorption was complete above 920 K. Galaktionowa[64] likewise concluded that H_2 in Ru is adsorbed (physically adsorbed) rather than dissolved and that desorption increases around 670–720 K owing to the conversion of Ru black into sponge. The enthalpy of chemisorption was reported to be −108.8 ± 8.4 kJ mol^{-1},[65] but we assume that this value refers to physical absorption. Bouten and Miedema[66] developed an empirical model for metal hydride thermodynamics. Their predicted enthalpy of formation was positive for Ru hydrides, which also indicates that they are unstable. Fisher[67]

TABLE I. Recommended Data for Elemental Ru

property	value	temp, K
unit-cell *a* dimen	2.704 ± 0.003 Å	298.15
unit-cell *c* dimen	4.281 ± 0.003 Å	298.15
thermal expansion *a* axis	7.0×10^{-6} K^{-1}	298–1773
thermal expansion *c* axis	11.1×10^{-6} K^{-1}	298–1773
mp	2546 ± 36 K	
bp	≃4400 K	
superconducting transition	0.48 ± 0.01 K	
Debye temp	530 ± 30 K	0
electronic heat capacity coeff	2.95 ± 0.15 mJ mol^{-1} K^{-2}	
heat capacity of solid	24.06 J K^{-1} mol^{-1}	298.15
entropy of solid	28.61 J K^{-1} mol^{-1}	298.15
heat capacity of gas	29.84 J K^{-1} mol^{-1}	298.15
entropy of gas	186.4 J K^{-1} mol^{-1}	298.15
heat capacity of liquid	51.4 J K^{-1} mol^{-1}	2613–2757
enthalpy of sublimation	649.6 ± 13 kJ mol^{-1}	298.15
free energy of sublimation	602.5 ± 16 kJ mol^{-1}	298.15
entropy of sublimation	157.8 ± 5.4 J K^{-1} mol^{-1}	298.15
vapor pressure	$\simeq 10^{-106}$ atm	298.15
enthalpy of fusion	38.8 ± 1.8 kJ mol^{-1}	2546
entropy of fusion	15.2 ± 0.7 J K^{-1} mol^{-1}	2546
liquid surface tension	2.34 ± 0.03 J m^{-2}	2546

studied the binding energy of H_2 adsorbed on the Ru(110) surface at low temperatures using angle-integrated ultraviolet photoemission and concluded that dissociative absorption occurs on massive Ru.

Whereas Ru and H_2 do not react to form a chemical compound, stoichiometric and nonstoichiometric intermetallic hydrides and deuterides of Ru can be prepared.[68] Carbonyl-containing hydrides[8] are beyond the scope of this review.

C. Phase Diagrams

1. General Comments

This section concerns phase diagrams for Ru with metals and non-metals. There is a very large amount of information on this subject, and it will not be discussed in great detail here since most of these systems have no published thermodynamic data other than phase equilibria results. Phase diagrams are mentioned here since their previous review[69] only covers to 1968. This discussion will be qualitative, and it is intended to be illustrative rather than exhaustive. Interested readers should consult the cited literature and the Gmelin update volume[69] for numerous additional references. Systems of Ru with chalcogenides, oxygen, halides, and oxysulfur and oxynitrogen ions will be treated separately.

The Engel–Brewer theory has been applied by several workers[70,71] to rationalize the unusually high thermodynamic stability of certain classes of alloys of transition metals. This model is based on a valence-bond approach and can be considered to be a generalized Lewis acid–base type of interaction.[70] Wijbenga[71] has compared predicted and experimental enthalpies of formation of platinum group metal compounds with Zr, Nb, Hf, and Ta. In most cases the agreement of theory with experiment is fairly reasonable. Miedema et al.[72] have used an alternate cell model approach that also predicts formation enthalpies reasonably well.

It should be noted that strong radiation fields can cause radiation damage in alloys that produces shifts in the phase boundaries due to disordering.[73a] At higher temperatures recrystallization can occur, but at lower temperatures these changes can be "frozen in".

The superconductivity of Ru, and its binary and ternary alloys, has recently been reviewed.[73b]

2. Systems with Other Platinum Group Metals

Ru and Os both form hcp (Mg-type) crystals, whereas Pt, Pd, Rh, and Ir crystallize in a face-centered cubic lattice (Cu type).[3] Ru and Os have the same type of structure, so they would be expected to occur together readily in nature as is observed.

Ru forms a continuous series of solid solutions with Os as expected.[35] Ru–Re alloys are also hcp and form a similar series of solid solutions,[33,74a] as does the ternary system Ru–Os–Re.[74a] In contrast, Ru–Rh, Ru–Ir, and Ru–Pt are peritectic-type systems with intermediate phases in some cases and solid solutions.[74b,75] Hellawell and Hume-Rothery[29] have investigated lattice spacings for dilute solutions of Rh and Pd in Ru. Decomposition of RuO_2–IrO_2 mixtures occurs above 1678 K and yields Ru–Ir solid solutions.[76]

3. Systems with Actinides

Inclusions of Mo–Ru–Tc–Rh–Pd solid solutions form when U–Pu oxide fuels are irradiated in a nuclear reactor. Inclusions that are in contact with the mixed-oxide fuel form a Pd–U–Pu–Rh–Ru alloy.[15] When uranium carbide fuels are used instead, some of the resulting phases produced are $U_2(Ru,Rh)C_2$, $(U,Ln)_a(Ru,Rh)_b$, and $(U,Ln)_c(Ru,Rh,Pd)_d$.[71] Here Ln represents lanthanide metals. Clearly phase equilibrium and thermodynamic data for M–Ru and M–Ru–C systems (where M represents an actinide) are essential for understanding the formation of such phases in nuclear reactors.

Phase diagrams for U–Ru mixtures have been determined by several workers including Park[58] and Abou-Zahra and Hammad.[77] Five intermetallic compounds are observed, which form congruently melting, peritectic, and eutectic mixtures. The observed compounds are U_2Ru, URu, U_3Ru_4, U_3Ru_5, and URu_3. Similarly, the Pu–Ru system contains Pu_3Ru, Pu_5Ru_3, PuRu, $PuRu_2$, and possibly other compounds.[78] The U–Ru–C systems contains U_2RuC_2 and URu_3C_x, where x has a maximum value of ≃0.7.[79] Solid compounds in the Th–Ru system are Th_7Ru_3, ThRu, $ThRu_2$, and another compound that probably is Th_3Ru_2.[80,81]

4. Systems with Lanthanides, Scandium, and Yttrium

The M–Ru systems (where M represents a lanthanide, scandium, or yttrium) are fairly complicated, and contain eutectic and peritectic mixtures. Most of these systems have not been studied in detail. Ru_2Sc, RuSc, and $RuSc_3$ were reported[59] for the Sc–Ru system.

Most of the lanthanides (except Ce, Yb, and probably Eu) form M_3Ru and M_5Ru_2 compounds. Their crystal structures are of the Fe_3C and Mn_5C_2 types.[82] The lanthanides (including Ce) form MRu_2 compounds of the $MgCu_2$ Laves phase type.[83,84] Other intermetallic compounds reported include Y_3Ru, YbRu, LuRu, some M_2Ru compounds, and probably Ce_7Ru_3.[82]

5. Systems with Other Transition and Non-Transition Metals

Phase diagram results are available for Ru with the 3d transition elements Ti, V, Cr, Mn, Fe, Co, and Ni.

The Ti–Ru system has a peritectic and a eutectic region and forms one intermetallic compound TiRu.[60] Changes in the Ti–Ru phase regions due to radiation damage have been discussed.[73a] The V–Ru alloy system is a simple eutectic with no intermediate phases.[38] Waterstrat discussed the Cr–Ru system for which published results are in disagreement.[85] The "A15" phase, which is generally considered to be Cr_3Ru, was found by him to be nonstoichiometric with a homogeneity range of $\simeq$30–33 at. % Ru. The Fe–Ru phase diagram is dominated by a large Fe solubility in Ru.[86a,b] Ru–Mn, Ru–Co, and Ru–Ni systems have complicated phase diagrams without any intermetallic compounds.[69]

Phase diagrams are available for Ru with the 4d transition elements Zr, Nb, Mo, and Ag. The Nb-Ru phase diagram has a minimum and a maximum melting point and also a eutectic. A compound, probably $NbRu_3$, forms peritectically.[32] Mo–Ru is a eutectic system, and Mo_5Ru_3 forms peritectically.[87,88] Mo_5Ru_3 forms an exceptionally hard film for a metallic conductor.[88] The Ag–Ru system has a simple eutectic at low Ag content.[89] It was not studied at higher Ru contents owing to the large difference between the melting points of Ag and Ru (Ag boils below the Ru melting point). ZrRu and $ZrRu_2$ form in the Zr–Ru system.[69,70] Lattice spacings for dilute solutions of Nb and Mo in Ru have also been reported.[29]

For the 5d transition elements, phase diagrams have been reported for ruthenium with Ta, W, and Au. The Ta–Ru system has a eutectic region and a rather complicated tetragonal to orthorhombic martensitic transformation near the equiatomic mixture.[90] W_3Ru_2 forms peritectically in the W–Ru system.[39] It is another example of an extremely hard electrical conductor.[88] Ru is only slightly soluble in Au (<1 wt %), and their liquids are probably immiscible.[89]

Ru is sparingly soluble in liquid Hg,[21] Ga,[91] and In[92] at high temperatures. The Ru–Ga system contains the compound Ga_3Ru.[91] Ru_2Be_3, $RuBe_2$, Ru_3Be_{10}, and $RuBe_{13}$ have been reported in the Ru–Be system, and RuAl, Ru_2Al_3, $RuAl_2$, $RuAl_3$, $RuAl_6$, and $RuAl_{12}$ in the Ru–Al system.[93]

6. Systems with Non-Metals

Chernogorenko et al. reported that Ru_2P, RuP, and RuP_2 form in the Ru–P system.[94] RuP_4 in known in both a low-temperature α-modification (CdP_4-type structure) and a high-temperature β-modification.[95] Ternary phosphides ZrRuP, NbRuP, and TaRuP have also been described.[96] They become superconducting (except possibly the Ta compound) below 3.8–13.3 K. The Ru–B system was reported to contain Ru_2B, RuB, Ru_7B_3, Ru_2B_3, and RuB_2.[93,97] Single-crystal structural data have been reported for Ru_7B_3.[98]

The Ru–Si system has not been completely characterized. Known compounds are Ru_2Si, Ru_3Si_2, RuSi (two structural forms, CsCl and FeSi types), and a fourth compound that is either Ru_2Si_3 or $RuSi_2$.[97,99] Several ternary silicides of the type $LnRu_2Si_2$ (Ln ≡ Gd, Dy, Ho, or Er) have been prepared and partially characterized.[100]

Scullman and Thelin[101a] prepared gaseous RuC by reacting Ru and C in a furnace at 3300 K and recorded its arc spectrum from 4100 to 4800 and 6000 to 8700 Å. These spectra are fairly complicated, and most of the band assignments are not known. Consequently, no attempt was made to derive thermodynamic values for RuC(g) from statistical thermodynamic methods. Dissociation energies have been reported for RuC(g), RuB(g), and RuSi(g).[101b,c] Ru carbonyls are beyond the scope of this review. However, we note that Behrens[102] used estimated vibration frequencies to calculate ideal gas thermodynamic properties for $Ru(CO)_5$.

D. Thermodynamic Data for Intermetallic Compounds

1. $URu_3(c)$ and $URu_3C_x(c)$

Data are available for URu_3(c) over wide temperature ranges. Holleck and Kleykamp[79] reported solid-state emf measurements for URu_3 from 1000 and 1140 K and later reinvestigated this system from 970 to 1120 K.[103] Their later data give a Gibbs energy of formation for this temperature interval of

$$\Delta G^\circ{}_{T,f}(URu_3) = -199.16 + 0.036T \qquad (6)$$

in kJ mol^{-1}. Wijbenga and Cordfunke[104] did similar measurements and obtained

$$\Delta G^\circ{}_{T,f}(URu_3) = -178.54 + 0.016\,29T \qquad (7)$$

for 1090–1180 K. These two sets of Gibbs energy data are in excellent agreement, with a maximum difference of 1.5 kJ mol^{-1} in the overlap region. Thermal data are available to convert these results to standard values at 298.15 K.[105]

Drop calorimetry enthalpy data are available up to 889.7 K, and calorimetric data exist at lower temperatures.[71,105] These data yield $C_{p,298}$ = 101.42 J K^{-1} mol^{-1} and $S^\circ{}_{298}(URu_3)$ = 144.60 J K^{-1} mol^{-1}. A third-law extrapolation of their[104] emf data yields $\Delta H^\circ{}_{298,f}(URu_3)$ = −150.80 ± 0.30 kJ mol^{-1} and $\Delta G^\circ{}_{298,f}(URu_3)$ = −153.45.[71] These data are for the formation reaction (8).

$$3Ru(c) + U(c) = URu_3(c) \qquad (8)$$

A similar calculation with Holleck et al.'s data[103] yields $\Delta H^\circ{}_{298,f}(URu_3)$ = −152.34 ± 2.43 kJ mol^{-1} and $\Delta G^\circ{}_{298,f}(URu_3)$ = −154.98 kJ mol^{-1}. Recommended values are the averages of $\Delta G^\circ{}_{298,f}(URu_3)$ = −154.2 ± 1.3 kJ mol^{-1} and $\Delta H^\circ{}_{298,f}(URu_3)$ = −151.6 ± 1.3 kJ mol^{-1}.

Edwards et al.[106] have reinvestigated URu_3, using Knudsen effusion with mass spectrometer target collection, from 1691 to 2100 K. Only $^{238}U^+$ was detected in the vapor; therefore, decomposition of URu_3 was assumed to produce U(g) and Ru(c). There was an excess of Ru present in the sample, so the effusion results refer to two-phase Ru–URu_3 mixtures. The thermodynamic data in Table I indicates that the Ru(g) vapor pressure should be only 0.6–1.9% of the U(g) value.

Unfortunately, the Gibbs energy and enthalpy of formation of URu_3 from this study[106] are about a factor of 3–4 smaller than results from the two solid-state emf studies (−49 ± 22 vs. −151.6 ± 1.3 kJ mol^{-1} for ΔH). There is no obvious reason for this discrepancy. We decided to accept the emf results since they are in excellent agreement. However, since both emf studies used the same type of cell, systematic errors are a possibility. It should also be noted that the emf results correctly predict that URu_3 forms in reactors whereas the decomposition pressures do not.

Holleck and Kleykamp[79] also reported high-temperature emf data for URu_3C_x from 860 to 1070 K which yield

$$\Delta G°_{T,f}(URu_3C_x) = -222.17 - 0.0293T \quad (9)$$

This equation gives $\Delta G°_{1000,f}(URu_3C_x) = -251.5 \pm 4.2$ kJ mol^{-1}. These data probably refer to the carbon-saturated phase $URu_3C_{0.7}$. No enthalpy or heat capacity data are available. Consequently, no attempt was made to extrapolate these data to lower temperatures.

2. *ThRu$_2$(c), ThRu(c), Th$_3$Ru$_2$(c), and Th$_7$Ru$_3$(c)*

Kleykamp and Murabayashi[107] did solid-state emf measurements for the known Th–Ru intermetallics from about 1020–1180 K. The Gibbs energy data in kJ mol^{-1} were represented by eq 10–13. These data yield

$$\Delta G°_{T,f}(ThRu_2) = -148.99 + 0.0407T \quad (10)$$

$$\Delta G°_{T,f}(ThRu) = -128.03 + 0.0305T \quad (11)$$

$$\Delta G°_{T,f}(Th_3Ru_2) = -281.37 + 0.0513T \quad (12)$$

$$\Delta G°_{T,f}(Th_7Ru_3) = -547.27 + 0.1351T \quad (13)$$

free energies of formation at 1000 K of $\Delta G°_{1000,f}(ThRu_2) = -108.3 \pm 1.5$ kJ mol^{-1}, $\Delta G°_{1000,f}(ThRu) = -97.5 \pm 1.3$ kJ mol^{-1}, $\Delta G°_{1000,f}(Th_3Ru_2) = -230.1 \pm 3.4$ kJ mol^{-1}, and $\Delta G°_{1000,f}(Th_7Ru_3) = -412.2 \pm 5.9$ kJ mol^{-1}. No attempt was made to extrapolate these data to lower temperatures owing to a lack of thermal data.

Holleck[108] studied the high-temperature phase equilibria for Th–Ru–C. He used these results, along with published data for Th–Ru and Th–C, to estimate that -225.9 kJ mol^{-1} $< \Delta G°_{1473,f}(ThRu_3C_{1-x}) < -117.2$ kJ mol^{-1} and -824.2 kJ mol^{-1} $< \Delta G°_{1473,f}(Th_3Ru_4C_5) <$ -464.4 kJ mol^{-1} at 1473 K.

3. *PuRu$_2$(c)*

Campbell et al.[109] used high-temperature solid-state electrolyte emf measurements for

$$Pu(l) + 2Ru(c) = PuRu_2(c) \quad (14)$$

from 935 to 1069 K. Their Gibbs energy data were represented by

$$\Delta G°_{T,f}(PuRu_2) = -112.1 + 0.0289T \quad (15)$$

and yield $\Delta G°_{1000,f}(PuRu_2) = -83.2 \pm 0.8$ kJ mol^{-1}. A reinvestigation by Campbell[110] gave $\Delta G°_{1000,f}(PuRu_2) = -28.4$ kJ mol^{-1} instead. No thermal data are available to extrapolate these results to 298 K.

Peterson[111] has recently performed Knudsen vapor pressure measurements for $PuRu_2$ at high temperatures. Only Pu(g) was present in the vapor in significant amounts.

Peterson[111] reported large differences between his sublimation results and Campbell et al.'s emf studies.[109,110] Part of these differences arises from Campbell et al. reporting data relative to molten Pu,[109,110] whereas Peterson's high-temperature data are relative to Pu vapor.[111] When this is taken into consideration, Campbell's early study and Peterson's results are in fairly good agreement. Each made an approximate third-law extrapolation assuming $(G°_{T,f} - H°_{298,f})/T$ for URu_3(c) is roughly equal to 3 times the value for Nb[111] or that the heat capacity of URu_3 was about equal to that for $PuC_{0.86}$ minus the heat capacity for 0.86C plus 2Ru(c).[110] The two sets of data in good agreement[109,111] yield $\Delta H°_{298,f}(PuRu_2) \simeq -124$ kJ mol^{-1} for formation from the solid elements.

TABLE II. Recommended Thermodynamic Data for Solid Ruthenium Intermetallic Compounds and fcc Ru

compd	$\Delta G°_{T,f}$, kJ mol^{-1}	$\Delta H°_{T,f}$, kJ mol^{-1}	$S°_T$, J K^{-1} mol^{-1}	T, K
URu_3(c)	-154.2 ± 1.3	-151.6 ± 1.3	144.60	298.15
$URu_3C_{0.7}$(c)	-251.5 ± 4.2			1000
ThRu(c)	-97.5 ± 1.3			1000
$ThRu_2$(c)	-108.3 ± 1.5			1000
Th_3Ru_2(c)	-230.1 ± 3.4			1000
Th_7Ru_3(c)	-412.2 ± 5.9			1000
$ThRu_3C_{1-x}$(c)	-172 ± 54			1473
$Th_3Ru_4C_5$(c)	-644 ± 280			1473
$PuRu_2$(c)		$\simeq -124$		298.15
Ru(c,fcc)	0.908			298.15
$ZrRu_2$(c)	-178 ± 11			1770
ZrRu(c)	-180 ± 13			1570

4. *Fe–Ru Alloys*

Stepakoff and Kaufman[112] investigated the thermodynamics of the Fe–Ru system, where no intermetallic compounds form. They measured heat capacities for three hcp alloys from about 61 to 300 K. Knudsen vaporization measurements were made for 11 Fe–Ru alloys at 1600 K.

They used there data to estimate the Gibbs energy of formation of face-centered cubic (fcc) Ru, from the stable state of hcp, from 0 to 1800 K. The difference between hcp and fcc was assumed to be the same as for Fe, with magnetic free energy differences taken into account. Results are $\Delta G°_{298,f}(Ru,fcc) = 908$ J mol^{-1}, based on reaction 16.

$$Ru(c,hcp) = Ru(c,fcc) \quad (16)$$

5. *Mo–Ru–Pd Alloys*

Yamawaki et al.[113] performed high-temperature emf measurements from 1200 to 1300 K for Mo–Ru–Pd alloys at seven compositions (in two tables the compositions were presumably incorrectly described as Mo–Ru–Rh). Owing to a lack of thermal data, these results were not extrapolated to lower temperatures.

6. *Other Alloy Systems with Thermodynamic Data*

Brewer and Wengert[70] used high-temperature phase equilibria for the C–Zr–Ru and Zr–Ru systems to estimate the Gibbs energies of formation of $ZrRu_2$ and ZrRu. They estimated $\Delta G°_{1770,f}(ZrRu_2) = -178 \pm 11$ kJ mol^{-1}, and $\Delta G°_{1570,f}(ZrRu) = -180 \pm 13$ kJ mol^{-1}. Ho and Viswanathan[49] reported heat capacities at very low temperatures for several Mo–Ru alloys. Low-temperature heat capacities are also available for Pd–Ru alloys (0.5 to 10.0 at. % Ru) and several Pd–Ru hydrides.[114a]

Table II contains a summary of thermodynamic data for ruthenium intermetallic compounds.

III. Comments on Second-Law, Third-Law, and Modified Second-Law Extrapolations of High-Temperature Thermodynamic Data

For several systems free energy of formation data were measured at very high temperatures, and we need to reduce these results to a standard temperature of 298.15 K. The usual methods to do this are second- and third-law extrapolations.

A. Second-Law Extrapolation

The second-law method involves integration of the Gibbs–Helmholtz equation

$$\int \mathrm{d}(\Delta G^\circ_{T,\mathrm{rxn}}/T) = -\int (\Delta H^\circ_{T,\mathrm{rxn}}/T^2)\,\mathrm{d}T \quad (17)$$

where the free energies and enthalpies of reaction are given by

$$\Delta G^\circ_{T,\mathrm{rxn}} = \sum \Delta G^\circ_{T,\mathrm{f}}(\text{products}) - \sum \Delta G^\circ_{T,\mathrm{f}}(\text{reactants}) \quad (18)$$

$$\Delta H^\circ_{T,\mathrm{rxn}} = \sum \Delta H^\circ_{T,\mathrm{f}}(\text{products}) - \sum \Delta H^\circ_{T,\mathrm{f}}(\text{reactants}) \quad (19)$$

Phase changes are also considered to be reactions in this formalism. In general, the $\Delta H^\circ_{T,\mathrm{f}}$ are temperature dependent. They can be obtained in some cases by drop calorimetry or estimated when no experimental data are available. Integration of eq 17 yields

$$\frac{\Delta G^\circ_{T,\mathrm{rxn}}}{T} - \frac{\Delta G^\circ_{298,\mathrm{rxn}}}{298.15} = -\int_{298.15}^{T} \frac{\Delta H^\circ_{T,\mathrm{rxn}}}{T^2}\,\mathrm{d}T \quad (20)$$

If $\Delta G^\circ_{T,\mathrm{rxn}}$ is known at elevated temperatures (from emf or decomposition pressure measurements, etc.), $\Delta G^\circ_{298,\mathrm{rxn}}$ can easily be calculated.

When long temperature extrapolations are involved, and the original free energy data available for only a restricted temperature interval, the second-law method can be quite sensitive to extrapolation errors.

B. Third-Law Extrapolation

The third-law method uses free energy functions that vary slowly, and it generally gives more accurate results. The third-law extrapolation equation for a reaction can be written

$$\Delta\left(\frac{\Delta G^\circ_{T,\mathrm{f}} - \Delta H^\circ_{298,\mathrm{f}}}{T}\right)_{\mathrm{rxn}} = \left(\frac{\Delta G^\circ_{T,\mathrm{f}} - \Delta H^\circ_{298,\mathrm{f}}}{T}\right)_{\mathrm{products}} - \left(\frac{\Delta G^\circ_{T,\mathrm{f}} - \Delta H^\circ_{298,\mathrm{f}}}{T}\right)_{\mathrm{reactants}} = \frac{\Delta G^\circ_{T,\mathrm{rxn}}}{T} - \frac{\Delta H^\circ_{298,\mathrm{rxn}}}{T} \quad (21)$$

Here $\Delta G^\circ_{T,\mathrm{rxn}}$ is known from high-temperature free energy measurements and $\Delta H^\circ_{298,\mathrm{f}}$ is being sought. If both high- and low-temperature thermal data are available for reactants and products, then $\Delta G^\circ_{T,\mathrm{f}} - \Delta H^\circ_{298,\mathrm{f}}$ will be known (it can also be calculated for gases by statistical thermodynamic methods) and $\Delta H^\circ_{298,\mathrm{rxn}}$ can be calculated. However, if only high-temperature enthalpy data from drop calorimetry are available and not low-temperature data, then $\Delta G^\circ_{T,\mathrm{f}} - \Delta H^\circ_{298,\mathrm{f}}$ will not be known. The drop calorimetry measurements give $\Delta H^\circ_{T,\mathrm{f}} - \Delta H^\circ_{298,\mathrm{f}}$ and $\Delta S^\circ_{T,\mathrm{f}} - \Delta S^\circ_{298,\mathrm{f}}$, so eq 21 can then be recast in terms of them

$$\frac{\Delta G^\circ_{T,\mathrm{rxn}}}{T} - \frac{\Delta H^\circ_{298,\mathrm{rxn}}}{T} = -\Delta S^\circ_{298,\mathrm{rxn}} - (\Delta S^\circ_{T,\mathrm{rxn}} - \Delta S^\circ_{298,\mathrm{rxn}}) + \left(\frac{\Delta H^\circ_{T,\mathrm{rxn}} - \Delta H^\circ_{298,\mathrm{rxn}}}{T}\right) \quad (22)$$

There are two unknowns in this equation, $\Delta H^\circ_{298,\mathrm{rxn}}$ and $\Delta S^\circ_{298,\mathrm{rxn}}$. $\Delta S^\circ_{298,\mathrm{rxn}}$ is usually treated as an adjustable parameter and the data optimized so that $\Delta H^\circ_{298,\mathrm{rxn}}$ shows the least variation with input $\Delta G^\circ_{T,\mathrm{rxn}}$ at various temperatures.

Unfortunately, owing to a lack of reliable data, the thermal data for Ru(c) above 272.5 K are estimated values. If $\Delta S^\circ_{298,\mathrm{rxn}}$ can be fixed from heat capacity data, as it was for Ru sublimation and URu_3(c), then a third-law extrapolation can still be performed with confidence to obtain $\Delta H^\circ_{298,\mathrm{rxn}}$. However, when low-temperature data are not available, there is a possibility that errors in the optimized $\Delta S^\circ_{298,\mathrm{rxn}}$ will incorporate errors from S°_T(Ru(c)), and this error will depend on the temperatures of the original free energy measurements. Free energy data above 1000 K could conceivably yield errors of several J K^{-1} mol^{-1} for $\Delta S^\circ_{298,\mathrm{f}}$ and 10–20 kJ mol^{-1} for $\Delta H^\circ_{298,\mathrm{f}}$ when used with estimated high-temperature data for Ru(c).

C. Modified Second-Law Extrapolation

In some cases we chose to use a modified extrapolation method that uses some of the second- and third-law extrapolation features, and we shall refer to it as a modified second-law extrapolation. High-temperature free energy of reaction data can be represented by

$$\Delta G^\circ_{T,\mathrm{rxn}} = \Delta H^\circ_{T,\mathrm{rxn}} - T\Delta S^\circ_{T,\mathrm{rxn}} \quad (23)$$

where ΔH and ΔS can either be assumed constant or temperature dependent over the experimental high-temperature interval. Drop calorimetry (relative enthalpy) results for the compound of interest and its elements can be subtracted to yield $\Delta S^\circ_{T,\mathrm{rxn}} - \Delta S^\circ_{298,\mathrm{rxn}}$ and $\Delta H^\circ_{T,\mathrm{rxn}} - \Delta H^\circ_{298,\mathrm{rxn}}$. These can be combined with $\Delta H^\circ_{T,\mathrm{rxn}}$ and $\Delta S^\circ_{T,\mathrm{rxn}}$ from eq 23 to yield

$$\Delta S^\circ_{298,\mathrm{rxn}} = \Delta S^\circ_{T,\mathrm{rxn}} - (\Delta S^\circ_{T,\mathrm{rxn}} - \Delta S^\circ_{298,\mathrm{rxn}}) \quad (24)$$

$$\Delta H^\circ_{298,\mathrm{rxn}} = \Delta H^\circ_{T,\mathrm{rxn}} - (\Delta H^\circ_{T,\mathrm{rxn}} - \Delta H^\circ_{298,\mathrm{rxn}}) \quad (25)$$

Results can then be combined to yield $\Delta G^\circ_{298,\mathrm{rxn}}$.

By doing the extrapolations for ΔH and ΔS directly, this method is less prone to extrapolation errors than second-law calculations for ΔG (which varies more rapidly with temperature). Admittedly, it is slightly more sensitive to the temperature dependences of $\Delta G^\circ_{T,\mathrm{rxn}}$ than a third-law extrapolation, but $\Delta S^\circ_{298,\mathrm{rxn}}$ is no longer a direct fitting parameter although it still is a parameter determined by the thermodynamic data. Also, as noted by Cubicciotti[114b] (who first described the method), it is very useful for graphical analysis of tabulated numerical data. We will use this procedure for RuS_2, $RuSe_2$, $RuTe_2$, and RuO_2 only. This method and second-law methods give almost identical results for RuS_2, $RuSe_2$, and $RuTe_2$; however, for RuO_2 the modified method is superior. When reliable high-temperature enthalpy data become available for Ru(c), we recommend that these data be reextrapolated by the bona fide third-law method. We do not recommend the modified method (nor the standard second-law method) for systems where free energy measurements are over short temperature intervals since $\Delta H^\circ_{T,\mathrm{rxn}}$ and $\Delta S^\circ_{T,\mathrm{rxn}}$ are too uncertain.

IV. Ru Chalcogenides, Arsenides, Antimonides, Oxysulfur Compounds, Halides, Oxyhalides, Nitrates and Nitrites, and Oxides

A. Properties of Chalcogenides, Arsenides, and Antimonides

The mineral laurite (Ru,Os)S_2 has been known at least since 1866. It has the pyrite structure,[2] as does pure RuS_2. Juza and Meyer[115] studied vapor pressures of sulfur over RuS_2–Ru mixtures at elevated temperatures. Except for slight changes near pure RuS_2 and pure Ru, the vapor pressures were independent of composition. This suggests that lower sulfides do not form. Knop noted that the phase "Ru_9S_8" is actually RuS_2 saturated with Ru.[116]

RuS_2 is generally prepared by direct reaction of the elements in the absence of air at elevated temperatures[115,116] or by reaction of $RuCl_6^{2-}$ salts with H_2S.[117]

Various crystal structure determinations for the cubic pyrite structure of RuS_2 are in very good agreement.[116,118-120] Sutarno et al.[119] compared their results to earlier studies of lower precision. The best value of "a" at room temperature is the average of 5.6110 ± 0.0011 Å. Svendsen[120] also reported lattice constants up to 1273 K; they yield a linear expansion coefficient of $\alpha_a = 4.7 \times 10^{-5}$ K^{-1}.

$RuTe_2$ also has the pyrite structure. Sutarno et al.[119] reported $a = 6.3906 \pm 0.0004$ Å at room temperature, Svendsen[121] obtained 6.3907 Å, and Zhao et al.[122] reported 6.3831 ± 0.0014 Å for samples prepared above 1000 K. Zhao et al. obtained higher values for samples prepared at lower temperatures. The recommended value is the average of $a = 6.3881 \pm 0.0044$ Å. Svendsen[121] also measured data up to 1273 K, which yields a linear expansion coefficient of 5.0×10^{-5} K^{-1}. Earlier studies at room temperature yield smaller a values.[123,124]

$RuTe_2$ is generally formed by direct reaction of Ru and Te at elevated temperatures, but reacting $RuCl_3$ with Te in flowing CO_2 also works.[122,125] Its melting point is above 1573 K.[121] Svendsen[121] measured high-temperature vapor pressures of tellurium above two-phase $RuTe_2$–Ru mixtures for compositions ranging from $RuTe_{2.00}$ to $RuTe_{1.96}$. Identical results were obtained for each composition, which indicates the absence of significant Ru–$RuTe_2$ homogeneity. Samples of Ru with <9 mol % Te had the same lattice constant as for Ru, which indicates the solubility of Te in Ru is low.[121]

Recently, Zhao et al.[122] described the preparation of a maracasite-type modification of $RuTe_2$ by reacting Ru or $RuCl_3$ with Te at lower temperatures (670–930 K). It transforms to the pyrite structure above about 890 K. Recommended lattice constants for the maracasite form are $a = 5.2915 \pm 0.0006$ Å, $b = 6.4043 \pm 0.0008$ Å, and $c = 4.0118 \pm 0.0005$ Å.

$RuSe_2$ is similarly prepared by reaction of Ru or $RuCl_3$ with Se at elevated temperatures, and it also has a pyrite structure.[123,125,126] Room-temperature lattice constants of $a = 5.933 \pm 0.002$[125] and 5.935 ± 0.001 Å[126] are in good agreement. Their average of 5.934 ± 0.001 Å is recommended. Murray and Heyding[126] reported that reacting Ru with Se in ratios of 1:1, 2:3, 1:2, and 2:5 at 850–1250 K produced only one intermediate phase $RuSe_2$. The lattice constant of $RuSe_2$ was independent of starting composition and quenching temperature. This indicates that the solubility of Se in Ru is small and that the range of variable composition for $RuSe_2$ is small.[126] Thomassen also was unable to prepare a lower selenide.[123]

RuS_2, $RuSe_2$, and $RuTe_2$ (pyrite form) have been investigated for superconductivity, and none of them exhibit it, at least above 0.32 K.[127] RuS_2 is a photoconducting material, and it has potential for the solar energy decomposition of H_2O to form H_2.[128]

Amorphous or poorly crystalline RuS_2 has been prepared by the "low-temperature" (525 K) reaction of $(NH_4)_2RuCl_6$ with sulfur.[117] Annealing the samples caused crystal growth that was complete by 1070 K. Lattice parameters for samples annealed above 750 K fall below our recommended values.

Foise et al.[129] studied the $Co_{1-x}Ru_xS_2$ and $Rh_{1-x}Ru_xS_2$ systems. Direct reaction of the elements gave single-phase samples for the Co–Ru–S system only when $x \geq 0.7$. Single-phase samples could be obtained for both systems when the mixed ammonium chloride double salts were reacted with H_2S and then annealed. All single-phase samples had the pyrite structure. Cell constants for $Rh_{1-x}Ru_xS_2$ ($0.5 \leq x \leq 1$) were $a = 5.607$ Å, which is equal to the pure RuS_2 value. Knop[116] studied one Ru–Pd–S composition and similarly obtained 5.610 Å.

The adsorption of H_2S on the Ru(110) surface has been investigated.[67] Heating the sample left a stable layer of absorbed S. This study is of interest for the mechanisms of sulfur poisoning of catalysts.

There are occasionally reports of other sulfides of ruthenium. For example, Taimni and Salaria[130] precipitated a sulfide from "ruthenium chloride" in an aqueous ammonium hydroxide–ammonium acetate solution, by addition of excess sodium sulfide. They identified the solid as $Ru_2S_3 \cdot 2H_2O$ solely on the basis of a Ru analysis, which agreed with the percentage ruthenium expected for this compound. Taimni and Tandon[131] later studied its thermal decomposition. Taimni and Rakshpal[132] similarly reported $Ru_2Se_3 \cdot 2H_2O$. Supporting evidence will be required before they can be accepted. There are also claims for RuS_3, RuS_6, and Ru_2S_3, but they may just be mixtures RuS_2 and S or RuS_2 and Ru.[2,3] Rudnev and Malofeeva[133] prepared crystalline $TlRu_2S_6$ (good elemental analysis) and claimed amorphous Ru_2S_3. At least some of these claims for Ru_2S_3 come from workers assuming that sulfide ions react with "hydrated ruthenium trichloride" to produce it. However, "$RuCl_3 \cdot mH_2O$" is usually mainly Ru(IV) oxychlorides (see below), and RuS_2 is a more likely product.

Dehnicke et al.[134] reported the preparation of $RuSCl_4$ by reaction of RuO_4 with SCl_2 in CCl_4. It probably has a ring structure and is very moisture sensitive.

Wöhler and Ewald[135] investigated the Ru–As system and prepared $RuAs_2$ by reaction of Ru or ruthenium chloride with As. Heyding and Calvert[136] prepared both RuAs (MnP-type structure) and $RuAs_2$ (marcasite structure). The unit-cell dimensions at room temperature are $a = 5.70 \pm 0.01$, $b = 3.25 \pm 0.01$, and $c = 6.27 \pm 0.01$ Å for RuAs and $a = 5.41 \pm 0.01$, $b = 6.17 \pm 0.01$, and c = 2.96 ± 0.01 Å for $RuAs_2$. These compounds have been studied very little. Zhuravlev and Kertes[137] reported that no intermetallic compounds form when Bi and Ru are fused together. RuSb has the MnP structure; $RuSb_2$ has a maracasite structure with a = 5.930, b = 6.637, and c = 3.168 Å.[138]

Of the compounds discussed in this section, only RuS_2, $RuSe_2$, and $RuTe_2$ (pyrite form) have published thermodynamic data.

B. Thermodynamic Data for Chalcogenides

1. $RuS_2(c)$

In 1933, Juza and Meyer[115] reported decomposition pressure data for reaction 26 for four temperatures from

$$RuS_2(c) = Ru(c) + S_2(g) \qquad (26)$$

1396 to 1481 K. In principle, these data can be extrapolated to 298.15 K to yield the standard state formation thermodynamics for eq 27, where the standard state for sulfur is the rhombohedral crystal.

$$Ru(c) + 2S(rh) = RuS_2(c) \qquad (27)$$

Decomposition pressure measurements were over a short temperature range (85 K) and a long extrapolation to 298 K was required using estimated heat capacities. Consequently derived thermodynamic properties were not very accurate. For example, Westrum et al.'s[139] and Kelley's[140] calculated values of $\Delta H°_{298,f}$ differ from each other by 25 kJ mol^{-1} and their $S°_{298}$ by 8.8 J K^{-1} mol^{-1}.

Fortunately, Svendsen[120] recently published more extensive thermodynamic data. He measured decomposition pressures from 1073 to 1505 K. The pressures are about 30–40% higher than Juza and Meyer's.[115] Drop calorimetry data were reported up to 1481 K. Also required are thermodynamic data for solid sulfur and sulfur vapor. Svendsen reported such results, based on an analysis of literature data, which were normalized by him to the CODATA 298.15 K results. We extrapolated RuS_2 results by the modified second-law method and obtained $\Delta H°_{298,f}(RuS_2) = -199.5 \pm 1.7$ kJ mol^{-1}, $\Delta G°_{298,f}(RuS_2) = -188.4 \pm 1.7$ kJ mol^{-1}, and $S°_{298}(RuS_2) = 55.2 \pm 1.7$ J K^{-1} mol^{-1}. Svendsen[120] estimated, from his enthalpy measurements, that $C_{p,298}(RuS_2) = 66.53$ J K^{-1} mol^{-1}. It turns out that Kelley's estimates[140] are close to experimental values, and our extrapolation agrees with Svendsen's second-law values.

2. $RuTe_2(c)$

Svendsen[121] has reported similar thermodynamic measurements for $RuTe_2(c)$. Decomposition pressure measurements were reported from 1276 to 1423 K both for $RuTe_2$ and for slightly Te-deficient samples. Svendsen did drop calorimetry up to 1273 K, reanalyzed literature data for $Te_2(g)$, and took data for Te(c) from Stull and Sinke.[41] The decomposition reaction is

$$RuTe_2(c) = Ru(c) + Te_2(g) \qquad (28)$$

and the formation reaction under standard conditions is

$$Ru(c) + 2Te(c) = RuTe_2(c) \qquad (29)$$

A modified second-law analysis of his results yields $\Delta H°_{298,f}(RuTe_2) = -140.0 \pm 0.8$ kJ mol^{-1}, $S°_{298}(RuTe_2) = 89.6 \pm 0.8$ J K^{-1} mol^{-1}, $\Delta G°_{298,f}(RuTe_2) = -128.6 \pm 0.8$ kJ mol^{-1}, and $C_{p,298}(RuTe_2) = 74.06$ J K^{-1} mol^{-1}. These results agree with Svendsen's second-law calculations.

TABLE III. Recommended Thermodynamic Data for Solid Ruthenium Chalcogenides (Pyrite Structure) at 298.15 K

thermodyn property	RuS_2	$RuSe_2$	$RuTe_2$
$\Delta G°_{298,f}$, kJ mol^{-1}	−188.4 ± 1.7	−138.0 ± 0.8	−128.6 ± 0.8
$\Delta H°_{298,f}$, kJ mol^{-1}	−199.5 ± 1.7	−146.4 ± 0.8	−140.0 ± 0.8
$S°_{298}$, J K^{-1} mol^{-1}	55.2 ± 1.7	85.4 ± 0.8	89.6 ± 0.8
$C_{p,298}$, J K^{-1} mol^{-1}	66.53	70.25	74.06
a, Å	5.611 ± 0.001	5.934 ± 0.001	6.388 ± 0.004
α_a, K^{-1}	4.7×10^{-5}		5.0×10^{-5}

Svendsen[121] also reported vapor pressures for Te(1) saturated with $RuTe_2(c)$.

3. $RuSe_2(c)$

Murray and Heyding[126] reported decomposition pressure measurements for eq 30 from 1006 to 1127 K.

$$RuSe_2(c) = Ru(c) + Se_2(g) \qquad (30)$$

No relative enthalpy data are available for $RuSe_2(c)$, so Svendsen's data for $RuS_2(c)$ and $RuTe_2(c)$ were averaged to produce an estimated value.[120,121] Data for Se(c) and $Se_2(g)$ were taken from Stull and Sinke.[41] The standard formation reaction is then

$$Ru(c) + 2Se(c) = RuSe_2(c) \qquad (31)$$

and $\Delta H°_{298,f}(RuSe_2) = -146.4 \pm 0.8$ kJ mol^{-1}, $S°_{298}(RuSe_2) = 85.4 \pm 0.8$ J K^{-1} mol^{-1}, $\Delta G°_{298,f}(RuSe_2) = -138.0 \pm 0.8$ kJ mol^{-1}, and $C_{p,298}(RuSe_2) = 70.25$ J K^{-1} mol^{-1}.

The actual errors for $RuSe_2$ may be larger since the relative enthalpies were estimated. Boerio et al.[141] have measured heat capacities of $RuSe_2$ up to room temperature. These data give $S°_{298}(RuSe_2)$ directly, so it will be possible to do a bona fide third-law extrapolation when they are published.

Table III contains a summary of recommended data for ruthenium chalcogenides.

C. Ru Oxysulfur Compounds

In aqueous solutions there is evidence for simple ruthenium sulfate complexes such as $RuSO_4$, $Ru(SO_4)^+$, $Ru(SO_4)_2^-$, and $Ru(OH)_2(SO_4)$ along with more complicated tetrameric forms with average Ru valences of +3.5, +4.0, etc. These aqueous species will be discussed later. Examination of solid ruthenium sulfates and double sulfates is of interest, both for their own sakes and for the information they provide about possible aqueous species.

There was an early claim by Claus that reddish amorphous $Ru(SO_4)_2$ is produced when "ruthenium chloride" is reacted with H_2S, digested with HNO_3, and then evaporated to dryness.[2] However, when ruthenium compounds are exposed to HNO_3, NO_2, or NO, ruthenium nitrosyl compounds generally form and they are fairly stable with regard to oxidation and reduction. Many of these complexes are orange, red, brown, or purple, and Claus's "$Ru(SO_4)_2$" was probably a complex ruthenium nitrosyl sulfate. In fact, this was suggested by Hepworth and Robinson.[142]

Antony and Lucchesi[143] prepared a red solution of "ruthenium sulfate" by dissolving $BaRuO_4$ in concentrated HCl, evaporating the solution to dryness, and extracting the residue into dilute H_2SO_4. However, either brown $Ru_2OCl_{10}^{4-}$ or red polymeric Ru(IV) could have formed instead, and these species will be described later.

A sulfate complex of RuO_2^{2+} has been suggested for the unstable green intermediate formed by reduction of RuO_4 in aqueous solution.[144] Hepworth and Robinson[142] found that irradiation of RuO_4 in SO_3 with ultraviolet light produces a dark brown solid upon removal of excess SO_3. The empirical composition of this compound is $RuO(SO_4)_2$ as determined by elemental analysis, and the valence of Ru was determined to be +6. This compound evolves SO_3 above about 420 K but is stable at lower temperatures in the absence of moisture. Dissolution of it in H_2O produces the insoluble hydrated dioxide, but in dilute H_2SO_4 a soluble Ru(IV) species forms. These workers thought the original compound was probably the pyrosulfate salt $RuO_2(S_2O_7)$, but no structural data were obtained. Fusion of it in $KHSO_4$ produced a clear green melt that dissolved in H_2O to form a clear green solution, and partial evolution of RuO_4 gas occurred.

References to green and brown aqueous solutions of ruthenium sulfates appear frequently. Brito and Lewis[145] studied the color of various polymeric species as a function of ruthenium valence in great detail. Their study was done in 1 mol L^{-1} SO_4^{2-} solutions (H_2SO_4 or Na_2SO_4). Reduction of RuO_4 with H_2O_2 gave ruby red Ru(IV). Further reduction with Ti^{3+} gave brown Ru(3.5), and even further reduction produced gray-green Ru(III). Oxidation of this Ru(III) gave either amber-brown Ru(3.5) or amber-brown to golden yellow Ru with average valences of $\simeq$3.7–3.8. Further reduction of Ru(3.5) probably produced Ru(3.25). These observations can be rationalized if reduction of RuO_4 produces tetramers of Ru with average valences of +4.0, +3.75, +3.5, and possibly +3.25. The presence of these tetramers is also indicated by numerous other studies, and this will be discussed later. There is also ample evidence that Ru(III) is monomeric, although short-lived polymers of it may be produced by reduction of other polymeric species.

Brito and Lewis' oxidation data[145] are also consistent with tertramers for Ru(3.5). However, the species with average valences of 3.7–3.8 could either be Ru(3.75) tetramers or Ru(3 2/3) trimers.

Aqueous solution and solid-state green and brown sulfato compounds have been studied in more detail by Ginzburg et al.[146–149] They studied the redox behavior of Ru(III) and Ru(IV) chloro compounds in aqueous sulfuric acid solutions. Heating Ru(IV) compounds at 523–573 K formed brown sulfates, whereas green sulfates formed at 423–463 K.[146] Both types of salts contained anionic complexes as indicated by ion exchange. When the Ru(IV) compounds were evaporated at 373–393 K, the product contained Ru(3.5). When Ru(III) compounds in this media were heated at 523–573 K, Ru(3.5) was also produced. The formation of this Ru(3.5) compound was confirmed in a later study.[149] Solid K^+ and Cs^+ salts of this substance were obtained.[147] Their aqueous solutions contain no free sulfate ions, IR absorption indicated bidentate coordination of the sulfates, and the complex ion was predominantly anionic. Addition of excess Ti^{3+} caused H_2O_2 formation, suggesting a –Ru–O–O–Ru (peroxide) or –Ru–O_2–Ru (superoxide) group. Chemical analysis of these salts indicated a polymeric compound with a Ru:sulfate ratio of 2:3 or 3:5 and a Ru:cation (K^+ or Cs^+) ratio of 1:1. The structures and exact chemical natures of these salts are uncertain.

The same authors later prepared two other types of ruthenium complex sulfates.[148] Reduction of RuO_4 in H_2SO_4 produced a soluble brown complex that was isolated as both K^+ and Cs^+ salts with Ru:SO_4^{2-}:M^+ ratios of about 1:1.4:1.1. Fusion of $K_4[Ru_2OCl_{10}]$ in $KHSO_4$ gave a green salt with a Ru:SO_4^{2-}:K^+ ratio of about 1:3.06:2.5. However, varying the fusion conditions and times results in compounds with Ru:SO_4^{2-} ratios of 1:2.5 to 1:2.0.

Ginzburg et al.[148] partially characterized these compounds by thermal decomposition and infrared absorption. They suggested that these compounds were brown $K_4H_6[Ru_4O_6(SO_4)_6]$ with two Ru(IV) and two Ru(III) atoms and green $K_8[Ru_3O(SO_4)_9]$ with all Ru(IV) atoms. Unfortunately, the crystals were not of suitable quality for X-ray structural determination. Similarly, Orlov et al.[150a] prepared a brown Ru(3.5) salt with the empirical formula $K_2H[Ru_2O_2(H_2O)_2(SO_4)_3]$, and its corresponding tri-*n*-dodecylammonium salt. Two units of Orlov et al.'s[150a] brown potassium salt have the same elemental composition as a dihydrate of Ginzburg et al.'s brown salt,[148] so they may be structurally related.

These green and brown sulfate complexes are definitely worth reinvestigating in more detail, and structural determinations could shed considerable light on the nature of polymeric species in aqueous solution. For example, Ginzburg et al.[148] formulated the brown complex as $K_4H_6[Ru_4O_6(SO_4)_6]$, which has a H^+ to (nonsulfate) O^{2-} ratio of 1:1. Conceivably it is actually a hydroxy compound, which would correlate with some claims for Ru(IV) and Ru(3.5) hydroxy tetramers in aqueous solutions. However, IR spectra provide no clear-cut evidence, in part because the –OH bending mode overlaps with the –SO bands. There is also no obvious –OH stretching line in the 3500–3700 cm^{-1} range.

Similarly, better identification of the green trimers might indicate whether Brito and Lewis'[145] solution data for Ru(3.7–3.8) in H_2SO_4 are for trimeric or tetrameric Ru species.

Only recently have monomeric double salts containing $Ru(H_2O)_6^{2+}$ and $Ru(H_2O)_6^{3+}$ octahedra been prepared.[150b] Slow cooling of alkali sulfate solutions containing *p*-toluenesulfonate yielded $K_2Ru(SO_4)_2{\cdot}6H_2O$, $Rb_2Ru(SO_4)_2{\cdot}6H_2O$, and $CsRu(SO_4)_2{\cdot}12H_2O$.

There are several claims in the older literature for lower valence ruthenium sulfites and double sulfites.[1,151,152] Aqueous solutions of "$RuCl_3$" or Ru(IV) were reacted with SO_2, sulfite salts, or bisulfite salts. The claimed reaction products include blue (probably hydrated) $Ru_2(SO_3)_3$, dark violet $K_2SO_3{\cdot}2Ru(OH)SO_3{\cdot}3H_2O$, a dark gray compound, possibly $K_2SO_3{\cdot}3RuSO_3{\cdot}6H_2O$, green-blue $7Na_2SO_3{\cdot}2RuSO_3{\cdot}mH_2O$, dark green $K_4[Ru(SO_4)_3]{\cdot}mH_2O$, yellowish white $Ru_2(SO_3)_3{\cdot}8Na_2SO_3{\cdot}3H_2O$, and dark blue amorphous $2RuSO_3{\cdot}Ru_2(SO_4)_3{\cdot}4Na_2SO_3$. Extraction of the Ru(II) double sulfites gave $RuSO_3$.

These sulfite salts were generally only characterized in terms of elemental analyses, and the structures of all of them are unknown. It may turn out that some of the reported double sulfites are actually mixtures without any definite stoichiometry. The evidence for the salts $RuSO_3$ and $Ru_2(SO_3)_3$ is sufficiently strong that an attempt should be made to prepare them and determine their crystal structures.

A number of sulfur dioxide complexes are also known. The first, $[RuCl(NH_3)_4(SO_2)]Cl$, was reported by Gleu et al. in 1938.[153] A number of them have since been described, and none contain a simple ruthenium ion. Many are ammonium compounds such as $[Ru(NH_3)_5(SO_2)]X_2$ where $X^- = Cl^-, Br^-$, or I^- or $[Ru(NH_3)_4(H_2O)(SO_2)]X_2$ where $X^- = NO_3^-, BF_4^-$, or $^1/_2S_2O_6^{2-}$. The remainder are mainly carbonyls such as $Ru(CO)_2(PPh_3)_2(SO_2)$ or triphenylphosphines $RuCl_2(PPh_3)_2(SO_2)$, where Ph represents the phenyl group. A triphenylstibine complex $[RuCl_2(SbPh_3)_2(SO_2)]_2$ is also known. Two recent detailed reviews are available;[154,155] they list known complexes, methods of preparation, reactions, crystal structure data, and spectroscopic properties.

There are no published thermodynamic data for the ruthenium oxysulfur compounds discussed in this section.

D. Anhydrous Binary Halides, Oxyhalides, and "Hydrated Ruthenium Trichloride"

There are several claims in the early literature that direct chlorination of Ru under various conditions can produce solid $RuCl_2$, Ru_2Cl_5, and $RuCl_3$.[2] Of these, only $RuCl_3$ has been definitely established. Chlorination of Ru is seldom complete: Wöhler and Balz[156] obtained samples containing 38.5–49.6% Cl, whereas Hyde et al.[157] obtained 46.0–50.8%. Pure $RuCl_3$ has 51.3% Cl. Carbon monoxide gas is generally added to the Cl_2 to enhance the reaction.[2,157-160] Low-temperature chlorination with added CO (423–483 K) initially produces yellow volatile $Ru(CO)_2Cl_2$, which decomposes at higher temperatures to form $RuCl_3$. $Ru(CO)_2Cl_2$ can also be produced by bubbling CO through an alcoholic "$RuCl_3 \cdot mH_2O$" solution.[161]

Joly[2] and Howe et al.[158] prepared incompletely chlorinated samples with Cl:Ru ratios of about 2:1. This dark brown "$RuCl_2$" was insoluble in H_2O but dissolved in aqueous alcohol to form solutions that were usually initially "claret" but gradually became azure blue. Since blue Ru(II) chloride solutions were well-known, Howe et al.[158] concluded that they had prepared the solid anhydrous ruthenium blue $RuCl_2$. Krauss and Kükenthal[160] did similar experiments and obtained batches corresponding to "$RuCl_2$" and "Ru_2Cl_5". They considered these samples to be complex mixtures.

Wöhler and Balz[156] measured decomposition pressures above chlorinated ruthenium corresponding to $RuCl_{1.8}$ to $RuCl_{2.8}$; this variable composition implies two solid phases are present. The vapor pressures were independent of composition, which could indicate that only one ruthenium chloride is present in the solid phase (or that lower chlorides react with Cl_2 produced by decomposition) and samples with less than 51.3% chloride are mixtures of $RuCl_3$ with Ru.

Shchukarev et al.[162] found that residues from high-temperature decomposition pressure measurements contained only $RuCl_3$ and Ru. Similarly, Bell et al.[163] showed that chloride-deficient samples are $RuCl_3$–Ru mixtures. Thus, direct chlorination produces only $RuCl_3$.

Hill and Beamish[164] obtained two products from direct chlorination. Their black chloride was insoluble in HCl, H_2O, and ethanol, whereas their "brown chloride" formed brown aqueous and reddish brown alcohol solutions. Hyde et al.[157] and Fletcher et al.[165] reinvestigated direct chlorination and obtained high-temperature α-$RuCl_3$ and low-temperature β-$RuCl_3$. Any contact of $RuCl_3$ with the silica reaction vessel at high temperatures produced dark brown Ru_2OCl_6, which is apparently identical with Hill and Beamish's[164] brown chloride. This oxychloride disproportionates to $RuCl_3$ and RuO_2 at higher temperatures.[157]

Hyde et al.[157] and Fletcher et al.[165,166] investigated these $RuCl_3$ polymorphs. β-$RuCl_3$ forms by chlorination below 720 K. However, it usually contains 1–30% α-$RuCl_3$.[157] β-$RuCl_3$ converts irreversibly to α-$RuCl_3$ at about 720 K. α-$RuCl_3$ can be prepared by chlorination of Ru at higher temperatures, but samples are usually contaminated with RuO_2 and oxychlorides.[157] However, sublimation of β-$RuCl_3$ in a Cl_2 stream gave pure α-$RuCl_3$ and a separate deposit of violet oxychlorides.[157] These violet oxychlorides may have been the "claret" precursors of Howe et al.'s[158] azure blue solutions.

$RuCl_3$ has also been prepared by reduction of Ru(IV) oxychlorides with ethanol,[157] by reacting $Cl_2(g)$ with $(NH_4)_2RuCl_6$ at 873 K or by direct reaction of RuO_2 and anhydrous HCl at 750–810 K.[167] However, reacting HCl with $Ru(OH)_3$ probably gives an oxychloride rather than the claimed $RuCl_3$.[160]

Solid $RuBr_3$ is usually prepared by direct reaction of Ru with Br_2 at about 750 K.[168,169] However, reaction of $Ru(OH)_3$ and HBr may have produced an oxybromide.[2,168] Von Schnering et al. prepared RuI_3 by direct but incomplete reaction at 620 K,[169] whereas Shchukarev et al.[170] obtained no reaction in a sealed tube at 770 K. Since technetium does not react with Cl_2 in a static system but does under flowing conditions,[171] a similar situation may apply to Ru and I_2. The quantitative reduction of upper valence states of Ru with HI or iodide salts in aqueous solution produces insoluble RuI_3 also.[2,170]

Gall and Lehmann[172] claimed preparation of $RuCl_2$, $RuBr_2$, and RuI_2 by H_2 reduction of Ru halides in absolute alcohol. Addition of $CHCl_3$ or $CHBr_3$ was necessary to get the corresponding Ru halide salt. Possibly these were actually oxyhalides rather than dihalides. As with the chloride, both $Ru(CO)_2Br_2$ and $Ru(CO)_2I_2$ are known.[2]

α-$RuCl_3$ forms black lustrous plates, is insoluble in most solvents, and is volatile above about 870 K.[165] It has a hexagonal-layered structure (α-$TiCl_3$ type) with $a = 5.98 \pm 0.005$ and $c = 17.17 \pm 0.02$ Å.[166] β-$RuCl_3$ is dark brown, fluffy, and soluble in ethanol.[165] It is also hexagonal (β-$TiCl_3$ type) with $a = 6.120 \pm 0.005$ and $c = 5.658 \pm 0.005$ Å.[166] The β-$RuCl_3$ becomes antiferromagnetic below about 600 K and α-$RuCl_3$ becomes antiferromagnetic below about 13 K. $RuBr_3$ was reported to be hexagonal with $a = 12.924$ and $c = 5.860$ Å; RuI_3 is also, with $a = 6.982$ and $c = 6.231$ Å.[169] A more detailed study indicated that $RuBr_3$ crystals are actually orthorhombic with $Ru_2Br_3^{3+}$ clusters.[173] Mössbauer isomer shift parameters for β-$RuCl_3$, $RuBr_3$, and RuI_3 are a linear function of the halide electronegativities, so they are not sensitive to the structural changes.[174]

As the temperature of $RuCl_3(c)$ is increased in the absence of moisture and oxygen, decomposition occurs according to reaction 32. The Cl_2 pressure is about 0.02 atm at 920 K and 1 atm at about 1145 K.[156,162,163,175,176] Sublimation (eq 33) also occurs in this temperature region but is an order of magnitude less important than decomposition by reaction 32.[162,176] Ru(c) is the stable solid phase above 1145 K so eq 34 occurs instead. Bell et al.[176] studied the vapor pressure above Ru(c) as a function of Cl_2 pressure at 1400–1800 K. The pressure dependence indicates the dominant gaseous species is Ru_xCl_3. Since $RuCl_3$ is the only known solid species, they assumed $x = 1$.

$$RuCl_3(c) = Ru(c) + {}^3/{}_2Cl_2(g) \qquad (32)$$

$$RuCl_3(c) = RuCl_3(g) \qquad (33)$$

$$Ru(c) + {}^3/{}_2Cl_2(g) = RuCl_3(g) \qquad (34)$$

Shchukarev et al.[177] found that the vapor pressure above $RuCl_3$ in a Cl_2 atmosphere was higher than expected and attributed this to the formation of an additional higher volatile chloride by eq 35. This "higher chloride" was condensed on a cold finger;[178] warming it produced a pressure rise at 243 ± 1 K which they attributed to decomposition of $RuCl_4(c)$ by the reverse of reaction 35. Analyzed samples of this material had a Cl:Ru ratio of 3.53:1 to 3.65:1, but some decomposition may have occurred during quenching.[178] Within the analytical precision of this difficult experiment, one could not distinguish $RuCl_4$ from Ru_2Cl_7 or Ru_2OCl_7 (if they exist). However, Bell et al.'s[176] study of vapor pressures with variable Cl_2 pressure established the formula $RuCl_4(g)$ as the principle vapor species between about 1000 and 1170 K, and $RuCl_3(g)$ dominates at higher temperatures. Above 1145 K $RuCl_4(g)$ forms by reaction 36. Hyde et al., however, suggested that some of these observations may be due to oxychlorides.[157]

$$RuCl_3(c) + {}^1/{}_2Cl_2(g) = RuCl_4(g) \qquad (35)$$

$$Ru(c) + 2Cl_2(g) = RuCl_4(g) \qquad (36)$$

Early workers found that RuO_4 could be reduced by aqueous HCl to "$RuCl_3$", and the reduction becomes easier upon addition of a few drops of ethanol.[2] Ruff and Vidic[179] found that aqueous HCl reduces RuO_4 to Ru(IV) rapidly and to Ru(III) more slowly. In contrast, HBr causes the Ru(IV) to Ru(III) reduction to occur more rapidly, and with HI the reduction is rapid and quantitative to Ru(III). In fact, the reduction of upper valence states of Ru to Ru(III) by iodides, generally known as the method of Crowell and Yost,[180] is one of the few quantitative reactions for Ru. Consequently, no upper valence iodides or oxyiodides have been prepared by aqueous reduction.

Reduction of RuO_4 by HCl, or dissolution of $RuO_2{\cdot}mH_2O$ in HCl followed by evaporation, yields "water-soluble" or "hydrated" ruthenium trichloride, "$RuCl_3{\cdot}mH_2O$", where m is usually given as 1–3. This material is probably the most widely used ruthenium chemical reagent. It appears to be called the "trichloride" because the Cl:Ru ratio is about 3:1. Freshly prepared solutions of "$RuCl_3$" have been reported to contain from 5.6 to 51% Ru(IV) species.[180–183] This indicates that reduction to Ru(III) may not be complete, that the isolated solid is extremely sensitive to oxidation, and that the extent of oxidation is quite variable. Commercial "$RuCl_3{\cdot}mH_2O$", which may have aged much longer, could well be nearly all Ru(IV) species.

Failure to recognize the presence of Ru(IV) has resulted in several errors in the literature. For example, many of the claims[2] that ruthenium blues contain Ru(I) arose from workers assuming that their "$RuCl_3{\cdot}mH_2O$" contained Ru(III) rather than Ru(IV). Duvigneaud and Reinhard-Derie[184] claimed to have prepared $Ru(OH)_3{\cdot}H_2O$ by precipitation of "$RuCl_3{\cdot}mH_2O$" solution with NH_4OH, but its brownish black color indicates that $RuO_2{\cdot}2H_2O$ from Ru(IV) precipitation was present in significant amounts (pure $Ru(OH)_3{\cdot}mH_2O$ is yellow).

Another common method for synthesis of "$RuCl_3{\cdot}mH_2O$" is oxidation of Ru metal by alkaline nitrate fusion, followed by reduction with HCl. However, ruthenium is extremely prone to formation of chemically stable nitrosyl compounds containing $Ru(NO)^{3+}$. For example, Belikin et al.[183] used this method and got about 41 ± 2% nitrosyl formation. Seddon[185] cited an example where a ruthenium ammine compound was obtained when "$RuCl_3{\cdot}mH_2O$" was the only possible nitrogen source.

Since much of the Ru in "$RuCl_3{\cdot}mH_2O$" is Ru(IV) and the Cl:Ru ratio is about 3:1, this suggests that the Ru(IV) is in the form of a hydroxy- or oxychloride. The simplest possibility is $Ru(OH)Cl_3$ that has been suggested by a number of workers.[182,183,186,187] However, Grube and Fromm[182] considered them to be $Ru(OH)Cl_3$–$RuCl_4$ mixtures. There is no convincing evidence that $RuCl_3{\cdot}mH_2O$ or $RuCl_4{\cdot}mH_2O$ exist as chemical entities, although both $Ru^{III}Cl_n{}^{3-n}$ and $Ru^{IV}Cl_n{}^{4-n}$ anions are well-known as double salts. Early claims for $RuCl_3{\cdot}HCl{\cdot}2H_2O$ or $HRuCl_4{\cdot}2H_2O$ have never been verified.[2]

A more likely possibility is that the non-nitrosyl portion of "$RuCl_3{\cdot}mH_2O$" consists of oxychlorides as described by Fletcher et al.[165] and Woodhead and Fletcher.[188] They dried "$RuCl_3{\cdot}mH_2O$" at 383 K and found the product was mostly Ru_2OCl_6, whereas heating it at 673 K in a Cl_2 stream gave even more Ru_2OCl_6. This has the right Cl:Ru ratio. Heating "$RuCl_3{\cdot}mH_2O$" in a vacuum produced a mixture of Ru_2OCl_5 and Ru_2OCl_4.[165] It is likely that "$RuCl_3{\cdot}mH_2O$" consists of a mixture of these compounds with nitrosylruthenium chlorides.

Ivanter et al.[187] studied the thermal decomposition of "$Ru(OH)Cl_3$" in the presence and absence of air. However, $Ru(OH)Cl_3$ is more likely a mixture of oxychlorides as described above. Pizzini et al.[189] and Lodi et al.[190] have studied thermal decomposition of "$RuCl_3{\cdot}mH_2O$". Samples annealed at 570 K contain about 8% Cl, but by 870 K the Cl content drops below 2% and the lattice constants approach those of RuO_2. The Cl content is lower at the surface than in the interior.[191] Incompletely thermally decomposed "$RuCl_3{\cdot}mH_2O$" can be considered to be nonstoichiometric oxychloride–RuO_2 mixtures.

It was earlier (section IV.C) noted that unstable ion $RuO_2{}^{2+}$ and its pyrosulfate have been suggested[142,144] as reduction products of RuO_4. The ruthenyl ion $RuO_2{}^{2+}$ also occurs in a number of salts. Deep red-purple $Cs_2[RuO_2Cl_4]$ and $Rb_2[RuO_2Cl_4]$ were prepared by addition of CsCl or RbCl to RuO_4 in concentrated HCl.[188,192,193] Analogous light brown $Cs_2[RuO_2Br_4]$ and light green $Cs_2[RuO_2(C_2O_4)_2]$ were prepared by the same type of reaction at 273 K.[194] A number of substituted ruthenyl complexes are also known (e.g., $[RuO_2(NH_3)_4]Cl_2$, $RuO_2(py)_2Cl_2$, $RuO_2(OH)_2(py)_2$, etc.).[9] All of these RuO_2^{2+} compounds that have been studied are diamagnetic and have an IR band around 830 cm^{-1}. This suggests, by analogy to *trans*-OsO_2^{2+} compounds, that all contain the *trans*-RuO_2^{2+} group.[9,194,195] The reaction of HCl gas with RuO_4 was claimed to produce reddish brown $H_2[RuO_2Cl_4]\cdot 3H_2O$.[196]

Jaber et al.[197] reduced "$RuCl_3\cdot mH_2O$" in HCl with Hg and then reoxidized it with $HClO_4$. They obtained Raman spectra consistent with $Ru_2O_2Cl_4$ and $Ru_2O_2Cl_6^{2-}$. This later species is equivalent to Alimarin et al.'s $[Ru_2O_2Cl_6(H_2O)_2]^{2-}$.[198]

The best known and most thoroughly characterized ruthenium oxyhalide salts contain $Ru_2OCl_{10}^{4-}$ and $Ru_2OBr_{10}^{4-}$ anions. Salts of the chloride form are brown; those of the bromide form are black. They can be prepared as follows: (1) by reacting RuO_4 with moderately concentrated hydrohalic acids in the presence of their corresponding alkali halides (recall that concentrated acid and short contact times yields $M_2[RuO_2X_4]$ salts, (2) by acidification of alkaline ruthenate salts with HCl or HBr, (3) by solution of $RuO_2\cdot 2H_2O$ in HCl or HBr and alkali chlorides; or (4) by recrystallization of M_2RuX_6 salts in moderately concentrated acid.[193] They form so readily that workers sometimes misidentify them when their presence is not expected. Oxidation of $RuCl_5(H_2O)^{2-}$ salts can also produce $Ru_2OCl_{10}^{4-}$.

There was much confusion in the early literature about the nature of these salts. The brown salt $K_4[Ru_2OCl_{10}]\cdot H_2O$ was originally thought to be a "hydrate isomer" of red $K_2RuCl_5(H_2O)$, since the percentages of all elements except hydrogen are nearly identical for these two salts. It was then known as brown or α-pentachlororuthenate. However, Charonnat[199] used iodide reduction to show that Ru(IV) and not Ru(III) was present. Similarly, Crowell and Yost[180] showed that the same was true for the bromide analogue. They were therefore reformulated as pentahalohydroxyruthenates: $M_2RuX_5(OH)$. Slightly earlier, Remy and Lührs[186] demonstrated, via Na amalgam titration, that Ru(IV) occurred in the brown salt, but they thought the formula was $K_4[Ru_2OCl_{10}]$. NH_4^+, K^+, Rb^+, and Cs^+ salts of both the chloride and bromide form are known.[193]

Charonnat[199] found that the brown salt lost H_2O at about 570 K, which is unlikely for a hydroxy salt but possible for the hydrated dimer structure. The formula $K_4[Ru_2OCl_{10}]\cdot H_2O$ was confirmed by Mathieson et al.'s powder pattern X-ray study.[200] It contains a μ-oxo-bridged dimer, with each Ru surrounded by five chlorides and a shared oxygen in a nearly octahedral environment. A molecular orbital description of the anion has been published.[201] Deloume et al. were unable to prepare the monohydrate but found the anhydrous salt has a very similar structure.[202a] Clark et al.[202b] have reported IR and resonance Raman spectra of the solid anhydrous K^+, Rb^+, and Cs^+ salts. This type of μ-oxo-bridged dimer is also known for Os, Re, and W.[203,204]

Raman spectra studies leave little doubt that the $Ru_2OCl_{10}^{4-}$ and $Ru_2OBr_{10}^{4-}$ ions can exist in aqueous solution.[197,203,205] However, their spectra in aqueous solutions show time-dependent changes. In certain pH regions and Cl/Ru ratios, $[Ru_2OCl_9(H_2O)]^{3-}$ or $[Ru_2OCl_8(H_2O)_2]^{2-}$ forms by dissociation. The species $[Ru_2OBr_8(H_2O)_2]^{2-}$ has also been reported.[198] Crisp and Seddon[206] reported isolation of several red-brown salts that proved to be of the type $M_3[Ru_2OCl_9(H_2O)]\cdot mH_2O$.[185] These other two types of salts are just partially dissociated forms of $[Ru_2OCl_{10}]^{4-}$. A mixed-valence dimer has been suggested as an intermediate in the reduction of $K_4[Ru_2OCl_{10}]\cdot H_2O$ in aqueous HCl.[207] During reduction, the solution initially becomes reddish black. Briggs' black salt "$K_2RuCl_5\cdot K_2RuCl_5(OH)$" has an appropriate empirical formula for this intermediate species,[208] but it may have just been a mixture of $K_4[Ru_2OCl_{10}]$ with K_2RuCl_6.

We earlier discussed the oxyhalide Ru_2OCl_6; by analogy Ru_2OBr_6 should also exist. The ions discussed in the previous paragraph are just these compounds with four additional coordination sites occupied by halides or by halides and H_2O. Dehand and Rosé[209] have described violet diamagnetic compounds $[Ru_2OCl_6(RCN)_4]$ with these four sites occupied by organonitrile ligands. These authors[210] also reported brown compounds possibly containing $[Ru_2Cl_7(OH)_3]^{2-}$. Nothing is known about their structures.

Fluorides and oxyfluorides are beyond the scope of this review; Colton and Canterford[17] have summarized much of their available data.

E. Double Halides and Hydrated Double Halides

There is a considerable amount of data concerning double halides of ruthenium. This section is concerned with what types of double halides and hydrated halides can form.

Alkali-metal hexahalo ruthenates $M_2[RuX_6]$ can be synthesized by a variety of procedures:[17] (1) oxidation of $M_2[RuCl_5\cdot H_2O]$ salts in concentrated HCl; (2) recrystallization of $Ru_2OCl_{10}^{4-}$ salts in concentrated HCl; (3) reduction of RuO_4 by concentrated HCl with MCl addition (restricting the reduction time gives $M_2RuO_2Cl_4$ salts); or (4) reaction of K_2RuO_4 with dilute HCl. Fergusson and Greenaway[211] prepared $M_2[RuBr_6]$, with $M^+ = K^+, Rb^+$, or Cs^+, by bubbling Br_2 gas through a HBr solution of Ru(III) or Ru(IV) chlorides or oxychlorides. If HBr or HBr plus ethanol were used instead, mixtures of $M_2[RuBr_6]$ and $M_3[Ru_2Br_9]$ were obtained.

The crystal structure of K_2RuCl_6 has been studied by several workers.[202a,212,213] It crystallizes in the fcc space group *Fm*3*m*. Adams and Mellor[212] and Deloume et al.[202a] report very similar lattice parameters, whereas Forcheri et al.[213] give a larger value. Deloume et al.'s results are probably the more accurate; their average Ru–Cl bond length is 2.318 ± 0.002 Å. Na^+, Rb^+, Cs^+, NH_4^+, etc. salts are also known.[9] Gutbier and Krauss[214] reported several red and black alkylammonium salts of $RuCl_6^{2-}$, but they were not studied in detail. Several "onium" salts have also been described.[215] Powder pattern data for $K_2[RuBr_6]$ indicates a cubic structure.[211]

IR spectra were reported for K_2RuCl_6,[195,216] as have magnetic properties for several M_2RuCl_6 and M_2RuBr_6 salts.[217] Most transition-metal hexahalometalates undergo a structural transition whose characteristic temperature increases from Cl^- to Br^- to I^- salts.[218]

Sinitsyn et al.[219] noted that there were conflicting claims about whether $M_2[RuCl_6]$ thermally decomposes initially to form $M_2[RuCl_5]$ or $M_3[RuCl_6]$, which then further decomposes at higher temperatures to $RuCl_3$ and MCl. They found that thermal decomposition of $K_2[RuCl_6]$ in Cl_2 or argon actually went by the mechanism eq 37 followed by eq 38. In air, however, decomposition of $K_2[RuCl_6]$ yields $RuO_2(c)$. Thermal decomposition of "onium" salts[215] proceeds by the different mechanism eq 39 where A denotes the "onium" ligands.

$$3M_2[RuCl_6](c) = 2M_3[RuCl_6](c) + \alpha\text{-}RuCl_3(c) + {}^3/_2Cl_2(g) \quad (37)$$

$$M_3[RuCl_6](c) = 3MCl(c) + Ru(c) + {}^3/_2Cl_2(g) \quad (38)$$

$$(AH)_2[RuCl_6](c) = 2HCl(g) + RuA_2Cl_4(c) \quad (39)$$

Pentachloroaquoruthenate(III) salts are also known, and the best characterized is the "red salt" $K_2[RuCl_5{\cdot}H_2O]$. These salts can be prepared by (1) mild reduction of $K_2[RuCl_6]$ in aqueous HCl; (2) reduction of $K_4[Ru_2OCl_{10}]$ or RuO_4 by ethanol in aqueous HCl; or (3) by oxidation or ruthenium blues.[193] Briggs,[208] Howe,[193] and Remy and Lührs[186] all reported analyses for samples corresponding to $2K_2[RuCl_5]{\cdot}3H_2O$, but Charonnat[199] doubted its existence. Briggs[208] also prepared samples that corresponded to $K_2[RuCl_5]{\cdot}2H_2O$ and $K_2[RuCl_5{\cdot}H_2O]$. Only the monohydrates have been characterized structurally, and the higher hydrates remain suspect.

X-ray diffraction data for $K_2[RuCl_5{\cdot}H_2O]$ and $Cs_2[RuCl_5{\cdot}H_2O]$ indicate orthorhombic crystals with each Ru surrounded by five chlorides and one H_2O.[220,221] The average Ru–Cl bond length is about 2.32 Å; the Ru–OH_2 bond length is 2.10 Å. Fergusson and Greenaway[211] prepared $Rb_2[RuCl_5{\cdot}H_2O]$, but they were unable to prepare bromo analogues. IR spectra[195,211] and magnetic properties[222,223] of several $M_2[RuCl_5{\cdot}H_2O]$ salts have been reported. Gutbier and Krauss[214] reported the preparation of many dark red to black crystalline alkylammonium salts of this type, but their structures and extents of hydration are unknown. Salts of $RuCl_4(H_2O)_2^-$ and $RuBr_4(H_2O)_2^-$ have also been claimed.[224]

Magnetic properties of K_2RuCl_5 have been reported,[222] but no description was given for its preparation. This type of salt was claimed to form during thermal decomposition of M_2RuCl_6 salts, but Sinitsyn et al. were unable to prepare them by this method.[219] They obtained material with that empirical formula by dehydration of $K_2[RuCl_5{\cdot}H_2O]$, but IR and powder-pattern structural data suggest a dimer structure $K_4[Ru_2Cl_{10}]$.[219]

Reddish brown $RuCl_6^{3-}$ and brown to dark brown $RuBr_6^{3-}$ salts are also known. They can be prepared by addition of Ru(III) salts to concentrated hydrohalic acid, followed by addition of an appropriate salt to cause precipitation. Salts prepared in this manner include $(C_6H_8N)_6[RuCl_6]{\cdot}3Cl$, $(C_6H_8N)_6[RuBr_6]{\cdot}3Br$, $[N(CH_2CH_2NH_3)_3][RuCl_6]{\cdot}HCl{\cdot}2H_2O$, $[N(CH_2CH_2NH_3)_3][RuBr_6]{\cdot}HBr$, $Al(H_2O)_6[RuCl_6]{\cdot}4H_2O$, $K_3[RuCl_6]$, and $Na_3[RuCl_6]{\cdot}12H_2O$.[199,223,225–228] The presence of HX molecules of solvation for the $N(CH_2CH_2NH_3)_3^{3+}$ salts was established by pH measurements.[226] Thermal decomposition of $K_2[RuCl_6]$ produced low temperature α-$K_3[RuCl_6]$, which transforms to β-$K_3[RuCl_6]$ at about 725 ± 23 K.[219] $Na_3[RuCl_6]$ has been reported in the NaCl–α-$RuCl_3$ phase diagram.[227]

X-ray structural data for $Al(H_2O)_6[RuCl_6]{\cdot}4H_2O$ and $(C_6H_8N)_6[RuBr_6]{\cdot}3Br$ confirm that Ru is surrounded by six halides in an octahedral environment.[225,228] The average Ru–Cl bond length is 2.375 ± 0.005 Å, and it is 2.514 ± 0.005 Å for Ru–Br. Many of the salts mentioned in the previous paragraph have been characterized by IR, electronic spectra, and magnetic measurements.[195,211,219,223,225,226]

Although Fergusson and Greenaway[211] tried to prepare $M_3[RuBr_6]$, most of their attempts yielded hexagonal crystals of $M_3[Ru_2Br_9]$ where $M^+ = K^+$, Rb^+, or Cs^+. There are many similar X-ray peaks in the powder patterns for monomeric and dimeric forms, so workers should be extra careful when studying bromide salts.

Fergusson and Greenaway[211] found that heating $M_2[RuCl_5{\cdot}H_2O]$ in a vacuum to 473 K gave a green powder which became brown at higher temperatures. They thought the green salt was $M_3[Ru_2Cl_9]$ since $Cs_3[Ru_2Cl_9]$ had been reported previously.[229] A dark brown salt prepared by Sinitsyn et al.[219] had the empirical formula "K_2RuCl_5" but probably contained the dimer $K_4[Ru_2Cl_{10}]$.

Bona fide $Cs_3[Ru_2Cl_9]$ has been prepared by solid-state reaction of CsCl with $RuCl_3$ at 973 K, and unit-cell dimensions are in excellent agreement.[229,230] Single-crystal data[230] indicated $Ru_2Cl_9^{3-}$ clusters with metal–metal interaction. Crisp and Seddon's salt "$M_3Ru_3Cl_9$" was later proved to contain Ru(IV).[185] Ivanova et al. invoked chloride-bridged anions $Ru_2Cl_9^{3-}$ to explain liquid extraction behavior of Ru(III).[231]

$Cs_3[Ru_2Cl_9]$ appears black by reflected light but red by transmitted light.[232] The Ru–Ru bond length is 2.725 Å, but Ru–Cl bond lengths vary from 2.391 (bridging) to 2.332 Å (terminal).[230] Bursten et al.[232] have done comparative molecular orbital calculations for $[RuCl_6]^{3-}$, $[Ru_2Cl_9]^{3-}$, and $[Ru_3Cl_{12}]^{4-}$ anions.

It is well-known that reduction of upper valence states of ruthenium in aqueous HCl by chemical or electrical methods produces the intensely colored compound(s) known as ruthenium blue(s). Since there may be several similar compounds with different Cl:Ru ratios, we shall use the plural. These compounds are extremely sensitive to oxidation and have never been unambiguously characterized in the solid state. There was much confusion in the early literature about the valence of ruthenium in these solutions, with various claims being made for Ru(I), Ru(II), and Ru(III).[1,2] Whereas the initial reduction is to Ru(II), there is no guarantee that oxidation to a slightly higher valence state has not happened when the blue compounds form. The initial reduction stage will be discussed in more detail in the aqueous chloride section.

Oxidation of ruthenium blues generally produces a yellow solution of Ru(III) chlorides,[233,234] sometimes with a green intermediate stage.[233,235,236] Analogous blue compounds are formed when ruthenium is reduced in the presence of Br^- or I^-.[1] Obviously, halide ions are incorporated into the structure of these blue compounds. Ruthenium blues bear no direct relationship to polymeric platinum blues that contain NH_3, amide, or amine groups.[237]

In halide-free solutions, ruthenium ions and RuO_4 can be reduced to the pink aquo complex of Ru(II). The aquo ion does not reduce H_2O, but it is very sensitive to traces of oxygen. Bernhard et al.[238] prepared a salt with noncomplexing *p*-toluenesulfonate that contained the pink aquo ion $Ru(H_2O)_6^{2+}$.

In contrast to $Ru(H_2O)_6^{2+}$ that does not reduce H_2O, ruthenium blues are oxidized by water with H_2 evolution.[239] This seems to be the main reason why the pure ruthenium blue ions have not been isolated and characterized as solid salts.

Dumas and Mercer[240] used ion exchange to separate monomeric yellow Ru(III) chlorides; $RuCl^{2+}$, *cis*- and *trans*-$RuCl_2^+$, and *cis*- and *trans*-$RuCl_3$. Waters are omitted from these formulas. Electrolytic reduction initially produced gray solutions, and, when the reduction was nearly complete, the solutions were pink and had the $Ru(H_2O)_6^{2+}$ spectrum. After 1.5–2 h the solutions became blue. They interpreted their one-electron reductions as initially yielding gray monomeric Ru(II) complexes. Thus, the reduction scheme is shown in eq 40. They considered the blue color formation to be due to polymerization and oxidation.

$$RuCl_m^{+3-m} + e^- = RuCl_m^{+2-m} = Ru^{2+} + mCl^- = \text{ruthenium blues} \quad (40)$$

Polymeric coordination compounds are frequently intensely colored and monomeric complexes lightly colored, but there are many exceptions to this generalization. A few examples of known Ru(II) complexes illustrate this point. Refluxing "$RuCl_3 \cdot mH_2O$" in dimethyl sulfoxide produces an orange-brown solution from which acetone precipitation gives a yellow solid $RuCl_2(Me_2SO)_4$.[241] Dissolution in H_2O and addition of $AgNO_3$ give the $Ru(Me_2SO)_4(H_2O)_2^{2+}$ ion. In ethanol–Me_2SO mixtures $Ru(Me_2SO)_6^{2+}$ forms. Crystal structure data for $RuCl_2(Me_2SO)_4$ indicate a distorted octahedron with cis chlorine atoms.[242] This is a bona fide monomeric and light colored ruthenium dichloride. Ammine complexes of the type $[Ru(NH_3)_6]X_2$, where X = Cl^-, Br^-, I^-, or BF_4^-, are various shades of yellow and are probably monomeric.[243] "$RuCl_3 \cdot mH_2O$" in HCl solution is reduced by $SnCl_2$ to an orange-red solution. Heating this solution produces ruthenium blues.[244] However, yellow-orange crystals can be precipitated from the orange-red initial solution. Farrugia et al. showed that the resulting $[N(CH_3CH_2)_4]_4[Ru(SnCl_3)_5Cl]$ contains monomeric, octahedral anions of $[Ru(SnCl_3)_5Cl]^{4-}$.[245] Similarly, the presumably monomeric metal salts of $Ru(CN)_6^{4-}$ are mostly white or pale in color;[246] in contrast the insoluble polymeric ruthenium purples ($Fe_4[Ru(CN)_6]_3$, $KFe[Ru(CN)_6]$, $NH_4Fe[Ru(CN)_6]$, etc.) are darkly colored.[247] $Ru(NO)^{3+}$ complexes, in which Ru is usually considered to be divalent, are obvious exceptions since they can be almost any color.[1,2]

The preceding paragraphs indicate that ruthenium blues are probably polymeric (i.e., two or more Ru atoms), probably incorporate halide ions in their structure, and have ruthenium valences of $2 \leq Z < 3$. In addition, they are unstable in aqueous solution owing to oxidation by water. Mercer and Dumas[234] also noted the presence of Ru metal when $K_2[RuCl_5(H_2O)]$ solutions are reduced and suggested that disproportionation of Ru is involved. Ion-exchange separation of the ruthenium blues indicated several discreet blue bands and one red band due to aqueous Ru^{2+}. Anionic, cationic, and neutral bands were present.[234] Thus, ruthenium blues are a mixture of species with different anion/cation ratios, and some uncomplexed $Ru(H_2O)_6^{2+}$ is also present in these solutions.

Attempts have been made to isolate a blue salt from these solutions. Howe[248] added CsCl to a ruthenium blue solution and precipitated a dark greenish blue solid of approximate composition $3CsCl \cdot 2RuCl_2 \cdot 2H_2O$. It was extremely air sensitive and may have simply been a mixture of salts. Adamson[249] tried the same type of experiment and obtained a Ru to Cl ratio of 1:(5.5 ± 0.3) so oxidation was a problem. Adamson thought that he had a mixture of low-spin octahedral $RuCl_5(H_2O)^{3-}$ and $RuCl_6^{4-}$, in equilibrium with high-spin tetrahedral $RuCl_4^{2-}$ in solution. However, this seems unlikely. Rose and Wilkinson[233] also tried the same type of experiment but the resulting solid always had an anion:cation ratio consistent with $[Ru_5Cl_{12}]^{2-}$ clusters. Following Bino and Cotton,[236] we consider their proposed cluster unlikely. Crisp and Seddon[206] reported red-brown salts with clusters of the types $RuCl_3^-$ and $Ru_3Cl_9^{3-}$. This claim, based on an inaccurate commercial analysis, was later retracted.[185]

Two studies provide definite information about the structure of ruthenium blues. Mercer and Dumas[234] separated three blue aqueous species by ion exchange and characterized them by charge determination (membrane equilibrium), anion to cation ratio, and redox behavior. These blue complexes were $Ru_2Cl_3^{2+}$, $Ru_2Cl_4^+$, and Ru_2Cl_5, which could be reversibly oxidized to yellow $Ru_2Cl_3^{3+}$, $Ru_2Cl_4^{2+}$, and $Ru_2Cl_5^+$. They also observed anionic blue complexes that could not be removed from the ion-exchange column. Bino and Cotton[236] tried to isolate a blue salt, but during solvent evaporation it turned green. Crystals of $[(C_2H_5)_4N]_2[H_7O_3]_2[Ru_3Cl_{12}]$ formed and contain the $[Ru_3Cl_{12}]^{4-}$ cluster. They thought it might be an oxidation product of an actual blue species but acknowledged that it could be an unrelated species.

The wavelength of the absorption maximum increases with increasing Cl to Ru ratio for Mercer and Dumas' blue and yellow dimeric complexes.[234] $Cs_3Ru_2Cl_9$, which is red by transmitted light,[232] fits into the Ru(III) dimer trend.

While the exact nature of the ruthenium blues is still uncertain, the above work indicates that mixtures of dinuclear and/or trinuclear complexes with variable Cl to Ru ratios is most likely.

Key et al.[250] prepared a black crystalline compound with the empirical formula $[C_6H_5NH_3]_5[Ru_3Br_{14}]$ for which no structural data are available. They suggested that it might have a linear trinuclear structure with bromine bridges linking the Ru(III) ions. Bino and Cotton's green salt is also trinuclear.[236]

F. Thermodynamic Data for Binary Ruthenium Halides

Of all of the compounds discussed in the last two sections, only the anhydrous binary chlorides have thermodynamic data. Their chemistry was discussed in section IV.D.

The pressure of $Cl_2(g)$ above α-$RuCl_3$ reaches 1 atm at about 1145 K. Below this temperature, the reactions are decomposition to the elements, sublimation to

$RuCl_3$(g), and oxidation of $RuCl_3$(g) to $RuCl_4$(g). See eq 32–36. Decomposition of $RuBr_3$ and RuI_3 to the elements also occurs, but the experimental conditions were not varied enough to detect other species in the vapor phase.[168,170]

Five studies of pressures above α-$RuCl_3$ cover the temperature ranges 723–1018 K,[156] 913–1093 K,[175] 773–1173 K,[162] and 923–1112 K.[163,176] The first of these studies[156] had much higher pressures than the other three, and much curvature to the data. Oxychlorides may have been present so that data set will not be considered further. Bell et al.[176] also reported pressures above Ru(c) in a Cl_2 atmosphere up to about 1800 K. Pressures above $RuBr_3$ were reported from 759 to 893 K[168] and above RuI_3 from 590 to 660 K.[170]

Thermodynamic data for the halogen gases at 298 K were taken from the 1977 CODATA tables: values at higher temperatures are from Stull and Sinke.[41] There are no available calorimetric data for solid or gaseous ruthenium halides so it was necessary to estimate them from other halides of similar valence type. Second-law extrapolations were used since the calculations are approximate anyway. Constant heat capacities were assumed at the mean temperature between 298 K and the experimental temperatures.

Heat capacities of various tri- and tetrahalides were taken from Kubaschewski and Alcock[251] and lanthanide trihalides from Myers and Graves.[252] Atypical values, as for $SbCl_3$, were rejected.[251] The estimated heat capacities are $C_{p,650}(\alpha\text{-}RuCl_3(c)) = 109 \pm 7$ J K^{-1} mol^{-1}, $C_{p,560}(RuBr_3(c)) = 115 \pm 16$ J K^{-1} mol^{-1}, $C_{p,460}(RuI_3(c)) = 107 \pm 4$ J K^{-1} mol^{-1}, and $C_{p,650}(RuCl_3(g)) = 76 \pm 6$ J K^{-1} mol^{-1}.

Shchukarev et al.[162] gave Cl_2(g) pressures and total pressures, so sublimation and decomposition can be easily separated. Extrapolation of their results to 298 K yields $\Delta G°_{298,f}(\alpha\text{-}RuCl_3) = -147.5 \pm 2.5$ kJ mol^{-1}, $\Delta H°_{298,f}(\alpha\text{-}RuCl_3) = -204.1 \pm 4.0$ kJ mol^{-1}, $S°_{298}(\alpha\text{-}RuCl_3) = 173.5 \pm 8.2$ J K^{-1} mol^{-1}, $\Delta G°_{298,f}(RuCl_3(g)) = -9.5 \pm 3.0$ kJ mol^{-1}, $\Delta H°_{298,f}(RuCl_3(g)) = -16.2 \pm 5.5$ kJ mol^{-1}, and $S°_{298}(RuCl_3(g)) = 340.5 \pm 10.6$ J K^{-1} mol^{-1}.

Bell et al.[163] reported pressures above $RuCl_3$(c) corrected for the presence of $RuCl_3$(g). Their data yield $\Delta G°_{298,f}(\alpha\text{-}RuCl_3) = -185.6 \pm 2.5$ kJ mol^{-1}, $\Delta H°_{298,f}(\alpha\text{-}RuCl_3) = -259.2 \pm 4.0$ kJ mol^{-1}, and $S°_{298}(\alpha\text{-}RuCl_3) = 116.2 \pm 8.2$ J K^{-1} mol^{-1}. Bell et al.[176] did not give their original pressures for $RuCl_3$(g) but only derived results. They are (corrected to our selected data): $\Delta G°_{298,f}(RuCl_3(g)) = 42.9 \pm 6.4$, $\Delta H°_{298,f}(RuCl_3(g)) = 50.0 \pm 13$ kJ mol^{-1}, and $S°_{298}(RuCl_3(g)) = 386.9 \pm 17$ J K^{-1} mol^{-1}. Similarly, they reported $\Delta G°_{298,f}(RuCl_4(g)) = -63.4 \pm 17$ kJ mol^{-1}, $\Delta H°_{298,f}(RuCl_4(g)) = -93.3 \pm 17$ kJ mol^{-1}, and $S°_{298}(RuCl_4(g)) = 374.1 \pm 21$ J K^{-1} mol^{-1}.

Remy and Köhn's[175] data were not determined over wide enough conditions to extract results for both $RuCl_3$(c) and $RuCl_3$(g). Decomposition is the dominant reaction in their temperature interval; the presence of $RuCl_3$(g) was corrected for by using the average results of Shchukarev et al.[162] and Bell et al.[176] Their data[175] yield $\Delta G°_{298,f}(\alpha\text{-}RuCl_3) = -142.9 \pm 2.5$ kJ mol^{-1}, $\Delta H°_{298,f}(\alpha\text{-}RuCl_3) = -200.4 \pm 4.0$ kJ mol^{-1}, and $S°_{298}(\alpha\text{-}RuCl_3) = 170.1$ J K^{-1} mol^{-1}.

The recommended values are the averages of the above data, and they are listed in Table IV. Results are moderately concordant for α-$RuCl_3$(c). For example, they indicate that the Cl_2 pressure will reach 1 atm at 1136,[175] 1180,[162] and 1125 K.[163] They also agree with the thermogravimetric analysis result of 1110 K in argon.[219] Danilov et al.[227] could not detect any thermal effect at this temperature and claimed that was due to a low enthalpy of fusion. Actually, at this temperature, decomposition to the elements occurs rather than fusion.

TABLE IV. Recommended Thermodynamic Data for Anhydrous Ruthenium Halides

compds	$\Delta G°_{298,f}$, kJ mol^{-1}	$\Delta H°_{298,f}$, kJ mol^{-1}	$S°_{298}$, J K^{-1} mol^{-1}
α-$RuCl_3$(c)	−158.7 ± 23	−221.2 ± 33	153.3 ± 32
$RuCl_3$(g)	16.7 ± 26	16.9 ± 33	363.7 ± 33
$RuCl_4$(g)	−63.4 ± 17	−93.3 ± 17	374.1 ± 21
$RuBr_3$(c)	−120.8 ± 10	−147.8 ± 12	166.5 ± 53
RuI_3(c)	−53.5 ± 9.2	−58.4 ± 8.0	186.3 ± 25

Table IV also contains data for $RuBr_3$ and RuI_3.[168,170] Recalculated decomposition pressure values yield $\Delta G°_{298,f}(RuBr_3(c)) = -120.8 \pm 10$ kJ mol^{-1}, $\Delta H°_{298,f}(RuBr_3(c)) = -147.8 \pm 12$ kJ mol^{-1}, and $S°_{298}(RuBr_3(c)) = 166.5 \pm 53$ J K^{-1} mol^{-1}. For the iodide $\Delta G°_{298,f}(RuI_3(c)) = -53.5 \pm 9.2$ kJ mol^{-1}, and $\Delta H°_{298,f}(RuI_3(c)) = -60.8 \pm 8.5$ kJ mol^{-1}. The reverse reaction, reaction of I_2(g) with Ru(c), was found to be very slow so Shchukarev et al.[170] did an enthalpy of combustion measurement as a check. It yielded $\Delta H°_{298,f}(RuI_3(c)) = -56.1 \pm 7.5$ kJ mol^{-1}. Using the average ΔH value gives $S°_{298}(RuI_3(c)) = 186.3 \pm 25$ J K^{-1} mol^{-1}.

Combustion enthalpy data for $RuCl_3$(c) and $RuBr_3$(c) would be very desirable as a check on the high-temperature measurements.

G. Nitrate and Nitrite Compounds with Comments on Nitrosyl Compounds

A detailed consideration of ruthenium nitrosyl compounds is beyond the scope of this review. However, they deserve some comment since they are more numerous for ruthenium than for any other element.[1] In addition, they readily form when ruthenium compounds come in contact with HNO_3, HNO_2, or NO. They are fairly resistant to oxidation, more so than most lower valence ruthenium compounds. The most common of them contain the $Ru(NO)^{3+}$ group. The NO can be removed by heating them with H_2O_2 or hydrazine[253] or by photolysis with UV light.[254] However, in a closed system the NO generated by photolysis can react with the Ru^{3+} produced and reform $Ru(NO)^{3+}$.[254]

There were disagreements in the early literature about the actual valence of ruthenium in these compounds.[2] The majority contain $Ru(NO)^{3+}$, and Ru was assumed to be trivalent. However, the Ru–NO bond is fairly short in most cases, which indicates that NO is donating electrons to Ru. Thus, they are now considered to be Ru^{2+} compounds. Actually, 5d electron $Ru(NO)^{4+}$, 6d $Ru(NO)^{3+}$, 7d $Ru(NO)^{2+}$, 8d $Ru(NO)^{+}$, and 10d electron $Ru(NO)_2{}^0$ groups all are known.[255,256] $Ru(NO)^{2+}$ compounds are produced by chemical or electrolytic reduction of $Ru(NO)^{3+}$;[255] $Ru(NO)^{4+}$ was obtained[256] by reaction of NOCl with "$RuCl_3 \cdot mH_2O$". Only $Ru(NO)^{3+}$ compounds will be discussed since they are the only ones likely to be encountered under conditions of interest to this review.

Nitrate ions do not react with Ru(IV), but they do react with Ru(III) quantitatively (eq 41),[253] and the

$$4Ru^{3+} + 4H^+ + NO_3^- = Ru(NO)^{3+} + 3Ru(IV) + 2H_2O \quad (41)$$

Ru(IV) formed is extensively hydrolyzed. Solid compounds formed contain $Ru(NO)X_5^{m-}$, where X can be almost any ligand and sometimes is of more than one type. Nitrate and nitrite complexes have been studied extensively[257-266] since nuclear reactor fuel elements containing Ru are usually dissolved in HNO_3 after their useful life. In these complexes X can be one or more of NO_3^-, NO_2^-, OH^-, or H_2O. In several cases approximate distributions of species have been obtained at various HNO_3 concentrations.[257,259,260,262]

Ruthenium nitrosyl halides have been studied in slightly less detail. However, data have been reported for all of the aquo chlorides (i.e., $Ru(NO)Cl(H_2O)_4^{2+}$, ..., $Ru(NO)Cl_5^{2-}$), for tetraamine halides and hydroxy halides, and for double salts of the type $M_2[Ru(NO)X_5]$ where M is a monovalent cation and X is a halide.[267-270] The nitrosyl containing fraction of most commercial "$RuCl_3{\cdot}mH_2O$" is probably in the form of aquo- or hydroxyaquoruthenium nitrosyl chlorides.

Several workers have found that water molecules in these ruthenium nitrosyl halides and nitrates behave as weak acids with dissociation constants of 10^{-3} to 10^{-8}.[257,258,268,271] The solubility of ruthenium nitrosyl nitrate is constant at about 5×10^{-5} mol L^{-1} from pH 3–9, but it is higher outside this pH region.[266] It is possible that $Ru(NO)(H_2O)(OH)_4^-$ or $Ru(NO)(OH)_5^{2-}$ is the soluble species at high pH values. At pH >11 there was partial decomposition of the nitrosyl complex to form a black oxide ($RuO_2{\cdot}2H_2O$?) after several months.[266] Double salts containing both anionic and cationic $Ru(NO)^{3+}$ complexes are also known.[272]

Although there are a large number of nitrite and nitrate complexes of nitrosylruthenium known, there is only a small amount of evidence for salts of these anions without a nitrosyl group. In fact, almost any such oxynitrogen compound with a Ru valence of 3 or less is probably a nitrosyl compound.

One case where a nitrite probably formed was when anhydrous α-$RuCl_3$ was dissolved in a molten $LiNO_2$–KNO_2 eutectic above 525 K.[273] NO and NO_2 were evolved. A yellow solid also formed, which when washed and dried was found to have the empirical composition $K_4[Ru(NO_2)_6]$, and it contains Ru(II). Powder pattern data and visible and UV spectra showed similarities to other transition-metal compounds of this type. It decomposes to RuO_2 at about 625 K.

Reduction of RuO_4 in aqueous $HClO_4$, HNO_3, or H_2SO_4 by chemical (especially H_2O_2) or electrolytic methods generally produces Ru(IV) solutions.[145,274-281] When H_2O_2 is used as the reducing agent, the $HClO_4$ concentration should be kept below 2 mol L^{-1} (to avoid oxidation to Ru(4.25))[274] or the H_2SO_4 concentration below 0.5 mol L^{-1} (to avoid reduction to Ru(III) or Ru(3.5)).[277,280] The stable soluble hydrolysis product is the tetramer $Ru_4(OH)_{12}^{4+}$ (or $Ru_4O_6^{4+}$), and this has been amply demonstrated by potentiometric pH titrations,[279] electrochemical methods,[254,278,281] and ion-exchange/Donnan membrane equilibrium.[278] It is also possible to depolymerize them to obtain monomeric $Ru(OH)_2^{2+}$ (or RuO^{2+}). These tetramers can be oxidized to Ru(4.25) tetramers[274] or reduced to Ru(3.75), Ru(3.5), etc.[254,278,281] See sections V.C. and V.D. for details.

Brêmard et al.[279] found that pH titration in either 0.5 mol L^{-1} $NaCH_3SO_3$ or $NaNO_3$ gave identical results; viz., the tetramer exists and the OH^-:Ru(IV) ratio is 3:1 in both ionic media (NaCl addition slightly reduces the OH^-:Ru ratio). Maya[254] found that the electrochemical behavior of the tetramer in HNO_3 was identical with that reported in $HClO_4$.[278] Since the $CH_3SO_3^-$ ion does not form complexes in aqueous solutions and ClO_4^- rarely does, the above information also implies that $Ru_4(OH)_{12}^{4+}$ in nitrate solutions exists as a completely dissociated or nearly completely dissociated salt.

Evaporation of Ru^{IV}–HNO_3 solutions produced a red amorphous solid.[282] By successive evaporations it was possible to get NO_3^-:Ru(IV) ratios of 2.56:1 to 1.10:1. Analysis for nitrogen indicated that all was present as NO_3^- (i.e., no nitrosyl group) and pH titration indicated the presence of one dissociable hydrogen per NO_3^- added (and the end product was hydrated RuO_2). The NO_3^- ions were easily removed by "nitron" precipitation. It is possible that these species were polymers of the type $Ru_4(OH)_n(NO_3)_{16-n}$ and the NO_3^- is very weakly bound. It might be worth redoing these experiments with $CH_3SO_3^-$ replacing NO_3^- to see whether a crystalline compound can be obtained. Brêmard et al.[283] found that Ru(IV) titrated with HNO_3 had a break in the pH curve at a Ru:NO_3 ratio of 1:4. However, spectrophotometric monitoring showed no changes, so these nitrates must be dissociated.

Fletcher suggested that reduction of RuO_4 by H_2O_2 in HNO_3 may proceed via a $RuO_2(NO_3)_2$ or $H_2[RuO_2(NO_3)_4]$ intermediate.[259] Wilson[280] also reported that reduction of 10^{-4} to 10^{-3} mol L^{-1} RuO_4 by H_2O_2 in $HClO_4$ proceeded via an unknown yellow intermediate, but by 10^{-2} mol L^{-1} RuO_4 is directly reduced to Ru(IV).

H. Binary Oxides of Ruthenium

This section is concerned with anhydrous binary oxides of ruthenium. Hydrated oxides and/or hydroxides will be treated separately.

A number of different solid oxides were claimed by early workers: RuO, Ru_2O_3, RuO_2, Ru_2O_5, RuO_4, and Ru_4O_9.[2] RuO and Ru_2O_3 were claimed to form when $Ru(OH)_2$ and $Ru(OH)_3$, respectively, were heated in an inert atmosphere.[2] However, it is doubtful whether $Ru(OH)_2$ has ever been prepared in anything like a pure form. When $Ru(OH)_3$ (usually contaminated with $RuO_2{\cdot}2H_2O$) is heated in air, RuO_2 forms, but, when it is heated in an inert atmosphere, it disproportionates to Ru(c) and RuO_2.[184,284,285] Thus, Ru_2O_3 cannot be prepared by this method. Similarly, Ru_4O_9 was reported to form when aqueous RuO_4 is heated at 373 K. However, other workers found the RuO_4 distills off unchanged[2] (and others reported that distillation from H_2O or dilute HNO_3 causes some reduction to a black solid,[286,287] probably $RuO_2{\cdot}2H_2O$). All claims for Ru_2O_5 refer to a hydrated form,[2,288] so they will be discussed separately.

Several studies of the Ru(c)–O_2(g) system have been made at elevated temperatures, and only RuO_2 has been detected as the solid oxide. Remy and Köhn[175] measured the decomposition oxygen pressures above RuO_2–Ru mixtures. The initial addition of Ru caused the O_2 pressure to drop, but further addition caused no change. Remy and Köhn interpreted the initial drop as solid solution formation and concluded that no lower oxides form. Bell and Tagami[289] found an initial decrease in O_2 pressure upon O_2 removal and attributed this to removal of absorbed O_2. McDaniel and Schneider[76] likewise could prepare only RuO_2. The solubility of Ru in RuO_2 is <1.5 mass % below 1070 K.[290]

Heating RuO_2 in a vacuum or an inert-atmosphere leads to decomposition to the elements, and only O_2^+ ions were detected in the vapor.[289,291] The residue is Ru(c) with some traces of oxygen.

Thermal decomposition of "$RuCl_3 \cdot mH_2O$" in air yields a polycrystalline mixture of RuO_2 and ruthenium oxychlorides.[189,190,292] Since Cl is present, the samples are oxygen deficient. Annealing in an oxygen atmosphere increases the oxygen content. Polycrystalline samples were found to contain up to several percent excess oxygen after annealing at 1073 K.[189] Crystal size and electrical conductivity increase with annealing temperature. Polycrystalline films have electrical conductivities about 10^3 smaller than that of single crystals and so do crushed and sintered single crystals.[189] Campbell et al.'s[23] DTA endotherm of RuO_2 without weight loss at 458 K may possibly be related to desorption of small amounts of absorbed O_2 or H_2O. The oxygen excess on polycrystalline RuO_2 exists as RuO_3, probably as part of a gross defect structure.[293,294]

When polycrystalline RuO_2 is heated in oxygen stream, volatilization occurs by formation of higher oxides. These thermodynamically unstable oxides decompose upon cooling to form single crystals (frequently twinned) of the dark blue "metallic oxide" RuO_2.[295-298] Several analyses indicate that these crystals are stoichiometric RuO_2.[298-301] Their electrical conductivity is greater than that of Hg and approaches that of Cu at low temperatures.[11,296-298,300] Attempts have been made to explain this by electronic band structure calculations.[302,303]

Ten separate X-ray structural determinations for RuO_2[285,296-301,304-306] are in fairly good agreement, with the six highest precision values being in near perfect agreement. These six studies[297-300,304,305] give $a = 4.4911 \pm 0.0008$ Å and $c = 3.1065 \pm 0.0003$ Å at room temperature. There are also structural data up to 975[304] and 1293 K.[306] Krishna Rao and Iyengar's results[304] are preferred since their room-temperature value agrees better with other studies. Their linear expansion coefficients are strongly temperature dependent. At 303 K, $\alpha_a = 7.01 \times 10^{-6}\ K^{-1}$ and $\alpha_c = -1.41 \times 10^{-6}\ K^{-1}$. RuO_2 has the rutile structure at all of these temperature.

It was mentioned above that volatile higher oxides form when RuO_2 is heated in an oxygen atmosphere. The dependence of the total pressure at various temperatures indicates that these species are RuO_3(g) and RuO_4(g).[307] At very high temperatures they also occur above Ru(c).[45] RuO_4 is well-known both as liquid and solid around room temperature, but it is metastable with regard to RuO_2(c) formation.

Alcock and Hooper[308] studied the vapor pressure above "Ru(c)" in an oxygen atmosphere at elevated temperatures and concluded that RuO(g) forms. However, under these conditions Ru forms a surface film of RuO_2, so their data really indicate RuO_3(g). RuO(g) has, however, been detected as a vapor species by arcing Ru powder in a dilute O_2 atmosphere (if too much O_2, the O_2^+ bands overlap with the RuO bands).[309,310] Scullman and Thelin[310] cast doubt on some of Raziunas et al.'s[309] band assignments. Ru^+, RuO^+, RuO_2^+, RuO_3^+, and RuO_4^+ have been produced by electron impact on RuO_4(g),[311] and their enthalpies of formation were calculated. RuO, RuO_2, RuO_3, and RuO_4 vapor have been detected above Ru(c) in an O_2 atmosphere at extremely high temperatures.[45]

When bulk Ru or sintered Ru powder are exposed to air for several days at room temperature to 473 K, a thin film (4–8 Å) of "native oxides" forms which prevents further oxidation.[312,313] Electron spectroscopy suggests that a lower oxide is present, and Sharma and Hines[313] suggested that it might be RuO. However, another and likely possibility is that the spectra of Ru and RuO_2 interfere owing to the very thin film thickness.[312] Oxidation of bulk or powered Ru at higher temperatures gives RuO_2, but oxidation of Ru black can occur as low as 390 K.[306]

A number of studies report the anodic and cathodic behavior of solid Ru and $RuO_2 \cdot mH_2O$ in acidic and basic solutions.[314-319] Under conditions of anodic O_2 evolution in acidic solutions RuO_4 is formed.[316] "Ru_2O_3" is frequently claimed as a reduction product of $RuO_2 \cdot 2H_2O$,[314,317,318] but the actual Ru(III) product could well be hydrated $Ru(OH)_3$ or RuO(OH). It will be discussed later with other hydrated oxides. Unstable and presumably hydrated RuO_3 has been claimed to be involved in anodic evolution of O_2.[315,319]

RuO_4 can be prepared by oxidizing almost any lower valence compound by chemical methods (e.g., oxidation by Cl_2 in alkaline solutions, fusing Ru powder with alkaline permanganate or hypochlorite, followed by acidification and distillation, etc.[2]). It is a true Ru(VIII) tetraoxide and not a diperoxide.[320]

Deville and Debray found that distillation of RuO_4 liquid at 381 K can cause violent decomposition, whereas Debray and Joly found that a less violent decomposition to RuO_2 occurs at 380 K.[2] Extrapolation of vapor pressure data gives a boiling point of 406 ± 5 K.[321]

Krauss[322] claimed that RuO_4 forms brown granular crystals when heated above its melting point, whereas condensation of vapor produces yellow needles. The yellow form was found to be more soluble than the brown form and had a lower melting point. However, Remy[323] found that both solid forms had the same solubility. Additional results by Nikol'skii[324] indicate they both have the same melting point. Thus there is probably only one crystalline form of RuO_4. Němec et al. probably had $RuO_2 \cdot mH_2O$ rather than "brown insoluble" RuO_4 as claimed by them.[325]

Debray and Joly reported the melting point of RuO_4 to be 298.7 K.[2] Other values are 298 K (yellow needles),[322] 298.6 ± 0.1 K,[324,326] and 299.6 K.[327] Intersection of the liquid and solid vapor pressure curves yields 297.6 ± 1.4 K.[321] The recommended value is 298.5 ± 0.5 K.

RuO_4 is a very strong oxidizing agent.[1,2] One of the few organic solvents is does not attack is CCl_4. The RuO_4–CCl_4 system contains a simple eutectic.[328] The enthalpy of solution of RuO_4 in CCl_4[328] is $\simeq$18.6 kJ mol^{-1}, and vapor pressure measurements indicate that Henry's law is obeyed by RuO_4.[329] RuO_4–OsO_4 form nearly ideal solutions.[327]

RuO_4 in aqueous solutions forms a very weak acid (adding base can cause partial reduction to Ru(VI) or

TABLE V. Thermodynamic Data for $RuO_2(c)$ at 298.15 K

method	temp, interval, K	$\Delta G^\circ_{298,f}$, kJ mol^{-1}	$\Delta H^\circ_{298,f}$, kJ mol^{-1}	S°_{298}, J K^{-1} mol^{-1}
combustn[a]			−305.0 ± 5.9	
decompositn[b]	1380–1776		−304.6	51.2
decompositn[c]	1173–1523		−300.0	58.7
decompositn[d]	985–1190		−300.8	61.3
emf[e]	780–1040		−342.3	15.7
emf[f]	723–1230		−320.1	39.1
emf[g]	873–1273		−312.5	50.8
recommended value[h,i]		−253.1 ± 8.2	−307.2 ± 7.8	52.2 ± 8.7

[a] Reference 343. [b] Reference 289. [c] Reference 296. [d] Reference 291. [e] Reference 344. [f] Reference 345. [g] Reference 346. [h] Recommended values are averages of all but ref 344. [i] A standard second-law extrapolation yields $\Delta G^\circ_{298,f} = -252.4 \pm 6.7$ kJ mol^{-1}, $\Delta H^\circ_{298,f} = -295.4 \pm 9.2$ kJ mol^{-1}, and $S^\circ_{298} = 89.1 \pm 38.1$ J K^{-1} mol^{-1}.

Ru(VII)).[329] Although Martin claimed that RuO_4 also behaves as a base in concentrated HNO_3,[329] Shiloh et al.'s[330] absorption spectra and electromigration results indicate no such basic behavior in HNO_3.

RuO_4 is moderately soluble in H_2O: 0.10 mol kg^{-1} at 273 K and 0.14 mol kg^{-1} at 348 K.[323] There is a relative solubility maximum at 298 K corresponding to the melting temperature of pure RuO_4 and a relative minimum at about 313 K. RuO_4 oxidizes H_2O; this is slow at low temperatures but faster at higher temperatures. Adding small amounts of Cl_2 stabilizes these solutions and only slightly affects the solubility.[323]

RuO_4 gas, liquid, and solid have been thoroughly characterized by IR, UV, and Raman spectra.[331-336] NMR spectra have been reported for RuO_4 (both ^{99}Ru and ^{101}Ru) in CCl_4.[337] Electron diffraction data indicates that gaseous RuO_4 is tetrahedral with Ru–O bond lengths of 1.706 ± 0.003 Å.[338] RuO_4 single crystals are monoclinic ($a = 9.47$, $b = 4.94$, and $c = 8.63$ Å; $\beta = 118°\ 3'$) and are isomorphic with OsO_4.[339] Since OsO_4 shows angular distortion in crystals,[340] it is likely that RuO_4 does also.

I. Thermodynamic Data for Oxides

1. $RuO_2(c)$

Heat capacity data for $RuO_2(c)$ are available only from 0.54 to 10 K.[341] They yield a Debye constant of 637 K, which is in poor agreement with a value from resistivity measurements of 900 ± 50 K.[342] Drop calorimetry data are available from 619.4 to 1174.6 K relative to 298.15 K.[301] Direct combustion of Ru(c) by $O_2(g)$ yielded an enthalpy of formation of $RuO_2(c)$ of −305.0 ± 5.9 kJ mol^{-1}.[343]

$RuO_2(c)$ decomposes directly to the elements when heated in a vacuum or in an inert atmosphere. Four detailed decomposition pressure measurements have been reported;[175,289,291,296] we extrapolated them to 298.15 K by the modified second law method. Three high-temperature emf studies were also analyzed by the same method.[344-346] Results at 298.15 K are listed in Table V. Remy's decomposition pressures[175] are quite discrepant and were not considered further. Ortner et al.'s[347a] rough pressure measurements yield $\Delta H^\circ_{298,f}(RuO_2) = -313$ kJ mol^{-1}, which is in good agreement with our recommended value.

2. $RuO(g)$, $RuO_2(g)$, $RuO_3(g)$, and $RuO_4(g)$

Raziunas et al.[309] calculated $C_{p,298} = 31.3$ J K^{-1} mol^{-1} and $S^\circ_{298} = 228.4$ J K^{-1} mol^{-1} for RuO ideal gas using their band spectra data. Scullman and Thelin[310] questioned some of those band assignments. Although Raziunas et al.[309] implied that they included electronic contributions in their calculations, their entropy is much too low. Statistical calculations by Brewer and Rosenblatt[347b] give $S^\circ_{298} = 247$ and Pedley and Marshall[347c] give 242 J K^{-1} mol^{-1}. Norman et al.[45] studied eq 42 from 1870 to 2020 K by Knudsen effusion–mass

$$Ru(c) + {}^1/{}_2O_2(g) = RuO(g) \tag{42}$$

spectrometry that yields enthalpy of formation data. We accept Pedley and Marshall's analysis[347c] that yields $S^\circ_{298}(RuO) = 242$ J K^{-1} mol^{-1}, $\Delta H^\circ_{298,f}(RuO) = 372 \pm 42$ kJ mol^{-1}, and $\Delta G^\circ_{298,f}(RuO) = 339 \pm 45$ kJ mol^{-1}.

Two statistical thermodynamic calculations[307,332] for RuO_4 ideal gas are in good agreement. They yield $C_{p,298}(RuO_4) = 75.92 \pm 0.02$ J K^{-1} mol^{-1} and $S^\circ_{298}(RuO_4) = 290.6 \pm 0.6$ J K^{-1} mol^{-1} and are our recommended values. Schäfer et al.[307] gave a least-squares fit of these heat capacities from 298.15 to 1500 K. They also reported similar results for $RuO_3(g)$ assuming the vibrational heat capacity was $\simeq {}^2/{}_3$ of the $RuO_4(g)$ value. Their calculations yield $C_{p,298}(RuO_3) = 61.67$ J K^{-1} mol^{-1} and $S^\circ_{298}(RuO_3) = 285.8 \pm 8.4$ J K^{-1} mol^{-1}.[307]

Below about 1850 K, $RuO_2(c)$ is the stable phase in an oxygen atmosphere. Total pressure measurement as a function of O_2 pressure[289,307] indicate that both eq 43 and 44 occur. At higher temperatures, or at low O_2 pressures above Ru(c), the reactions 45 and 46 also need to be considered.[45,289,307] $RuO_2(g)$ was only observed by Norman et al.[45] around 2000 K.

$$RuO_2(c) + {}^1/{}_2O_2(g) = RuO_3(g) \tag{43}$$

$$RuO_2(c) + O_2(g) = RuO_4(g) \tag{44}$$

$$Ru(c) + {}^3/{}_2O_2(g) = RuO_3(g) \tag{45}$$

$$Ru(c) + O_2(g) = RuO_2(g) \tag{46}$$

Bell and Tagami[289] studied vapor pressures for reactions 43 and 44 from 1075 to 1776 K. Schäfer et al.[307] did similar measurements from about 1000 to 1500 K. They separated their results into RuO_3 and RuO_4 pressures. Alcock and Hooper[308] studied vapor pressures above solid RuO_2 (not above Ru as thought by them) from 1473 to 1673 K. Norman et al.[45] used Knudsen-effusion mass spectrometry to study reactions 45 and 46.

The above data sets were extrapolated to 298.15 K by the third-law method using statistical thermodynamic properties of gaseous RuO_3 and RuO_4[307,332] and our recommended results for $RuO_2(c)$. They yield enthalpies of formation of $RuO_3(g)$ of −76.6,[289] −62.3,[307] −75.3,[308] and −68.8 kJ mol^{-1}.[45] The recommended value is the average of $\Delta H^\circ_{298,f}(RuO_3) = -70.8 \pm 6.6$ kJ mol^{-1}. Enthalpies of formation of $RuO_4(g)$ are −202.8[289] and −189.7 kJ mol^{-1}.[307] The recommended average is $\Delta H^\circ_{298,f}(RuO_4) = -196.3 \pm 9.2$ kJ mol^{-1}. Use of the statistical entropy values then gives $\Delta G^\circ_{298,f}(RuO_3) = -55.8 \pm 9.1$ kJ mol^{-1} and $\Delta G^\circ_{298,f}(RuO_4) = -152.1 \pm 9.3$ kJ mol^{-1}. Norman et al.[45] estimated an entropy of formation of RuO_4 vapor from their results that is consistent with our recommended value.

TABLE VI. Thermodynamic Data for RuO_4(g,l,c,aq) at 298.15 K

property	$\Delta H°$(initial)[a]	$\Delta H°$(final)[a]	$\Delta S°$(initial)[b]	$\Delta S°$(final)[b]
f,g	−196.3 ± 9.2	−192.7 ± 4.0	−148.1 ± 0.6[c]	−148.1 ± 0.6[c]
f,l	−229.7 ± 8.4	−235.7 ± 4.2		
f,c	−244.3 ± 7.1	−244.4 ± 4.4		
f,aq	−240.6 ± 4.6	−238.1 ± 4.7		
fus	8.5 ± 2.5	8.7 ± 3.3	28.4 ± 9.2	27.7 ± 0.5
subl	51.2 ± 2.5	51.7 ± 3.3	135.8 ± 8.8	136.6 ± 0.5
vap	42.7 ± 0.8	43.0 ± 3.3	107.7 ± 2.9	108.9 ± 0.5
vol	46.4 ± 0.8	45.4 ± 3.3	136.0 ± 3.3	133.9 ± 0.5
sol,c	7.2 ± 0.0	6.3 ± 3.3	7.2 ± 0.4	2.7 ± 0.5
sol,l	−2.2 ± 0.4	−2.4 ± 3.3	−24.3 ± 1.3	−25.0 ± 0.5

[a] Units are kJ mol^{-1}. [b] Units are J K^{-1} mol^{-1}. [c] Not adjusted since this is the only phase for which absolute values of formation entropies can be assigned.

Norman et al.[45] studied reaction 46 from 1740 to 2040 K. At the mean temperature of 1890 K, $\Delta H°_{1890,f}(RuO_2)$ = 118.8 ± 4.2 kJ mol^{-1}, $\Delta G°_{1890,f}(RuO_2)$ = 130.7 ± 4.2 kJ mol^{-1}, and $S°_{1890}(RuO_2)$ = 339 J K^{-1} mol^{-1}. Plotting $S°_{298}$ for Ru, RuO, RuO_3, and RuO_4 gas suggests that $S°_{298}(RuO_2) \simeq 270$ J K^{-1} mol^{-1} for the vapor. This is in fair agreement with Brewer and Rosenblatt's[347b] statistical thermodynamic value, using an assumed electronic ground state, of 261 J K^{-1} mol^{-1}. The average of 265 ± 5 J K^{-1} mol^{-1} is accepted. If, as a rough approximation, we let $\Delta H°_{298,f}(RuO_2) \simeq \Delta H°_{1890,f}(RuO_2)$, then $\Delta G°_{298,f}(RuO_2) \simeq 110$ kJ mol^{-1} for the vapor.

A check on the statistical thermodynamic calculations was made by reanalyzing the high-temperature results for RuO_3(g) and RuO_4(g) by the modified second-law method. This calculation yields $S°_{298}(RuO_3)$ = 280.7 ± 5.6 J K^{-1} mol^{-1} and $S°_{298}(RuO_4)$ = 280.3 ± 6.3 J K^{-1} mol^{-1}. Results from the two methods are in reasonably good agreement, which increases our confidence in them.

3. Self-Consistent Results for RuO_4(g), RuO_4(l), RuO_4(c), and RuO_4(aq)

In addition to the gas phase data for RuO_4 discussed in the previous section, thermodynamic data are available for its liquid, solid, and aqueous solutions. These data are interrelated by phase transition results.

Nikol'skii and Ryabov[326] measured enthalpies of reduction of RuO_4(l) and RuO_4(c) with NH_3 to form RuO_2(c) and Ru(c). Recalculation to our RuO_2(c) results yields $\Delta H°_{298,f}(RuO_4(l))$ = −229.7 ± 8.4 kJ mol^{-1} and $\Delta H°_{298,f}(RuO_4(c))$ = −244.3 ± 7.1 kJ mol^{-1}. Mercer and Farrar[348] used calorimetric measurements to obtain $\Delta H°_{298,f}(RuO_4(aq))$ = −240.6 ± 4.6 kJ mol^{-1}.

Nikol'skii[321] measured RuO_4 vapor pressures above solid RuO_4 from 273.7 to 298 K and liquid to 364 K. Vapor pressures were measured for aqueous solutions from 286 to 364 K.[349,350] Slight deviations from Henry's law were observed above about 0.02 mol L^{-1}. They observed a change in slope in Henry's law constants around 298 K, which corresponds to the RuO_4 melting point. There is no reason why the Henry's law constant should change at 298 K, so we refit their data in this region to obtain an average enthalpy of volatilization. Remy[323] reported solubilities for aqueous RuO_4 from 273 to 348 K. Small amounts of Cl_2 were added to stabilize these solutions and prevent reduction of RuO_4; Remy showed that adding Cl_2 had little effect on solubility. He reported the density of the saturated solution at 293 K. By assuming densities were linear with concentration and that expansibilities of these dilute solutions were the same as pure water, we converted his molarities to molalities. An enthalpy of solution of liquid RuO_4 was also reported by Mercer and Farrar.[348]

TABLE VII. Final Data for RuO(g), RuO_2(g,c), RuO_3(g), and RuO_4(g,l,c,aq) at 298.15 K

oxide	$\Delta G°_{298,f}$, kJ mol^{-1}	$\Delta H°_{298,f}$, kJ mol^{-1}	$S°_{298}$, J K^{-1} mol^{-1}
RuO(g)	339 ± 45	372 ± 42	≃242
RuO_2(g)	≃110	≃119	≃265 ± 5
RuO_3(g)	−55.8 ± 9.1	−70.8 ± 6.6	285.8 ± 8.4
RuO_4(g)	−148.5 ± 4.1	−192.7 ± 4.0	290.6 ± 0.6
RuO_4(c)	−159.5 ± 4.6	−244.4 ± 4.4	154.0 ± 1.1
RuO_4(l)	−159.1 ± 4.6	−235.7 ± 4.2	181.7 ± 1.1
RuO_4(aq)	−154.0 ± 5.0	−238.1 ± 4.7	156.7 ± 1.1
RuO_2(c)	−253.1 ± 8.2	−307.2 ± 7.8	52.2 ± 8.7

These data yield enthalpies of sublimation (c → g), vaporization (l → g), solution (c → aq or l → aq), and volatilization (aq → g). Table VI summarizes these results. A $\Delta H°_{298,f}$ can be assigned for each phase, but $\Delta S°_{298}$ are for phase transitions only. These entropies of transition can then be used to generate absolute values since the entropy of RuO_4(g) is known from statistical thermodynamic calculations.

Various combinations of thermodynamic data can be taken to calculate the same quantity. For example, the enthalpy of formation of RuO_4(g) at 298.15 K is known directly from high-temperature vapor pressure measurements. However, it also is equal to the enthalpy of formation of the solid plus the enthalpy of sublimation. It also equals the enthalpy of formation of liquid plus the enthalpy of vaporization etc. Similar relationships hold for the other quantities. When all possible combinations were compared, it was seen that $\Delta H°_{298,f}(RuO_4(l))$ and $\Delta S°$ for the solution of the solid are slightly discrepant from other measured values. They were given low weight, and various combinations of the other data made to calculate each thermodynamic value. These combinations were averaged to obtain new values for each property, and the calculations were repeated until self-consistency was achieved. Table VI compares the input and final self-consistent enthalpy and entropy results for RuO_4. Table VII summarizes data for all of the binary oxides.

J. Double Oxides, Hydroxides, and Ruthenium Red and Brown

This section is a brief discussion of double oxides, hydroxides, and ruthenium red and brown. It is not intended to be exhaustive but is only designed to show what kinds of clusters and valence states occur. This will provide evidence as to what kinds of species could exist in aqueous solutions. Hydrated oxides and/or hydrated hydroxides that precipitate from aqueous solution will be discussed in the aqueous chemistry section.

When RuO_4 is added to aqueous hydroxide solutions, reduction to perruthenate or ruthenate ions can occur depending on temperature and concentration of base. Perruthenate salts can be made by using 0.1–1.0 mol L^{-1} base and chilling immediately after mixing. Several days at room temperature gives ruthenate salts.[2,318,351] Green perruthenate solutions are generally considered to contain RuO_4^- ions and yellow-orange to orange-red ruthenate solutions RuO_4^{2-} ions. For pH values much below 10 for RuO_4^- and 12 for RuO_4^{2-}, they disproportionate to form $RuO_2{\cdot}mH_2O$ or $Ru_2O_5{\cdot}mH_2O$ and RuO_4.[352] The RuO_4/RuO_4^- and RuO_4^-/RuO_4^{2-} redox potentials are independent of pH[351,353] in basic solutions so it is usually assumed that all three species have similar stoichiometries.

Silverman and Levy[351,354] determined the crystal structure of black $KRuO_4$. It has the scheelite structure with $a = 5.60 \pm 0.002$ Å and $c = 12.991 \pm 0.002$ Å. Bond lengths and crystal parameters are almost identical with those for KIO_4. The Ru atom is surrounded by four oxygens in a very nearly regular tetrahedron. They estimated an ionic radius of 0.54 Å for Ru^{7+} from these data.

A number of solid ruthenate salts have been described: K_2RuO_4, Rb_2RuO_4, $Rb_2RuO_4{\cdot}H_2O$, Cs_2RuO_4, $Cs_2RuO_4{\cdot}H_2O$, $Na_2RuO_4{\cdot}2H_2O$, Ag_2RuO_4, $MgRuO_4{\cdot}mH_2O$, $CaRuO_4{\cdot}mH_2O$, $SrRuO_4{\cdot}mH_2O$, and $BaRuO_4{\cdot}H_2O$.[2,355] Popova et al.[356] determined powder pattern structures for $CaRuO_4{\cdot}2H_2O$, $BaRuO_4{\cdot}H_2O$, $SrRuO_4{\cdot}H_2O$, and $PbRuO_4{\cdot}H_2O$. The Ca salt was reported to be cubic, and Ba and Sr salts were reported to be hexagonal and Pb salt tetragonal. The only one with single-crystal structural data is the red salt "$BaRuO_4{\cdot}H_2O$", which does not contain a ruthenate ion.[357] It has a rhombohedral cell with a hexagonal subcell due to stacking defects. This salt contains dihydroxotrioxoruthenate (VI) ions with a trigonal-bipyramid configuration: $[RuO_3(OH)_2]^{2-}$ with Ru–O bonds of 1.755 Å and Ru–OH bonds of 2.02 Å. "$SrRuO_4{\cdot}H_2O$" is isostructural so it should be similar. No anhydrous salts have been studied in enough detail to see if they contain RuO_4^{2-} tetrahedra.

Aqueous solutions of RuO_4 behave as a weak acid, which is usually written as H_2RuO_5.[329,351] Consistency with the "$BaRuO_4{\cdot}H_2O$" structural information is obtained if H_2RuO_5 is actually $RuO_3(OH)_2$. Carrington and Symons[358] studied the reduction of perruthenate by NaOH solutions and found it necessary to invoke $RuO_4(OH)_2^{3-}$ as a steady-state intermediate. It might be worth trying to reinterpret their data on the basis of $RuO_3(OH)_2^-$ instead.

It is difficult to explain isolation of $KRuO_4$ rather than $KRuO_3(OH)_2$, and no pH dependences for redox couples involving RuO_4^{2-}, RuO_4^-, and RuO_4 unless one of the following two possibilities is true: (1) RuO_4^m (m = 0, 1–, or 2–) solutions actually consist of a mixture of RuO_4^m and $RuO_3(OH)_2^m$ (similar to aqueous CO_2 containing H_2CO_3). "H_2RuO_5" is a weak acid, and "$H_2RuO_5^-$" and "$H_2RuO_5^{2-}$" would be expected to be even weaker acids. The lack of a pH dependence in redox couples would then be due to the $RuO_3(OH)_2^m$ forms with m = 1–, 2– being acids that are too weak to significantly dissociate at the pH values studied (pHs of 9 to 12). (2) The other possibility is either $RuO_3(OH)_2^m$ or RuO_4^m is present initially, but it slowly transforms to the other structural form. Whichever the case may be, we will write the solution species as H_2RuO_5 and RuO_4^m for the purpose of thermodynamic calculations. A detailed Raman spectra investigation might help to clarify the speciation.

Several solid oxides have been reported for Ru(V). They have the empirical formulas Li_7RuO_6,[359] $BaM_{1/3}Ru_{2/3}O_3$ with M = Mg, Ca, Cd, or Sr,[360] Na_3RuO_4,[361] and La_2LiRuO_6.[362] Greatrex et al.[363] described a number of double perovskites of Ru(V). Some of these compounds contain $Ru_2O_9^{8-}$ or $Ru_4O_{16}^{12-}$ clusters.[360,361] The double perovskites[363] have Ru surrounded by oxygens. Synthesis of $Bi_3Ru_3O_{11}$ has been claimed, which must contain +4 and +5 or +4 and +6 Ru.[364]

Various double oxides of Ru(IV) are well-known. They include $BaRuO_3$ with its strings of face-sharing RuO_6^{8-} octahedra,[365,366] Ln_2RuO_5 (Ln = Pr to Tb) with its chain structure,[367] various pyrochlores such as $Y_2Ru_2O_7$ and $Bi_2Ru_2O_7$,[368,369] and a number of more complicated Na^+ and Bi^{3+} double oxides.[364,370] Recently, salts with the empirical formula $Ln_2[Ru(OH)_6]_3{\cdot}mH_2O$ (Ln = lanthanide) have been reported,[371] but they could be oxyhydroxides instead.

Mixed-valence clusters of Ru(III) and Ru(IV) are known: KRu_4O_8 contains RuO_6 octahedra,[372] whereas $Ru_3O_{12}^{13-}$ clusters occur in $Ba_4NbRu_3O_{12}$ and $Ba_4TaRu_3O_{12}$.[373]

The above double oxides show that monomeric, dimeric, trimeric, and tetrameric clusters of Ru are known, and they can be homovalent or mixed valent ($3^2/_3 \le Z \le 7$). Probable trimers and tetramers were described in the sulfate section, and monomers, dimers, and trimers in the chloride and oxychloride sections. Similar situations may occur in aqueous solutions; the above considerations indicate that tetramers are the highest order clusters to be expected (outside of colloids).

Another compound of some interest is ruthenium red, which is prepared by reacting "hydrated $RuCl_3$" with aqueous ammonia in the presence of air.[2] It is used extensively in optical microscopy to stain tissue, and it even stains isolated DNA. For electron microscopy the tissue is usually also reacted with OsO_4 to provide a stronger contrast.[374,375] A one-electron oxidation of it produces ruthenium brown, which probably has a nearly identical structure.[376,377]

Joly thought ruthenium red was $Ru_2Cl_4(OH)_2{\cdot}7NH_3{\cdot}3H_2O$,[2] whereas Morgan and Burstall[378] claimed it was $[Ru(OH)Cl(NH_3)_4]Cl{\cdot}H_2O$. Sterling[379] reported it was $[Ru_3Cl_8(OH)_3(NH_3)_{12}(H_2O)_3]$ on the basis of crystal structure determination. However, his experimental description (i.e., pink crystals with much amorphous brown material) suggests an oxidation or degradation product was actually studied.

Fletcher et al.[376] investigated stoichiometry, oxidation states, IR, absorption spectra, and electrochemistry. They suggested that ruthenium red contains the cation $[(NH_3)_5Ru{-}O{-}Ru(NH_3)_4{-}O{-}Ru(NH_3)_5]^{6+}$ with an average Ru oxidation state $^{10}/_3$; ruthenium brown then contains $[(NH_3)_5Ru{-}O{-}Ru(NH_3)_4{-}O{-}Ru(NH_3)_5]^{7+}$.

This structure was confirmed by a structure determination of the ruthenium red salt $[Ru_3O_2(NH_3)_{14}](S_2O_3)_3{\cdot}4H_2O$.[375] The Ru-O-Ru-O-Ru backbone is nearly linear, and the ion is cylindrically shaped. Resonance Raman spectra[375,377] indicates that ruthenium brown has the same structure and that both cations have basically the same shape in solutions. These are examples of mixed-valence oxygen-bridged trimers in solution.

V. Aqueous Solutions and Hydrated Oxides/Hydroxides

A. Upper Valence States: Ru(VI), Ru(VII), and Ru(VIII)

When RuO_4 is dissolved in aqueous solution it behaves like a weak acid. Its dissociation is usually written as in eq 47, but, as noted earlier, H_2RuO_5 may

$$H_2RuO_5 = H^+ + HRuO_5^- \qquad (47)$$

actually be $RuO_3(OH)_2$. Two studies have been made of its dissociation constant using liquid extraction with CCl_4 from alkaline solutions of RuO_4.[329,351] These measurements were done rapidly to avoid reduction of RuO_4 by the base. RuO_4 in CCl_4 obeys Henry's law so it is not necessary to correct for nonideal behavior.[329]

Martin[329] obtained a dissociation constant of $(6.8 \pm 0.3) \times 10^{-12}$ mol L^{-1} at 293 K. The NaOH concentration was varied from 0.000 94 to 0.0094 mol L^{-1}; reduction of RuO_4 was observed only at higher NaOH concentrations. Silverman and Levy[351] obtained $(1.3 \pm 0.2) \times 10^{-12}$ mol L^{-1} at 298 K, and the NaOH concentration was varied from 0.011 to 0.043 mol L^{-1}. In neither case was there a trend with NaOH concentration and, consequently, none with ionic strength. The data are too sparse to determine whether a significant temperature dependence was present. Consequently, the values were averaged on the natural log scale, $\ln K'_{2,1} = -26.54 \pm 0.83$, and assumed equal to the zero ionic strength value at 298.15 K. (For $K_{i,j}$ values given in this paper, the first subscript indicates the number of dissociable ligands present in the reactant and the second subscript for the product. Obviously $K_{i,j} = K_{j,i}^{-1}$. Also, thermodynamic constants are denoted by $K^\circ_{i,j}$, whereas $K'_{i,j}$ indicates an "apparent" constant or concentration product.)

The Gibbs energy of formation of $H_2RuO_5(aq)$ is given by

$$\Delta G^\circ_{298,f}(H_2RuO_5(aq)) = \Delta G^\circ_{298,f}(RuO_4(aq)) + \Delta G^\circ_{298,f}(H_2O(l)) = -391.2 \pm 5.0 \text{ kJ mol}^{-1} \qquad (48)$$

For $HRuO_5^-(aq)$

$$\Delta G^\circ_{298,f}(HRuO_5^-(aq)) = \Delta G^\circ_{298,f}(H_2RuO_5(aq)) - RT \ln K^\circ_{2,1} = -325.4 \pm 7.1 \text{ kJ mol}^{-1} \qquad (49)$$

Martin[329] reported that $K'_{0,1} = (5.7 \pm 0.8) \times 10^{-15}$ mol^{-1} L for the protonation of RuO_4. Goldberg and Hepler[18] used this value to obtain $\Delta G^\circ_{298,f}(HRuO_4^+(aq))$. However, Shiloh et al.[330] cast doubt on the existence of this behavior so we do not report a value for this species.

Reduction of RuO_4 by aqueous base can produce both RuO_4^- and RuO_4^{2-} ions depending on conditions.[351] RuO_4^- usually forms first and eventually converts to RuO_4^{2-}. The rate of RuO_4^{2-} formation increases with pH. For example, 30% RuO_4^{2-} is present after 1 day in 1 mol L^{-1} NaOH, but 100% forms by then in 4 mol L^{-1} and higher base concentrations.[380] Adding hypochlorite stabilizes RuO_4^- under some conditions. Acidification of these solutions causes rapid disproportionation. Impurities present in most commercial NaOH will reduce RuO_4^- to RuO_4^{2-} or even to $RuO_2{\cdot}2H_2O(s)$, especially if the NaOH was stored in polyethylene bottles.[380,381] RuO_4^{2-} is stable in aqueous solution, but only under fairly alkaline and nonreducing conditions. Under more oxidizing conditions RuO_4^- can also be stabilized.

Electron exchange between RuO_4^- and RuO_4^{2-} takes place in less than 5 s.[382] Radiolysis of alkaline RuO_4^{2-} with X-rays produces $RuO_2{\cdot}mH_2O$ with RuO_4^- being an intermediate.[383]

Several attempts have been made to interpret spectra of RuO_4^- and RuO_4^{2-} ions. Some of the expected charge transfer bands have been identified, but others have not.[358,384-386] They are not well enough characterized to distinguish RuO_4^{n-} from $RuO_3(OH)_2^{n-}$.

Silverman and Levy[351,353] determined the reduction potential for eq 50 in aqueous base (pH 9–12.1) at 298

$$RuO_4 + e^- = RuO_4^- \qquad (50)$$

K and at ionic strengths of 0.04 and 0.10 mol L^{-1}. Polarographic measurements gave 1.00 ± 0.02 V at $I = 0$. They were pH-independent one-electron reductions. Similar measurements by Lam et al.[318] gave 0.997 ± 0.008 V at $I = 1$ and pH 11–12. Eichner[387] obtained 0.99 V for pH <12 using a vitreous carbon electrode. Connick and Hurley[388] reported 0.99 ± 0.02 V by using the RuO_4/RuO_4^- potential and an equilibrium involving $RuO_2{\cdot}mH_2O$. We prefer to use their results[388] to obtain values for the solid phase instead.

Best value for RuO_4/RuO_4^- potential is 0.996 ± 0.005 V. Then, $\Delta G^\circ_{298,rxn} = -96.1 \pm 0.5$ kJ mol^{-1} and

$$\Delta G^\circ_{298,f}(RuO_4^-(aq)) = \Delta G^\circ_{298,f}(RuO_4(aq)) + \Delta G^\circ_{298,rxn} = -250.1 \pm 5.5 \text{ kJ mol}^{-1} \qquad (51)$$

Similar measurements have been made for eq 52 which also has a reversible one-electron potential in basic solution. Silverman and Levy[351,354] obtained 0.59 V

$$RuO_4^- + e^- = RuO_4^{2-} \qquad (52)$$

from data at $I = 0.04$ and 0.10 extrapolated $I = 0$, Connick and Hurley[389] also obtained 0.59 V by direct potential measurement, and Eichner[387] got 0.57 V. Luoma and Brubaker[390] studied the equilibrium

$$K = \frac{[RuO_4^{2-}][MnO_4^-]}{[RuO_4^-][MnO_4^{2-}]} \qquad (53)$$

Using Carrington and Symons's results[391] for the MnO_4^-/MnO_4^{2-} couple yields 0.594 ± 0.003 V for reaction 52. Best value for the RuO_4^-/RuO_4^{2-} aqueous potential is the average of 0.586 ± 0.011 V. Thus

$$\Delta G^\circ_{298,f}(RuO_4^{2-}(aq)) = \Delta G^\circ_{298,f}(RuO_4^-(aq)) + \Delta G^\circ_{298,rxn} = -306.6 \pm 6.6 \text{ kJ mol}^{-1} \qquad (54)$$

Avdeev et al.[392] studied the electrical reduction of RuO_4 in H_2SO_4 solutions. Reduction initially proceeded by eq 55 where RuO_2^{2+} is the unstable green interme-

$$RuO_4 + 2e^- + 4H^+ = RuO_2^{2+} + 2H_2O \qquad (55)$$

diate discussed earlier. A smaller than expected consumption of electricity was observed for reaction 55, which they attributed to decomposition of RuO_2^{2+} and/or only an electroactive substance being reduced. They reported a two-electron reduction of this RuO_2^{2+} to Ru(IV) at various H_2SO_4 concentrations. Interpolation to unit H^+ activity gives 1.29 ± 0.02 V for the formal reduction potential. They considered the final reduction product to be RuO^{2+} ($Ru(OH)_2^{2+}$ for our purposes), but their pH dependence of H^+:e^- (1:2) indicates that $Ru_4(OH)_{12}^{4+}$ is more likely. However, since this potential may involve sulfate complexes of uncertain compositions, it was not used for thermodynamic calculations. RuO_4^{3-} was suggested as an intermediate in the reduction of RuO_4^{2-} by γ-radiolysis,[383] but no thermodynamic data are available for it.

The reduction of RuO_4^- by OH^- occurs by the overall reaction[358,393a] eq 56 but follows the kinetic rate law of eq 57 for 10^{-2} to 10^{-3} mol L^{-1} RuO_4^-. This rate law is

$$2RuO_4^- + 2OH^- = 2RuO_4^{2-} + H_2O + {}^1/_2O_2(g) \qquad (56)$$

$$-\frac{d[RuO_4^-]}{dt} = K^*[RuO_4^-]^2[OH^-]^3 \qquad (57)$$

higher order in OH^- than expected from reaction stoichiometry, and a rather complicated mechanism has been proposed to account for this.[358] At lower RuO_4^- concentrations, Nikitina et al.[393b] found that the reduction kinetics were more complicated and also lower order in $[OH^-]$.

Mercer and Farrar[348] studied the oxidation of Ru(c) using Br_2(l) in aqueous NaOH solution. The solution became green initially due to RuO_4^- formation, but within 10 min all of this was converted to RuO_4^{2-} as indicated by spectroscopic data. Their measurements yield $\Delta H°_{298,f}(Na_2RuO_4(aq)) = -937.6 \pm 3.3$ kJ mol^{-1}. Thus

$$\Delta H°_{298,f}(RuO_4^{2-}(aq)) = \Delta H°_{298,f}(Na_2RuO_4(aq)) - 2\Delta H°_{298,f}(Na^+(aq)) = -457.0 \pm 3.4 \text{ kJ mol}^{-1} \qquad (58)$$

Combining this result with the free energy data yields $S°_{298}(RuO_4^{2-}(aq)) = 64.9 \pm 34$ J K^{-1} mol^{-1}.

No direct measurement is available for the enthalpy of formation of aqueous RuO_4^-. However, Luoma and Brubaker[390] studied reaction 59 whose equilibrium

$$RuO_4^- + MnO_4^{2-} = RuO_4^{2-} + MnO_4^- \qquad (59)$$

constant is given by eq 53. The equilibrium constant was measured at 293.2, 297.9, and 305.2 K. Their data yield $\Delta H°_{298,rxn} = -13.3$ kJ mol^{-1} and $\Delta S°_{298,rxn} = -33.0$ J K^{-1} mol^{-1}. However

$$\Delta H°_{298,rxn} = \Delta H°_{298,f}(RuO_4^{2-}) + \Delta H°_{298,f}(MnO_4^-) - \Delta H°_{298,f}(RuO_4^-) - \Delta H°_{298,f}(MnO_4^{2-}) \qquad (60)$$

Using NBS technical note 270-4 values[394] for MnO_4^- and MnO_4^{2-} gives $\Delta H°_{298,f}(RuO_4^-(aq)) = -332.4 \pm 18$ kJ mol^{-1}, assuming moderate uncertainties for MnO_4^- and MnO_4^{2-} data. Then, $S°_{298}(RuO_4^-(aq)) = 224.9 \pm 79$ J K^{-1} mol^{-1}.

Although the entropies of RuO_4^{2-} and RuO_4^- are fairly uncertain, they certainly fall within the range for other ions of these types. In fact, semiempirical correlations of entropies of oxyanions would probably yield better estimates.

B. Hydrated Oxides and/or Hydroxides

We earlier discussed anhydrous oxides and double oxides of Ru (sections IV.H and IV.J). Only RuO_2 and RuO_4 are known as pure binary solid oxides, but ternary oxides were described with Ru valences from $3^2/_3 \le Z \le 7$. This present section considers hydrated oxides $Ru_xO_y\cdot zH_2O$ and hydroxides $Ru(OH)_x\cdot yH_2O$. A number of claims were made in the earlier literature for hydrated oxides and hydroxides of Ru(II), Ru(III), Ru(IV), and Ru(V).[1,2] Many of these claims are suspect especially for Ru(II) and Ru(V).

A black amorphous Ru(IV) substance is well-known from reduction of upper valence RuO_4^{n-} or by making Ru(IV) solutions less acid to cause precipitation. It has been formulated at various times as $Ru(OH)_4$, $RuO_2\cdot mH_2O$, $RuO_2\cdot 2H_2O$, etc. and $RuO(OH)_2\cdot H_2O$ could be added to this list. Connick and Hurley[389] and Gortsema and Cobble[276] reported samples with empirical compositions of $RuO_2\cdot 2H_2O$. Fletcher et al.[395] got samples with 1.0–1.3 waters by using H_2O_2 reduction of RuO_4. In contrast, $RuO_2\cdot H_2O$ was obtained with H_2 reduction.[396] It should be noted that H_2O_2 reduces RuO_4 to Ru(IV) in aqueous noncomplexing acidic media, but in fairly basic media H_2O_2 reduces it to RuO_4^{2-}.[389]

Thin films of $RuO_2\cdot mH_2O$ show a strong and continuous IR band from the visible end to about 45 μm which masks any vibration bands due to H_2O or OH. This was attributed to the presence of electronic conduction bands.[395] Since $RuO_2\cdot mH_2O$ can be prepared with $1 \le m \le 2$ and since the water is lost gradually upon heating (more rapidly above 470 K),[395,396] these are probably hydrated oxides rather than hydroxides. They will be treated as $RuO_2\cdot 2H_2O$ for the purpose of thermodynamic calculations, but individual samples could be lower hydrates.

Precipitated solids from Ru(III) solutions have been described as yellow, brown, green, or black.[2,184,253] Pure "$Ru(OH)_3\cdot H_2O$" is probably yellow, but it is so sensitive to traces of O_2 that darker colors are usually found due to partial oxidation to Ru(IV). Duvigneaud and Reinhard-Derie[184] cited a thesis by Hanke in which a yellowish green Ru(III) hydroxide was precipitated that contained the 3560 cm^{-1} IR band for OH. They[184] gave the formula as $Ru(OH)_3\cdot H_2O$, but $RuO(OH)\cdot 2H_2O$ is also possible. We will assume the formula $Ru(OH)_3\cdot H_2O$ for thermodynamic calculations. These are equivalent to Ru_2O_3 in the older literature.[1,2]

Bardin and Tkhan[397] and Trojánek[398] studied reduction of RuO_4^{2-} in alkaline media using cyclic voltammetry, and both reported that "Ru_2O_5" formed during reduction. It was unstable in concentrated base and rapidly disproportionated to $RuO_2\cdot 2H_2O$ and RuO_4^{2-}. Neither Eichner[387] or Lam et al.[318] detected this "Ru_2O_5" intermediate. Lam et al. also found evidence that reduction of RuO_4^{2-} in base changed mechanisms about pH 12.1. They suggested that unstable $Ru(OH)_6^{2-}$ occurs during reduction of RuO_4. "$Ru(OH)_3$" has also been claimed from reduction of RuO_4^{2-} in base, but it readily oxidized to Ru(IV).[398] The above information indicates that "Ru_2O_5" and "$Ru(OH)_3$" can sometimes form by chemical or electrolytic reduction in basic solutions, but they readily disproportionate or oxidize to $RuO_2\cdot 2H_2O$.

In acidic solutions of $HClO_4$, HNO_3, etc. it is well-known that reduction of RuO_4 by H_2O_2 produces soluble polymeric Ru(IV) species, and the same products also form at lower H_2SO_4 concentrations. Most reducing agents produce what appears to be RuO_2^{2+} as an unstable intermediate during reduction of RuO_4 in H_2SO_4. It is much easier to detect the RuO_2^{2+} if a several fold excess of RuO_4 is present or if slow addition of reducing agent is used.[144,399] Its not clear if RuO_2^{2+} is a direct reduction product of RuO_4 or whether reaction of Ru(IV) with excess RuO_4 produces it. Reaction of freshly prepared Ru(IV) with RuO_4 gives RuO_2^{2+} readily, whereas aged Ru(IV) solutions do not.[144] This may possibly indicate that only monomeric but not polymeric Ru(IV) can give this reaction. RuO_2^{2+} gradually decomposes to Ru(IV) and RuO_4 over a several hour period. Electrolytic reduction of RuO_4 in H_2SO_4 at about 1.35 V vs. NHE gives RuO_2^{2+} also.[392]

Acidification of RuO_4^- and RuO_4^{2-} salts is generally assumed to yield $RuO_2{\cdot}mH_2O$ by disproportionation. However, a careful and detailed study by Nowogrocki and Tridot[352] showed that $Ru_2O_5{\cdot}mH_2O$ is produced instead. They acidified RuO_4^- and RuO_4^{2-} solutions and monitored them by spectrophotometry, pH, and conductance measurements. All of these data indicate formation of $Ru_2O_5{\cdot}mH_2O$ (assuming that a hydrated oxide forms and not a hydroxide). The appropriate reactions seem to be eq 61 and 62 where "am" denotes

$$2RuO_4^{2-} + 3H^+ = RuO_4^- + {}^1/_2Ru_2O_5(am) + {}^3/_2H_2O(l) \quad (61)$$

$$3RuO_4^- + 3H^+ = 2RuO_4 + {}^1/_2Ru_2O_5(am) + {}^3/_2H_2O(l) \quad (62)$$

an amorphous solid. Since RuO_4^- produced in reaction 61 also decomposes, the "global" decomposition reaction for RuO_4^{2-} is eq 63. We shall treat Ru_2O_5 as being unhydrated since its extent of hydration is unknown.

$$3RuO_4^{2-} + 6H^+ = RuO_4 + Ru_2O_5 + 3H_2O \quad (63)$$

Avdeev et al.[392] produced a black hydrous oxide by controlled potential reduction of RuO_4 in 0.5 mol L^{-1} H_2SO_4 at 1.12 V. Coulometric analysis indicated a valence of +4.95 ± 0.05 for this material. It is insoluble in H_2O and H_2SO_4, but it dissolves in H_2SO_4 containing Ru(IV) to produce a Ru polymer with average valence of $\simeq$4.2.[400] This solution species is probably just an oxidized form of the tertamer $Ru_4(OH)_{12}^{4+}$ described earlier. El Guebely and Haissinsky[401] also found that Ru_2O_5 could be produced by reduction of RuO_4 or oxidation of $RuO_2{\cdot}mH_2O$, but the evidence for it in that study is less convincing. It was not detected in the reduction of RuO_4 by $NaBH_4$.[399]

The above discussion should indicate the source of much of this confusion. Both $RuO_2{\cdot}mH_2O$ and $Ru_2O_5{\cdot}mH_2O$ can form under similar conditions; both are black and amorphous; and the number of associated waters may be variable. All of this makes it difficult to characterize them. Either of them can form by reduction of RuO_4^- and RuO_4^{2-} under slightly different conditions in acidic media, but in basic solution $RuO_2{\cdot}mH_2O$ seems to be the final product. Actually, available data are for fairly acid and for fairly basic solutions, so it is not clear below which pH Ru_2O_5 becomes stable.

Connick and Hurley[389] studied the alkaline solution equilibrium eq 64 where we assumed the dihydrate

$$3RuO_4^{2-} + 4H_2O = 2RuO_4^- + RuO_2{\cdot}2H_2O(am) + 4OH^- \quad (64)$$

formed. At zero ionic strength they obtained

$$K° = \frac{[RuO_4^-]^2[OH^-]^4}{[RuO_4^{2-}]^3} = (6 \pm 3) \times 10^{-9}\ mol^3\ L^{-3} \quad (65)$$

where the uncertainty limit is our estimate from their scatter. The water activity was assumed $\simeq$1 in this calculation. Thus, $\Delta G°_{rxn} = -RT \ln K° = 46.9 \pm 1.0$ kJ mol^{-1} and $\Delta G°_{298,f}(RuO_2{\cdot}2H_2O) = -692.1 \pm 14$ kJ mol^{-1}. They[388] later studied eq 66 in acid solution by using a

$$4RuO_4^- + 4H^+ = 3RuO_4 + RuO_2{\cdot}2H_2O(am) \quad (66)$$

Ru powder catalyst. It appears that $RuO_2{\cdot}mH_2O$ rather than Ru_2O_5 can form when the Ru catalyst is present. They obtained

$$K° = \frac{[RuO_4]^3}{[RuO_4^-]^4[H^+]^4} = (2.5 \pm 2.9) \times 10^{27}\ mol^{-5}\ L^5 \quad (67)$$

from which we obtain $\Delta G°_{rxn} = -156.4 \pm 1.9$ kJ mol^{-1} (again, using our uncertainty estimate from their scatter). Thus, $\Delta G°_{298,f}(RuO_2{\cdot}2H_2O) = -694.8 \pm 12$ kJ mol^{-1}.

Eichner[387] and Lam et al.[318] studied eq 68 where re-

$$RuO_4^{2-} + 2e^- + 4H_2O = RuO_2{\cdot}2H_2O(am) + 4OH^- \quad (68)$$

actions have been rewritten in terms of the dihydrate. A two-electron reduction was indicated by controlled potential coulometry,[387] and the change in potential with pH indicates H^+:e^- (2:1).[318] Eichner's results[387] yield a value of $\Delta G°_{298,f}(RuO_2{\cdot}2H_2O)$ that is significantly less negative than Connick and Hurley's results.[388,389] Lam et al.'s Figure 9 gives $\Delta G°_{rxn} \simeq -60$ kJ mol^{-1} so $\Delta G°_{298,f}(RuO_2{\cdot}2H_2O) \simeq -686$ kJ mol^{-1} from that study.[318] The recommended value is the average of −691.0 ± 13 kJ mol^{-1} excluding Eichner's results.

Data for Ru(III) hydroxide have been recalculated for the assumed stoichiometry $Ru(OH)_3{\cdot}H_2O$. Eichner[387] reported that eq 69 occurs at −0.15 V so $\Delta G°_{298,f}(Ru(OH)_3{\cdot}H_2O) = -756.4$ kJ mol^{-1}. Eichner also studied eq 70 which yields $\Delta G°_{298,f}(Ru(OH)_3{\cdot}H_2O) = -830.8$ kJ mol^{-1}.

$$RuO_2{\cdot}2H_2O + e^- + H_2O = Ru(OH)_3{\cdot}H_2O + OH^- \quad (69)$$

$$Ru(OH)_3{\cdot}H_2O + 3e^- = Ru(c) + 3OH^- + H_2O \quad (70)$$

In both cases the number of electrons involved was determined by controlled potential coulometry. Rest or open circuit potentials for "RuO_2" electrodes in acid occur at about 0.90–0.95 V[10,402] and have been interpreted as corresponding to eq 71. The average of

$$RuO_2{\cdot}2H_2O + H^+ + e^- = Ru(OH)_3{\cdot}H_2O \quad (71)$$

these rest potentials yields $\Delta G°_{298,f}(Ru(OH)_3{\cdot}H_2O) = -780.3$ kJ mol^{-1}. Horkans and Shafer[317] gave $E = 0.65$ V for eq 72 which yields $\Delta G°_{298,f}(Ru(OH)_3{\cdot}H_2O) = -760.6$ kJ mol^{-1}.

$$Ru(OH)_3{\cdot}H_2O + 3H^+ + 3e^- = Ru + 4H_2O \quad (72)$$

The average of the three values in best agreement −766 ± 13 kJ mol^{-1} is recommended. Eichner's discrepant value[387] for reaction 70 was rejected since the reaction on which it is based has been disputed.[397]

We have less confidence in this value than for most others for several reasons: (1) $Ru(OH)_3{\cdot}H_2O$ is so readily oxidized that most samples are probably mixtures with $RuO_2{\cdot}2H_2O$.[403] (2) Reactions 71 and 72 were hypothesized by workers, and for reaction 72 no determination of electrons or hydrogen ions was involved. However, rest potentials do show the expected reversible slope of 0.059 V $(pH)^{-1}$, from pH 1 to pH 12, for reaction 71.[10] (3) "RuO_2" electrodes are prepared by thermal decomposition of "$RuCl_3{\cdot}mH_2O$", and it is unclear under which working conditions full hydration to $RuO_2{\cdot}2H_2O$ occurs. In fact, Galizzioli et al.[404a] noted differences in the potential/current responses between fresh (unhydrated) RuO_2 film electrodes and those (probably hydrated) that had undergone potential cycling. Thermally prepared RuO_2 is more stable with regard to reduction than (presumably hydrated) RuO_2 formed anodically on Ru.[404a] This causes a possible uncertainty of up to 36 kJ mol^{-1} in ΔG. We consider our value for $Ru(OH)_3{\cdot}H_2O$ to be provisional until better results become available. The uncertainty in ΔG°_f means that redox potentials involving $Ru(OH)_3{\cdot}H_2O$ could be uncertain by up to $0.190/Z$ V, where Z is the number of electrons involved.

It is also possible to obtain approximate data for Ru_2O_5. Bardin and Tkhan[397] reported data for eq 73

$$2RuO_4^{2-} + 3H_2O + 2e^- = Ru_2O_5 + 6OH^- \quad (73)$$

at various NaOH concentrations. These data yield $\Delta G^\circ_{298,f}(Ru_2O_5) = -417.3 \pm 14$ kJ mol^{-1}. Avdeev et al.[392] also obtained half-wave potentials for eq 74 where their

$$2e^- + Ru_2O_5(am) + 6H^+ = 2Ru(OH)_2^{2+} + H_2O(l) \quad (74)$$

pH dependence of E indicates this reaction stoichiometry (i.e., the reduction product is monomeric $Ru(OH)_2^{2+}$ and not the stable tetramer $Ru_4(OH)_{12}^{4+}$). These data yield $\Delta G^\circ_{298,f}(Ru_2O_5) = -467.7 \pm 36$ kJ mol^{-1} by using reduction wave data and -450.3 ± 36 kJ mol^{-1} for oxidation wave data. The average of -445 ± 26 kJ mol^{-1} is recommended. Data for aqueous $Ru(OH)_2^{2+}$ will be obtained in the next section.

Avdeev et al.'s reduction potentials[392] for reaction 74 are 1.10–1.19 V, and potentials in this same range have been reported from the oxidation of $Ru_4(OH)_{12}^{4+}$ to Ru(4.25) or Ru(4.38), where all are solution species.[404b] However, some of these solutions may be colloidal. The pH dependences for potential data[392] indicate solid Ru_2O_5 formation was more likely than aqueous Ru(4.25) or Ru(4.38). However, the chemistry of Ru(V) is sufficiently uncertain that data for Ru_2O_5 should be used with caution.

A nonstoichiometric hydrated oxide approaching the composition RuO has been reported to form as a thin film when Ru undergoes repeated potential cycling in H_2SO_4 solutions.[404c] X-ray emission spectroscopy and oxide layer thickness measurements were used to analyze this film. Similarly, Lenza et al.[404d] claimed that Ru(OH), $Ru(OH)_2$, and $RuO{\cdot}H_2O$ surface films form under similar conditions. As was the case for the "native oxides" discussed earlier, the exact chemical species are uncertain owing to difficulties in analyzing very thin films.

Thermodynamic data for $RuO_2{\cdot}2H_2O(am)$ and $Ru(OH)_3{\cdot}H_2O(am)$ indicate that both are metastable, although the Gibbs energies of decomposition are negative by amounts only slightly exceeding the experimental uncertainties. These data indicate that $RuO_2{\cdot}2H_2O(am)$ should spontaneously dehydrate and that $Ru(OH)_3{\cdot}H_2O(am)$ should disproportionate to RuO_2, Ru, and H_2O. These reactions do not occur at an observable rate at room temperature, but they do occur when samples are heated.[184,284,395,396]

C. Solubility of $RuO_2{\cdot}2H_2O$ and $Ru(OH)_3{\cdot}H_2O$, and Hydrolyzed Aqueous Species

It has long been known that soluble Ru(IV) hydrolyzed species in aqueous media are usually polymerized. Reduction[405] of Ru(IV) produced a species with average valence of +3.5, and thus the degree of polymerization must be a multiple of 2. Cady[404b] observed valences of 4.2, 4.25, 4.28, and 4.38 upon oxidation of polymeric Ru(IV) in $HClO_4$ and trifluoroacetic acid, and Brito and Lewis[145] reported valences of 3.0, 3.5, 3.7, and 3.8 in 1 mol L^{-1} H_2SO_4. Since these valences are uncertain by about 0.1 unit, 4.2, 4.25, and 4.28 could refer to the same species, as could 3.7 and 3.8. It is now known that Ru(IV) can exist as tetramers, so the actual valences must be 3.50, 3.75, 4.00, and 4.25. A valence of 4.38 was also observed by Maya,[254] who suggested that this value could result from a process involving two molecules of the tetramer in a second-order electrochemical process. Cady[404b] found that all solutions with average valences above +4.00 were colloidal, as were some but not all Ru(IV).

Maya[254] suggested that preferential oxidation of hydroxyls bound to Ru(IV) tetramers could be involved instead of oxidation of Ru atoms. Similarly, oxidation of bound water was suggested when oxidizing Ru(IV) or Ru_2O_5.[400,406] It is thus possible that some reported Ru(4.25) solutions actually contains Ru(IV) with associated peroxides. This may be why Ce^{4+} oxidation results sometimes give incorrect valence determinations for Ru.[145,407] However, since Ru(4.25) can also be produced by reduction of RuO_4[404b] and by equilibrating $Ru_2O_5{\cdot}mH_2O$ with Ru(IV),[400] solutions of Ru(4.25) can sometimes form.

Direct evidence for the tetrameric nature of Ru(IV) in aqueous acid also exists. Reduction of RuO_4 by H_2O_2 in $HClO_4$ gave a species with a charge of 4.04 ± 0.17 as determined by Donnan membrane equilibrium[408] and a charge per Ru atom of 1.05.[278] Thus, its formula is $Ru_4(OH)_{12}^{4+}$; an identical formulation was given from careful analysis of pH titration curves in methanesulfonate and in nitrate solutions.[279] This same OH^-:Ru(IV) ratio had been reported earlier in $HClO_4$.[409] Reduced valence tetramers have lower OH^-:Ru(IV) ratios and will be discussed in the next section. As noted by Brêmard et al.,[279] $Ru_4(OH)_{12}^{4+}$ could well be $Ru_4O_6{\cdot}mH_2O^{4+}$. We will assume it is a hydroxide as do most workers.

It is possible to depolymerize the soluble Ru(IV) tetramers under rather gentle ion-exchange conditions to form a monomer.[276,410] The spectra of monomer and tetramer are quite similar, but there are significant molar extinction coefficient differences at 4800 Å. Vdovenko et al.[277] found spectral changes occurring even after 240 days in 1 mol L^{-1} $HClO_4$, which indicates that repolymerization of the monomer could take several years. Two separate studies of the charge/species and charge/ruthenium using ion exchange[276,277] confirm that the monomer is $Ru(OH)_2^{2+}$ (or RuO^{2+}). Similarly, the solubility of this monomer[276,411] is consistent with two OH^-'s causing precipitation. The presence of Cl^- ions slightly reduces the OH^-:Ru(IV) ratio[279] and so may induce depolymerization of the tetramer.

Speciation in Ru(II) and Ru(III) solutions has been studied also. Cady,[404b] working in Connick's laboratory, used ion-exchange separation to establish that a monomeric Ru^{3+} aquo ion exists. Early studies showed that the Ru^{3+}/Ru^{2+} redox couple[275,405] was independent of pH over a large pH range (now known to be true below pH 2.9[412]), which suggests that the Ru^{2+} aquo ion exists also. This has been confirmed recently by the preparation and structural characterization[238] of pink $Ru(H_2O)_6(tos)_2$ and lemon yellow $Ru(H_2O)_6(tos)_3{\cdot}3H_2O$, where tos represents the *p*-toluenesulfonate(1−) anion. The Ru(II) salt was prepared by Pb reduction of RuO_4 in aqueous H_2SiF_6, followed by ion-exchange separation and elution with Htos. The Ru(III) salt was prepared by O_2 oxidation of Htos solutions of Ru(II). Both solid salts are air stable in contrast to their aqueous solutions, and both contain $Ru(H_2O)_6^{n+}$ octahedra.

Attempts were made to prepare other Ru aquo cation salts without success.[238] ClO_4^- oxidized Ru^{2+} quantitatively, SiF_6^{2-} and PF_6^- contain enough free F^- to give mixed anion complexes, and $Ru(H_2O)_6(BF_4)_2$ was prepared but gradually decomposed at room temperature.

The Ru(III)/Ru(II) aqueous redox couple in noncomplexing media is independent of pH below pH 2.9, but the reduction potential depends on pH at higher pH values.[412] The slope was consistent with a H^+:e^- (1:1) reduction so the hydrolysis reaction was assumed to be eq 75.[412] A similar conclusion was reached by

$$Ru(H_2O)_6^{3+} = Ru(OH)(H_2O)_5^{2+} + H^+ \quad (75)$$

Harzion and Navon[413] using spectrophotometric pH titrations. Optical spectra were consistent with a monohydroxide cation.

Brêmard and Tridot[414] did a careful analysis of pH titration of Ru^{3+} in 0.5 mol L^{-1} $NaCH_3SO_3$ and in 0.5 mol L^{-1} $NaNO_3$. Their results indicated that Ru^{3+} forms the mononuclear complex $Ru(OH)_2^+$ (or RuO^+) from about pH 1.2 to over pH 4. For most of these aqueous species the coordinated H_2O's are not listed, and they will not be included when doing thermodynamic calculations. However, enough H_2O will be present to complete octahedral coordination in most cases (e.g., $Ru(OH)_2^+$ is probably $Ru(OH)_2(H_2O)_4^+$).

An apparent contradiction is thus present; different methods indicate either one[412,413] or two[414] OH^-'s per Ru(III) are coordinated over essentially the same pH region. The above two conclusions can be reconciled only if both types of complexes can form under very similar conditions and have slow interconversion kinetics (but an alternative is that one or more of the studies are in error). In fact, Wan and Lunsford[415] suggested that a shift in the 2950-Å absorption maximum with pH may be due to converting $Ru(OH)(H_2O)_5^{2+}$ to $Ru(OH)_2(H_2O)_5^+$ (misprint for $Ru(OH)_2(H_2O)_4^+$?). Precipitation of $Ru(OH)_3{\cdot}mH_2O$ occurs between pH 4 and pH 5, depending on Ru(III) concentration.[413,414]

Brêmard et al.[279] found that the OH^-:Ru(IV) ratio is only slightly affected by the presence of Cl^-, so Ru(IV) solubility data in HCl may still be valid. However, for Ru(III) in 0.5 mol L^{-1} NaCl, the OH^-:Ru ratio decreases to 1 below pH 4 and becomes 0 below pH 2.5.[414] Thus, reported solubility measurements for Ru(III) in Cl^- media are of little value. Since $HClO_4$ oxidizes Ru(III) and liberates Cl^-, this medium should be avoided also.

Reduction of $Ru_4(OH)_{12}^{4+}$ in noncomplexing media produces an unstable polymeric Ru(III) species that decomposes fairly rapidly to the thermodynamically stable monomer.[278,281] VanHoudt[281] suggested that the original decomposition product was $Ru_4(OH)_4^{8+}$ which rapidly converts to a dimeric species and later to a monomer. This will be discussed later.

Solubility values for monomeric Ru(IV) are given by

$$RuO_2{\cdot}2H_2O(am) = Ru(OH)_2^{2+} + 2OH^- \quad (76)$$

for which

$$K_s = [Ru(OH)_2^{2+}][OH^-]^2 \quad (77)$$

is the solubility product. Gortsema and Cobble[276] reported $K'_s = (5.9 \pm 1.1) \times 10^{-28}$ mol^3 L^{-3} at 298 K and $I = 0.1$ mol L^{-1} $HClO_4$. Brandštetr et al.[411] reported (7.8 ± 0.8) × 10^{-28} for $I = 0.005$ mol L^{-1} and (8.2 ± 0.9) × 10^{-28} for $I = 0.0015$ mol L^{-1} at 293 K in HCl. These data are not extensive enough to give temperature dependences. Extrapolation to $I = 0$ with ln K'_s vs. $I^{1/2}$ gives $K^\circ_s = 8.5 \times 10^{-28}$ mol^3 L^{-3}, and therefore, $\Delta G^\circ_{298,f}(Ru(OH)_2^{2+}(aq)) = -221.8 \pm 13$ kJ mol^{-1}.

Starik[416] and Starik and Kositsyn[417] reported solubilities of Ru(III) and Ru(IV) in dilute HCl solutions based on determining the pH at which sparingly soluble true colloids are absorbed on glass. Their data for Ru(III) are not usable since Cl^- was present and it is known to destroy the Ru(III) hydroxy complexes.[414] Starik's method has been criticized in detail[418] and defended in an unfriendly reply.[419]

Starik and Kositsyn's[417] results were presented by them for different assumed reaction stoichiometries. For polymeric Ru(IV)

$$4RuO_2{\cdot}2H_2O(am) = Ru_4(OH)_{12}^{4+} + 4OH^- \quad (78)$$

$$K_s = [Ru_4(OH)_{12}^{4+}][OH^-]^4 \quad (79)$$

Their results in dilute HCl yield $K'_s = (0.5 \pm 0.16) \times 10^{-44}$ mol^5 L^{-5}. Their reported solubilities[417] tend to increases with lower initial Ru(IV) concentration, which may indicate that partial depolymerization occurs at higher HCl to Ru(IV) ratios. Actually, their K'_s values show less variation with Ru concentration for $[OH^-]^3$ than for either $[OH^-]^2$ or $[OH^-]^4$! (Could this be due to Cl^- complexes?) Their value is in fairly good agreement with Brêmard et al.'s results of (5.0 ± 0.34) × 10^{-44} in 0.5 mol L^{-1} $NaNO_3$ and 0.5 mol L^{-1} $NaCH_3SO_3$.[279] An approximate extrapolation to infinite dilution with the Davies equation[420] yields $\Delta G^\circ_{298,f}(Ru_4(OH)_{12}^{4+}(aq)) = -1877 \pm 58$ kJ mol^{-1}. Brêmard et al.[283] earlier reported a solubility for $[Ru^{IV}][OH^-]^4$ that is several orders of magnitude smaller than our accepted value, but few experimental details were given.

Solubility of Ru(III) is given by

$$Ru(OH)_3{\cdot}H_2O(am) = Ru(OH)_2^+ + OH^- + H_2O \quad (80)$$

for which

$$K_s = [Ru(OH)_2^+][OH^-][H_2O] \quad (81)$$

Starik and Kositsyn[417] and Pshenitsyn and Ginzburg's[421a] precipitation pH data were done in Cl^- media so cannot be used to extract solubilities. Brêmard et al.'s study[414] gave $K'_s = (2.5 \pm 1.2) \times 10^{-16}$ mol^2 L^{-2} in 0.5 mol L^{-1} $NaCH_3SO_3$ assuming a unit water activity. Their earlier study[283] yields a similar value, but insufficient data were provided to do an accurate recalculation. Similar considerations apply to Pshenitsyn and Ginzburg's potentiometric pH titration in sulfate solution.[421b] Extrapolation of Brêmard et al.'s value[414] to infinite dilution with Davies' equation[420] yields $\Delta G^\circ_{298,f}(Ru(OH)_2^+(aq)) = -280.9 \pm 21$ kJ mol^{-1}.

Our evaluated thermodynamic data yield a calculated $E^\circ = 1.430 \pm 0.050$ V for the standard reduction potential of eq 82 and $E^\circ = 1.404 \pm 0.039$ V for eq 83 in aqueous acidic media. Wehner and Hindman[274] re-

$$4RuO_4 + 20H^+ + 16e^- = Ru_4(OH)_{12}^{4+} + 4H_2O \quad (82)$$

$$RuO_4 + 6H^+ + 4e^- = Ru(OH)_2^{2+} + 2H_2O \quad (83)$$

ported 1.40 ± 0.05 V for the equivalent of reaction 82, using oxidation and reduction potential measurements in 1 mol^{-1} $HClO_4$, and this agrees with our calculated value.

We also discussed evidence above that monomeric Ru(IV) slowly polymerizes to form the thermodynamically stable tetramer (eq 84). Our evaluated data yield

$$4Ru(OH)_2^{2+} + 4H_2O = Ru_4(OH)_{12}^{4+} + 4H^+ \quad (84)$$

a polymerization constant of $\simeq 10^7$. However, this value is uncertain by several orders of magnitude. This polymerization constant indicates that the tetramer dominates above about pH 3, whereas at lower pHs the monomer is more important. However, polymerization of the monomer is very slow,[277] so both forms can exist metastably for lengthy periods of time outside their thermodynamically stable pH regions.

The solubility studies cited above are all for freshly precipitated or dissolved hydroxides and, in the case of monomeric $Ru(OH)_2^{2+}(aq)$, involve slow polymerization.[277] As the chemical natures of the species in solution change upon aging so should the solubilities. The recent publication by Varshal et al.[422] is the major contribution to the study of Ru(IV) solubility in aged solutions.

Varshal et al.[422] studied Ru(IV) solubilities in 0.1 mol L^{-1} $NaClO_4$ at various pH values at 298 K as a function of time. They investigated both saturation "from above" (i.e., precipitation of hydrated oxide when solution pH values are increased) and saturation "from below" (dissolution of hydrated oxide). Solubilities of Ru(IV) "from above" were always higher than those "from below", but the differences decrease as the pH increases. They tabulate solubilities "from above" after 105 days and "from below" after 92 days. Solubility differences of 1 or 2 orders of magnitude were generally observed. At most pH values the solubilities "from above" were still slowly decreasing with time even after these long equilibrations, and solubilities "from below" were still slowly increasing, so at least part of these differences should diminish with time.

Solubilities "from above" show very little variation from pH 1 to pH 4, they decrease rapidly to pH 5, they are nearly constant to about pH 8, and then they start increasing. Solubilities "from below" decrease steadily from pH 1.2 to about pH 4.5, are nearly constant to pH 7.2, and the increase at higher pH values. A combination of electrophoresis and an analysis of the variation of solubility with pH suggested that $Ru(OH)_2^{2+}(aq)$ and $Ru(OH)_4(aq)$ coexist at low pH values, $Ru(OH)_4(aq)$ dominates around the minimum, and $Ru(OH)_5^-(aq)$ forms at higher pH values.[422] $Ru(OH)_3^+(aq)$ also may have been present. Differences between solubilities "from above" and "from below" were attributed by these authors to differences in the extent of polymerization and in the irreversible formation of oxo bridges during aging of the precipitates. Their black amorphous precipitate ($RuO_2 \cdot H_2O$ after being dried at 383 K) had IR bands corresponding to water molecules bonded with weak hydrogen bonds, and this agrees with our deduction that precipitates of this type are hydrated oxides and not hydroxides.

In principle, these solubility data could yield free energies of formation for $Ru(OH)_3^+(aq)$, $Ru(OH)_4(aq)$, and $Ru(OH)_5^-(aq)$. However, we choose not to calculate them at this time for two reasons. First, even after their fairly long equilibrium times of 92 and 105 days, slow solubility changes are still occurring. The slopes of the solubility curves with time are not constant at most pH values so it is difficult to predict equilibrium values. Second, it is not known whether the soluble species are monomeric, dimeric, etc. or polydisperse. Measurements of charge per Ru and charge per species would help to clarify this point.

D. Aqueous Oxidation–Reduction of $Ru_4(OH)_{12}^{4+}$

It is well-known that reduction of RuO_4 in aqueous $HClO_4$ generally produces polymeric Ru(IV) (ref 145, 275, 277, 280, 408). If this reduction is done in H_2SO_4 solutions, the valence of the product depends on the acid concentration.[145,277,280,407,423] For H_2SO_4 concentrations of 0.5 mol L^{-1} and lower, Ru(IV) is the product. For higher H_2SO_4 concentrations, Ru(III) or Ru(3.5) is the usual product, although trimeric species with Ru(3.33), Ru(3.67), etc. apparently can be produced by oxidation of Ru(III).[145,277] This greater ease of reduction implies sulfate complexes are formed, but their stoichiometry is unknown. Consequently, they will not be considered any further. This section is concerned with noncomplexing media: $HClO_4$, CH_3SO_3H, HNO_3, H_2SO_4 below 0.5 mol L^{-1}, *p*-toluenesulfonic acid, etc.

Polymeric Ru species are known with average valences of about 4.25 and possibly 4.38.[254,274,400,404b] Since their stoichiometry is uncertain, no thermodynamic data will be derived for them. However, redox data are available relating them to $Ru_4(OH)_{12}^{4+}$ and RuO_4,[254,400,404b] so values of $\Delta G^\circ_{298,f}$ may be forthcoming when their chemistry becomes clarified.

A number of studies have been performed for the reduction of $Ru_4(OH)_{12}^{4+}$ in acidic media (ref 254, 275, 277, 278, 281, 404b, 405, 424a–c). Most reductions have been done in $HClO_4$, but HNO_3[254] and H_2SO_4[277] have also been investigated. Most of these studies were for $I = 1$ mol L^{-1}. However, Vdovenko et al.[277] used $I = 1.5$ mol L^{-1} H_2SO_4 and $I = 0.5$ mol L^{-1} $HClO_4$, and Lazarev et al.[424a] used $I = 2$ mol L^{-1} perchlorate. Techniques used include polarography, chemical reduction, cyclic voltammetry, and controlled-potential coulometry. In these studies, three reduction waves are generally observed. The first two polarographic waves are of approximately equal height, and their sum is equal to that of the third. The third corresponds to reduction of Ru(III) to Ru(II), so the first two must be reductions of $Ru_4(OH)_{12}^{4+}$ to polymeric Ru(3.5) and Ru(3.0).[277,281,405] Ru(3.5) has been confirmed in these solutions using coulometric analysis,[275] step coulometry,[278] and cyclic voltammetry.[254] Cyclic voltammetry also indicated the presence of Ru(3.75)[254] from a prior reduction step.

Under conditions of step coulometry the Ru(IV) → Ru(3.5) reduction is reversible over 80% of the range;[278] cyclic voltammetry also indicates both Ru(IV) → Ru(3.75) and Ru(IV) → Ru(3.5) are reversible.[254] Thus, we can use their potentials to calculate valid thermodynamic data. Slight deviations from reversibility near Ru(3.5) are probably due to slow oxidation of Ru(3.5) by $HClO_4$. Potentials for the reduction of Ru(IV) → Ru(3.75) and Ru(3.75) → Ru(3.5) do not depend on the ruthenium concentration, so no depolymerization occurs at these stages and for this time scale.[278,424b]

Atwood and deVries[405] were only able to determine that between one and three H^+'s were involved per one-electron reduction of Ru(IV). Wallace and Probst[278] believed that reduction of Ru(IV) to Ru(3.75) involved a mixture of $H^+:e^-$ (1:1 and 2:1) processes and that a total of two H^+ is used in going to Ru(3.5). However, VanHoudt,[281] Lazarev and Khvorostin,[424a] and Schauwers et al.[424b] found $H^+:e^-$ (2:1) reductions. We will accept their results *for the purpose of thermodynamic calculations.* Schauwers et al.[424b] noticed a slight change in the pH dependences for pH >1 so some additional hydrolysis may occur under those conditions. Following VanHoudt[281] we consider the reversible reductions to be eq 85 and 86.

$$Ru_4(OH)_{12}^{4+} + e^- + 2H^+ = Ru_4(OH)_{10}^{5+} + 2H_2O \quad (85)$$

$$Ru_4(OH)_{10}^{5+} + e^- + 2H^+ = Ru_4(OH)_8^{6+} + 2H_2O \quad (86)$$

Wallace and Propst[278] reported 0.621 V for reaction 85 in $I = 1$ mol L^{-1} ClO_4^-, Maya[254] reported 0.59 V in NO_3^-, and Schauwers et al.[424b] reported 0.650 V in $HClO_4$. Using the average of 0.620 ± 0.030 V yields $\Delta G°_{298,f}(Ru_4(OH)_{10}^{5+}(aq)) = -1462.4 \pm 61$ kJ mol^{-1}. Values for the sum of reactions 85 and 86 range from 0.64 to 0.70 V with one outlier[405] at 0.56 V. Averaging all but the outlier gives $E = 0.662 \pm 0.019$ V.[274,275,277,278,281,424b] Then, reduction of $Ru_4(OH)_{12}^{4+}$ yields $\Delta G°_{298,f}(Ru_4(OH)_8^{6+}(aq)) = -1056.0 \pm 62$ kJ mol^{-1}.

The next reduction wave generally observed corresponds to eq 87 for which reduction potentials range

$$Ru_4(OH)_8^{6+} + 2e^- + 4H^+ = Ru_4(OH)_4^{8+} + 4H_2O \quad (87)$$

from 0.39 to 0.55 V.[254,274,275,277,278,281,405,424a,b] Eliminating the highest value[274] gives an average of 0.447 ± 0.048 V. The large scatter in this value arises because $Ru_4(OH)_4^{8+}$ depolymerizes fairly rapidly and because it is slowly oxidized by the $HClO_4$ used in most of these studies. These data yield $\Delta G°_{298,f}(Ru_4(OH)_4^{8+}(aq)) = -193.5 \pm 72$ kJ mol^{-1}, but the uncertainty could be larger owing to the above difficulties.

Schauwers et al.[424b] obtained $E = 0.493$ V for eq 88

$$Ru_4(OH)_8^{6+} + e^- + 2H^+ = Ru_4(OH)_6^{7+} + 2H_2O \quad (88)$$

using rotating disk Pt electrodes. Thus, $\Delta G°_{298,f}(Ru_4(OH)_6^{7+}(aq)) = -629.2 \pm 63$ kJ mol^{-1}. For all of these tetramers with Ru(III) to Ru(3.75), one extra figure is given for ΔG solely to reproduce E values.

Wallace and Propst,[278] VanHoudt,[281] and Schauwers et al.[424b] should be consulted for additional subtleties of the reduction mechanism. It appears that Ru(III) tetramers probably rapidly disproportionate to dimers, followed by slower dissociation to monomers. Likewise polymeric Ru(III) can apparently be reduced to Ru(2.5).[281] These polymeric Ru(II) and Ru(III) species are thermodynamically very unstable and gradually convert to the stable monomers.[424b] Interpretation of the lower valence species is rendered more difficult by the fact most studies are in $HClO_4$. $HClO_4$ rapidly and quantitatively oxidizes Ru(II) and more slowly oxidizes Ru(III) to Ru(IV). Another detailed study using a noncomplexing and nonoxidizing anion could clarify the remaining points. However, all of the mixed valence tetramers are apparently unstable and spontaneously disproportionate to $Ru_4(OH)_{12}^{4+}$ and Ru^{3+}.

E. Aqueous Ru(IV) Sulfate Complex

It was earlier mentioned that polymeric Ru(IV) sulfates are known, but monomeric Ru(IV) complexes have received less attention. Vdovenko et al.[277,425] used ion-exchange measurements for aqueous monomeric $Ru(OH)_2^{2+}$ sulfate. Measurements at different H_2SO_4 concentrations indicate only a single complex is forming. The stability constant was determined from $I = 0.25$ to 2.00 mol L^{-1} and at 293.2, 298.2, and 308.0 K.[425] Their data were incorrectly extrapolated by them to $I = 0$, and their entropies are inconsistent with input data. Reextrapolation of stability constants for eq 89

$$Ru(OH)_2^{2+} + SO_4^{2-} = Ru(OH)_2SO_4 \quad (89)$$

to $I = 0$, using ln K' vs. $I^{1/2}$, yields $K°_{0,1} = 62.2$ for reaction 89 and $\Delta H°_{rxn,298} = 10.2$ kJ mol^{-1}. These data then yield $\Delta G°_{298,f}(Ru(OH)_2SO_4) = -976.5 \pm 13$ kJ mol^{-1}.

F. Aqueous Ru(IV) Chloride Complexes

Various types of Ru(IV) chloride complexes have been described already. $Ru_2OCl_{10}^{4-}$ and $Ru_2OBr_{10}^{4-}$ and their partially dissociated forms have also been described, and their dissociation and redox behavior will be described in the next section. $Ru_2O_2Cl_4$ and $Ru_2O_2Cl_6^{2-}$ have been little investigated and lack thermodynamic data.[197] I^- reduces Ru(IV) to insoluble RuI_3, so no soluble simple complexes of I^- are reported.

A number of RuX_6^{2-} (X = Cl^-, Br^-) solid salts were described earlier, and aqueous solutions of them are known at high halide concentrations. The same octahedral species seem to be present both in solution and in the solid state.[426] $RuCl_6^{2-}$ can also be produced by oxidation of Ru(III) with Cl_2, including Cl_2 generated by pulse radiolysis.[427] $RuCl_6^{2-}$ shows stable spectral features in solutions with Cl^- concentrations above 5 mol L^{-1},[428] and partial formation of it occurs above 0.6 mol L^{-1} in acid solutions.[429]

The initial hydrolysis of $RuCl_6^{2-}$ has been said to yield $RuCl_5(H_2O)^-$,[430] but Raman spectra suggest that eq 90

$$2RuCl_6^{2-} + 6H_2O = Ru_2O_2Cl_4(H_2O)_4 + 4H^+ + 8Cl^- \quad (90)$$

may happen instead.[197] Other complexes of the type $Ru(OH)_2Cl_n(H_2O)_{4-n}^{2-n}$ (n = 1–4) are known; they will be assumed to be monomeric since most workers consider them to be so, but some could well be dimers.[431,432] Only the monomeric complexes have published thermodynamic data.

Wehner and Hindman[433] studied changes that occur when HCl is added to Ru(IV) perchlorate. For $[Cl^-] < 0.1$ and $[H^+] < 0.4$ mol L^{-1}, red Ru(IV) became violet and then yellow. When $[Cl^-] > 0.1$ and $[H^+] > 0.4$ mol L^{-1}, the color change sequence was red → yellow → violet → yellow. They used spectroscopic, kinetic, and stability constant measurements to show that the violet species was probably $Ru(OH)_2Cl_2(H_2O)_2$, and the final yellow species were probably $Ru(OH)_2Cl_3(H_2O)^-$ and $Ru(OH)_2Cl_4^{2-}$. Ion-exchange measurements in HCl gave evidence for $Ru(OH)_2Cl_2(H_2O)_2$, $Ru(OH)_2Cl_4^{2-}$, and $RuCl_6^{2-}$.[429] High voltage electrophoresis separation of equilibrated samples[434] gave convincing evidence for $Ru(OH)_2Cl(H_2O)_3^+$, $Ru(OH)_2Cl_2(H_2O)_2$, $Ru(OH)_2Cl_3(H_2O)^-$, and $Ru(OH)_2Cl_4^{2-}$. They also found evidence for monohydroxy species $Ru(OH)(H_2O)_5^{3+}$, $Ru(OH)Cl(H_2O)_4^{2+}$, and $Ru(OH)Cl_5^{2-}$ and the trihydroxy species $Ru(OH)_3Cl_3^{2-}$ and $Ru(OH)_3Cl_2(H_2O)^-$. It seems likely that the trihydroxy species were polymeric and the monohydroxy species may have been $Ru_2OCl_n^{6-n}$ ions. In most of the following discussion, water molecules will be left out of these formulas.

Bromo complexes of Ru(IV) have been studied much less. Biryukov et al.[435] suggested, by analogy with chloride complexes, that the blue complex is $Ru(OH)_2Br_2(H_2O)_2$. It converts into a crimson complex, conceivably $Ru(OH)_2Br_3(H_2O)^-$ or $Ru(OH)_2Br_4^{2-}$.

Ru(IV) chloro complexes have been reported to reach thermodynamic equilibrium at room temperature after several days to weeks;[431,433,434] Ru(III) chloro complexes take even longer.[434] However, at 348 K equilibrium is reached in about 20–30 min.[431] Consequently, those studies for which "equilibrium constants" were reported without sufficient time being allowed[429,436] were rejected as invalid.

The association equilibria are of the type

$$K_{n,n+1} = \frac{[Ru(OH)_2Cl_{n+1}{}^{1-n}]}{[Ru(OH)_2Cl_n{}^{2-n}][Cl^-]} \tag{91}$$

for

$$Ru(OH)_2Cl_n{}^{2-n} + Cl^- = Ru(OH)_2Cl_{n+1}{}^{1-n} \tag{92}$$

Ohyoshi et al.[437] reported values of $K'_{0,1}$, $K'_{1,2}$, and $K'_{2,3}$ for room temperature and $I = 0.46$ and 0.92 mol L^{-1}. They used 2-week equilibrations. Wehner and Hindman[433] reported $K'_{3,4} = 1.9 \pm 0.1$ at $I = 6$, which agrees with Alimarin et al.'s value[198] of 2.12 ± 0.10 mol^{-1} L. Averaging these data and extrapolation to $I = 0$ using Davies' equation[420] yields $K°_{0,1} = 24.5 \pm 3.9$, $K°_{1,2} = 2.6 \pm 0.3$, $K°_{2,3} = 0.65 \pm 0.05$, and $K°_{3,4} = 12 \pm 1$ mol^{-1} L. These $K°_{n,n+1}$ values are each uncertain by about 10% based upon internal consistency. It is quite possible that the actual uncertainties are much larger due to uncertainties in the extrapolations. Values of $K_{n,n+1}$ at 363 K seem concordant[432,438] with lower temperature data.

These data then yield $\Delta G°_{298,f}(Ru(OH)_2Cl^+) = -361.0 \pm 14$, $\Delta G°_{298,f}(Ru(OH)_2Cl_2) = -494.7 \pm 14$, $\Delta G°_{298,f}(Ru(OH)_2Cl_3^-) = -624.9 \pm 14$, and $\Delta G°_{298,f}(Ru(OH)_2Cl_4^{2-}) = -762.4 \pm 14$ kJ mol^{-1}. These values and other aqueous species and hydrous oxides described earlier are summarized in Table VIII. Although the error limits are fairly large for the aqueous species, this has little effect on thermodynamic calculations since only relative values are required in most cases and the experimental redox potentials are reproduced. Additional thermodynamic data will be discussed in the remaining sections. Unfortunately, for them, only relative free energies can be obtained and not absolute values.

TABLE VIII. Thermodynamic Data for Ru Aqueous Species and Hydrated Oxides at 298.15 K

species	$\Delta G°_{298,f}$, kJ mol^{-1}	$\Delta H°_{298,f}$, kJ mol^{-1}	$S°_{298}$, J K^{-1} mol^{-1}
$H_2RuO_5(aq)$	-391.2 ± 5.0		
$HRuO_5^-(aq)$	-325.4 ± 7.1		
$RuO_4^-(aq)$	-250.1 ± 5.5	-332.4 ± 18	224.9 ± 79
$RuO_4^{2-}(aq)$	-306.6 ± 6.6	-457.0 ± 3.4	64.9 ± 34
$RuO_2 \cdot 2H_2O(am)$	-691.0 ± 13		
$Ru(OH)_3 \cdot H_2O(am)$	-766 ± 13		
$Ru_2O_5(am)$	-445 ± 26		
$Ru(OH)_2^{2+}(aq)$	-221.8 ± 13		
$Ru(OH)_2^+(aq)$	-280.9 ± 21		
$Ru_4(OH)_{12}^{4+}(aq)$	-1877 ± 58		
$Ru_4(OH)_{10}^{5+}(aq)$	-1462.4 ± 61		
$Ru_4(OH)_8^{6+}(aq)$	-1056.0 ± 62		
$Ru_4(OH)_6^{7+}(aq)$	-629.2 ± 63		
$Ru_4(OH)_4^{8+}(aq)$	-193.5 ± 72		
$Ru(OH)_2SO_4(aq)$	-976.5 ± 13		
$Ru(OH)_2Cl^+(aq)$	-361.0 ± 14		
$Ru(OH)_2Cl_2(aq)$	-494.7 ± 14		
$Ru(OH)_2Cl_3^-(aq)$	-624.9 ± 14		
$Ru(OH)_2Cl_4^{2-}(aq)$	-762.4 ± 14		

G. Hydrolysis and Reduction of Aqueous $Ru_2OCl_{10}^{4-}$

Solid salts of $Ru_2OCl_{10}^{4-}$ were described earlier and have a $Cl_5RuORuCl_5$ structure with an oxygen bridge. Raman spectra indicate that this same ionic structure is present in aqueous solutions.[197,203,205] It sometimes forms when Ru(III) chlorides are being oxidized.[197,439] Solutions of it readily undergo hydrolysis except at high HCl concentrations. Alimarin et al.[440] studied absorption spectra changes with time for different HCl concentrations. For examples, 2–4 mol L^{-1} HCl solutions reached equilibrium in 3–4 h, whereas 4 months were required in <0.08 mol L^{-1} HCl.

Bol'shakov et al.[441] suggested that hydrolysis of $Ru_2OCl_{10}^{4-}$ leads to bridged diol structures. However, the detailed Raman investigation of Deloume et al.[205] indicate rather that two Cl^- can dissociate and the dimer then depolymerizes. Let $t = [Cl^-]/[Ru]$. Then, if $[H^+] > 10$ mol L^{-1} and $t > 1.1 \times 10^4$, $Ru_2OCl_{10}^{4-}$ is dominant. If $10 > [H^+] > 6$ mol L^{-1} and $t > 500$, then reaction 93 is in equilibrium. Similarly, if $3 > [H^+] > 0.5$ mol L^{-1} and $t > 500$, eq 94 now occurs. When $[H^+] < 3$ mol L^{-1} and $t < 500$, depolymerization occurs by eq 95.

$$[Ru_2OCl_{10}]^{4-} + H_2O = [Ru_2OCl_9(H_2O)]^{3-} + Cl^- \tag{93}$$

$$[Ru_2OCl_9(H_2O)]^{3-} + H_2O = [Ru_2OCl_8(H_2O)_2]^{2-} + Cl^- \tag{94}$$

$$[Ru_2OCl_8(H_2O)_2]^{2-} + H_2O = 2[Ru(OH)_2Cl_4]^{2-} + 2H^+ \tag{95}$$

Both chemical and electrochemical reduction of $[Ru_2OCl_{10}]^{4-}$ have been investigated.[207,439,442] These studies indicate that reduction occurs irreversibly to a mixed-valence dimer Ru(3.5), which subsequently decomposes to monomeric Ru(III) and Ru(IV). Reduction potentials cannot be used to extract thermodynamic data since the exact nature of the Ru(3.5) species is unknown. Several determinations have also been made of the Ru(IV)/Ru(III) reduction potential in aqueous HCl for monomeric Ru complexes.[442-444] Although the reduction potentials are in fair agreement, reactants and products are complicated mixtures so no useful thermodynamic results are obtained.

H. Ru^{3+}/Ru^{2+} Aqueous Reduction Potential

Reduction of Ru^{3+} to Ru^{2+} in aqueous acidic media has been studied numerous times.[145,275,277,404b,405,412,445-450] This reduction is reversible and independent of pH below about pH 2.9 and has been studied at a variety of ionic strengths in $HClO_4$, H_2SO_4, HCF_3SO_3, trifluoroacetic acid, and *p*-toluenesulfonic acid.

Most of the reduction potentials either fall near 0.20–0.22 V or near 0.1 V. The potentials near 0.1 V were all measured in moderately concentrated $HClO_4$. $HClO_4$ quantitatively and rapidly oxidizes Ru(II) to Ru(III) and oxidizes Ru(III) to Ru(IV) in about 1 day.[274,278,404b,445,451] Oxidation of Ru(III) is much slower near 273 K.[404b] With excess $HClO_4$ the initial reduction product is mainly ClO^- (probably as HOCl),[451] but most workers found large amounts of Cl^-.[274,278,404b,445] The reduction potential of about 0.1 V in these solutions is close to the 0.08 V for reduction of the $RuCl^{2+}$ complex,[448] which should form in these solutions. Consequently data for this potential in $HClO_4$ solutions were rejected.[275,404b,405,424a] Values in 0.5 mol L^{-1} $HClO_4$ are only about half as low,[277,446] presumably since oxidation rates are slower at lower $HClO_4$ concentrations. Cady's value[404b] in trifluoroacetic acid was rejected because of low precision. Values in moderately concentrated H_2SO_4 are also slightly low, probably because of complex formation, and were also rejected.[145,277,446] The remaining reliable values[240,412,447-450] were least-squared to yield

$$E = 0.239 - 0.028(I)^{1/2} \qquad (96)$$

where $E° = 0.239 \pm 0.007$ V.

There were claims in the older literature that Ru^{2+} can reduce water (actually H^+ is reduced in these acid solutions). This potential value of 0.239 V indicates that water reduction cannot occur. However, it is well-known that Ru(II) chlorides can do so, with H_2 evolution.[239] Dumas and Mercer's potentials[240] indicates that the ability to reduce water increases with the Cl^-:Ru(II) ratio for monomeric complexes and dimeric Ru(2.5) complexes are even stronger reducing agents.[234]

Using the reduction potential for eq 97 in aqueous solution gives $\Delta G°_{298,f}(Ru^{2+}(aq)) - \Delta G°_{298,f}(Ru^{3+}(aq)) = -23.06 \pm 0.68$ kJ mol^{-1}. Unfortunately, $\Delta G°_{298,f}$ for

$$Ru^{3+} + e^- = Ru^{2+} \qquad (97)$$

neither Ru^{2+} nor Ru^{3+} are known, so no absolute values can be assigned to either (no experimental values are available to the Ru^{2+}/Ru couple). We will represent $\Delta G°_{298,f}(Ru^{2+}(aq))$ by ψ in the following discussions. Ru^{2+} is not observed to spontaneously disproportionate in acidic noncomplexing media. That is

$$3Ru^{2+} = Ru(c) + 2Ru^{3+} \qquad (98)$$

does not occur. This gives the inequality

$$\Delta G°_{298,f}(Ru^{3+}(aq)) \geq {}^3\!/_2\Delta G°_{298,f}(Ru^{2+}(aq)) \qquad (99)$$

Combining this equation with the known difference from the Ru^{3+}/Ru^{2+} potential gives $\Delta G°_{298,f}(Ru^{2+}(aq)) \leq 46.1 \pm 0.7$ kJ mol^{-1}. Unfortunately, if this constraint is used, it leads to unrealistic values for potentials involving Ru^{3+} [18] and some apparently incorrect thermodynamic predictions. This suggests that the fact that Ru^{2+} is not observed to disproportionate could be due to kinetic rather than thermodynamic inhibitions. A value for ψ will be estimated in section V.M.

Buckley and Mercer[447a] also studied reaction 97 at 288.15, 292.55, and 298.55 K at $I = 0.103$ mol L^{-1}. These data were used by them to calculate ΔH and ΔS for the reduction of H^+ by Ru^{2+}, but they reported $-\Delta H/R$ and not ΔH as claimed.

Bernhard et al.[447b] recently investigated the $Ru(H_2O)_6^{3+}/Ru(H_2O)_6^{2+}$ exchange rate using NMR.

I. Hydrolysis Constants

Böttcher et al.[412] reported $pK'_{0,1} = 2.90 \pm 0.05$ for reaction 75 which we shall rewrite as eq 100. Published

$$Ru^{3+} + H_2O = Ru(OH)^{2+} + H^+ \qquad (100)$$

data are for $I = 1$ mol L^{-1} and 298 K. Harzion and Navon[413] obtained $pK'_{0,1} = 2.4 \pm 0.2$ at 293 K. We will use the average $pK_{0,1}$ value in calculations after extrapolation to $I = 0$ with Davies' equation:[420] $pK°_{0,1} = 2.24 \pm 0.25$. Then, $\Delta G°_{298,f}(Ru(OH)^{2+}(aq)) = (\psi - 201.3) \pm 2.0$ kJ mol^{-1}.

Hydrolysis constants are available for a number of other Ru complexes, and a few will be mentioned by way of comparison with the above value. For $Ru(NO)(NO_3)_3(H_2O)_2$, two studies[257,258] give $pK'_{0,1} = 2.6 \pm 0.4$ which is identical with the hydrolysis constant for uncomplexed Ru^{3+}. Two studies for $Ru(NH_3)_5(H_2O)^{3+}$ yield $pK'_{0,1} = 4.0 \pm 0.2$, so it is a slightly weaker acid.[452,453]

Mercer et al.[268] studied several other systems. Hydrolysis of $Ru(NO)Cl_4(H_2O)^-$ had $pK'_{0,1} = 6.0$. The first hydrolysis constant of $Ru(NO)Cl_3(H_2O)_2$ is $pK'_{0,1} = 5.0$, and its second hydrolysis constant is $pK_{1,2} = 7.5$. Thus, chloronitrosyl compounds are weaker acids than the aquo complex.

J. Aqueous Ru(II) and Ru(III) Sulfates

Stability constant measurements have been reported[446] by ion-exchange method for eq 101 in aqueous

$$Ru^{2+} + SO_4^{2-} = RuSO_4 \qquad (101)$$

$HClO_4$–H_2SO_4 solutions. Excess hydrazine was added to these solutions to reduce aqueous Ru species to Ru(II) and to maintain it in that valence state. Small amounts of Cl^- were produced in this process, and complexing with hydrazine was assumed to be insignificant. Data measured with a truly noncomplexing and nonoxidizing medium would be very desirable as a check.

Their 1967 study was assumed to be more reliable.[446] Results at 293, 298, and 308 K coincided, so $\Delta H_{rxn} = 0$ for reaction 101. Least squaring their data gave

$$\ln K'_{0,1} = 5.409 - 1.508(I)^{1/2} \qquad (102)$$

so $K^\circ_{0,1} = 223\ \mathrm{mol^{-1}\ L}$. Thus, $\Delta G^\circ_{f,298}(\mathrm{RuSO_4(aq)}) = (\psi - 757.9) \pm 0.5\ \mathrm{kJ\ mol^{-1}}$.

Lazarev and Khvorostin[454] studied complex formation between Ru^{3+} and SO_4^{2-} by using polarography at $I = 2\ \mathrm{mol\ L^{-1}}$ and 298 K. Their results are consistent with the association equilibria eq 103 and 104. Liquid extraction with long-chain amines also indicated the presence of $Ru(SO_4)_2^-$ in H_2SO_4 solutions.[455]

$$Ru^{3+} + SO_4^{2-} = RuSO_4^+ \qquad (103)$$

$$RuSO_4^+ + SO_4^{2-} = Ru(SO_4)_2^- \qquad (104)$$

An approximate extrapolation of their association constants to infinite dilution yields $K^\circ_{0,1} = 89 \pm 19\ \mathrm{mol^{-1}\ L}$, $\Delta G^\circ_{298,f}(\mathrm{Ru(SO_4)^+(aq)}) = (\psi - 732.5) \pm 1.2\ \mathrm{kJ\ mol^{-1}}$, $K^\circ_{1,2} = 12.7 \pm 5.5\ \mathrm{mol^{-1}\ L}$, and $\Delta G^\circ_{298,f}(\mathrm{Ru(SO_4)_2^-(aq)}) = (\psi - 1483.3) \pm 2.1\ \mathrm{kJ\ mol^{-1}}$. A more extensive study of the Ru(III) sulfate complexes would be welcome.

K. Does Ru^+ Occur in Aqueous Solutions and More about Ruthenium Blues

We earlier discussed evidence for the nature of ruthenium blues and concluded that they are probably dimeric or trimeric (or both) ruthenium halide complexes, with a ruthenium valence between $2 \leq Z < 3$ and possibly of mixed valence. Garif'yanov and Luchkina[456] prepared a blue solution and claimed it was a mixture of monomeric chloride complexes of Ru(III). However, these monomeric complexes have been separated and they are either yellow or red,[457] so a Ru(III) monomeric complex is not the blue species. Neither are Mercer and Dumas' yellow Ru(III) dimers.[234] Starik and Barbanel' likewise claimed Ru(III) chlorides produced the blue color but acknowledged that blue Ru(I) and Ru(II) species could also be present.[458]

There are several claims in the older literature that these blue solutions actually contain Ru(I).[181,459–463] In each case the claim is based on reduction of water-soluble "$RuCl_3$" and determination of the valence change. We early noted that freshly prepared "$RuCl_3{\cdot}mH_2O$" can contain up to 51% Ru(IV). Sawyer et al.[464] reported that commercial "$RuCl_3{\cdot}mH_2O$" contained 85% Ru(IV). Clearly, the earlier studies actually indicate the valence of the blue solution initially was closer to two. Several of these earlier studies described their "$RuCl_3$" solutions as being dark brown or red-brown;[459,461] these colors are characteristic of $Ru_2OCl_{10}^{4-}$ and of Ru(IV) polymers.

Reduction of well-characterized Ru(III) and Ru(IV) chloro complexes[233,465] using controlled potential coulometry confirms that the blue solutions involve an initial reduction to Ru(II). These blue solutions also contain significant amounts of uncomplexed $Ru(H_2O)_6^{2+}$; about 60% was found in one study.[445] $Ru(H_2O)_6^{2+}$ was isolated by ion-exchange methods and was shown to have a 2+ charge and to be monomeric.[445]

Direct reduction of ruthenium blue solutions to the metal gave valence changes of 1.92 ± 0.02 and 2.2 ± 0.02, but the latter value could be slightly high due to catalytic evolution of H_2.[233]

Most workers find that attempts to get complete reduction to Ru(II) give some metal formation.[234,235] Whether this metal is produced by a direct two-electron reduction of Ru(II) or by disproportionation of very unstable Ru(I)[235,463] is not known. This is certainly worth additional study. However, if Ru(I) does form during reduction, it rapidly disproportionates or is oxidized by H_2O. Ru(I) has been claimed as a kinetic intermediate in the catalyzed oxidation of V(IV) by IO_3^-, but no direct evidence for it was obtained.[466] Ru(I) compounds can exist when electron-donating ligands are present.[1,7,9]

L. Ru(II) and Ru(III) Monomeric Chloride Complexes

Solutions of Ru(III) chlorides undergo aging as indicated by changes of color and spectral changes. Associated with this are changes in structure (i.e., cis to trans conversions) and in the number of coordinated chlorides. Several studies reported changes after dissolution of "$RuCl_3{\cdot}mH_2O$" in water or HCl solution.[181,467,468] However, these solutions actually contain much Ru(IV). Thus, the observed changes involved both Ru(III) and Ru(IV) chloro complexes and also changes due to oxidation.

Fine[457] did a detailed study of the aging of $K_2[RuCl_5{\cdot}H_2O]$ in 0.1 mol L^{-1} HCl. The spectral changes indicated $RuCl_5^{2-}$ rapidly dissociates to $RuCl_4^-$, $RuCl_4^-$ then dissociates to an isomer of $RuCl_3$; this isomer converts partially to the other geometric isomer and a Cl^- is lost to form $RuCl_2^+$; partial isomerization of $RuCl_2^+$ occurs; and another Cl^- is then lost to form $RuCl^{2+}$. Not surprisingly this complicated series of changes reaches equilibrium slowly.

The studies of Fine[457] and Ohyoshi et al.[434] indicate that several weeks or longer are required to reach thermodynamic equilibrium for Ru^{3+} in HCl. Changes were still occurring after 7 weeks, but they were fairly small after about 10 days. Similar results were reported by Hrabikova et al.,[469] who also noted that heating the solution speeded up equilibrium. Addition of borate, phosphate, sulfate, bromide, nitrate, lactic acid, oxalic acid, and nitrilotriacetic acid had almost no effect on the equilibrium,[434,469] which implies chloride complexes are quite strong. The anionic complexes reach equilibrium or near equilibrium fairly rapidly, whereas neutral and cationic complexes can take weeks to months.[457]

Slow equilibrium has obvious disadvantages such as that long times are required to reach equilibrium, so the danger of oxidation by air or by ClO_4^- used to adjust ionic strength is increased. A major advantage is that complicated mixtures can be physically separated and their individual concentrations determined. These separations have been done by both ion-exchange[404b,457] and high voltage electrophoresis.[434]

Connick and co-workers[404b,457,470–472] described the separation and identification of Ru^{3+}, $RuCl^{2+}$, $RuCl_2^+$ (cis and trans), and $RuCl_3$ (cis and trans). The charge/atom and charge/species were determined by ion exchange for charged species, and the molecular weight of $RuCl_3$ was determined by freezing point depression. Approximate cis/trans equilibrium ratios were also determine for $RuCl_2^+$, $RuCl_3$, and $RuCl_4^-$,[457,473] but they are not known accurately enough to warrant distinction of geometric isomers in thermodynamic calculations. The cis and trans isomers were tentatively identified on the basis of the rates in which they were eluted from an ion-exchange column.[457] Dielectric constant measurements for *cis*- and *trans*-$RuCl_3$ in ethyl acetate indicate that the isomer that elutes first is *trans*-$RuCl_3$,[474] in agreement with the relative elution rates for most cis and trans complexes.

Adamson[475] found that the ligand exchange rates for Cl^- bound to Ru follows the order Ru(II) > Ru(III) > Ru(IV). Partial reduction to blue solutions sped up the Ru(III) equilibrium. He thought that this catalytic effect was due to Ru(I), but Ru(II) is more likely.[448]

The $Ru(H_2O)_6{}^{3+}$ *p*-toluenesulfonate crystal is lemon yellow[238] and perchlorate solutions of Ru^{3+} are amber yellow.[405] Thus, Ru^{3+} is yellow. $RuCl^{2+}$ is also yellow,[240] and $RuCl_2{}^+$ is bright yellow.[457] Mercer and Dumas' unstable dimeric Ru(III) complexes[234] $Ru_2Cl_3{}^{3+}$, $Ru_2Cl_4{}^{2+}$, and $Ru_2Cl_5{}^+$ are also yellow. $RuCl_3$ is deep orange, $RuCl_4{}^-$ rose colored, $RuCl_5{}^{2-}$ bright red, and $RuCl_6{}^{3-}$ dark red.[457] Claims of green solutions during oxidation of Ru(II) or reduction of Ru(IV) cannot be due to these monomeric or dimeric species.

Association equilibria for Ru(III) which Cl^- have the general form of eq 105 where n = 0–5. The only reported value for the first association constant is $K°_{0,1} = 148 \pm 6$ mol^{-1} L,[448] based on Ru(II) catalysis of the equilibrium. This value yields $\Delta G°_{298,f}(RuCl^{2+}(aq)) = (\psi - 120.6) \pm 0.8$ kJ mol^{-1}.

$$RuCl_n{}^{3-n} + Cl^- = RuCl_{n+1}{}^{2-n} \qquad (105)$$

Fine[457] and Connick and Fine[472] studied the next three equilibria in HCl solutions by using ion-exchange separation after long-term equilibration. Ohyoshi et al.[437] used two-week equilibrations in $ClO_4{}^-$ media; longer times were not used because of the danger of oxidation. Two weeks is time to come close enough to equilibrium so that no serious errors should result. Values of $K'_{1,2}$ and $K'_{2,3}$ from these studies are concordant to 10–15%, but uncertainty for $K'_{3,4}$ is about 40%.

Extrapolation of their combined data to infinite dilution yields $K°_{1,2} = 37 \pm 5$ mol^{-1} L, $\Delta G°_{298,f}(RuCl_2{}^+(aq)) = (\psi - 260.9) \pm 1.0$ kJ mol^{-1}, $K°_{2,3} = 3.5 \pm 0.3$ mol^{-1} L, $\Delta G°_{298,f}(RuCl_3(aq)) = (\psi - 395.3) \pm 1.2$ kJ mol^{-1}, $K°_{3,4} = 0.7 \pm 0.25$ mol^{-1} L, and $\Delta G°_{298,f}(RuCl_4{}^-(aq)) = (\psi - 525.7) \pm 2.0$ kJ mol^{-1}. Fine[457] reported some very approximate values of $K'_{4,5}$ and $K'_{5,6}$ from spectroscopic measurements, but they were very dependent on ionic strength. Connick's later values[473] are presumably to be preferred: $K'_{4,5} \simeq 0.14$ and $K'_{5,6} \simeq 0.1$ mol^{-1} L at I = 5 mol L^{-1}. Marques and Simões' values[476] or $K'_{5,6}$ in 6.36 and 6.46 mol L^{-1} HCl are 0.0415 and 0.0417 mol^{-1} L. A very approximate extrapolation to infinite dilution yields $K°_{4,5} \simeq 0.5$ and $K°_{5,6} \simeq 0.4$ mol^{-1} L. We consider these last two values to be order of magnitude estimates only. Thus, $\Delta G°_{298,f}(RuCl_5{}^-(aq)) = (\psi - 655.3) \pm 4.0$ and $\Delta G°_{298,f}(RuCl_6{}^{3-}(aq)) = (\psi - 784.3) \pm 5.5$ kJ mol^{-1}.

Dumas and Mercer[240] studied rates of hydrolysis of $RuCl^+$ and *cis*- and *trans*-$RuCl_2$, which were produced by reduction of the corresponding Ru(III) complexes. Hydrolysis of $RuCl_2$ is quite rapid, $K^* = 0.15$ s^{-1}, but hydrolysis of $RuCl^+$ is slow enough that $RuCl^{2+}/RuCl^+$ reduction potentials can be measured. The only studies we considered reliable were those in which the $RuCl^{2+}$ starting material was purified by ion exchange.[240,412,447a] The average reduction potential for eq 106 is $E° = 0.082 \pm 0.005$, which yields $K°_{0,1} = 0.32 \pm 0.05$ mol^{-1} L for eq 107. Then, $\Delta G°_{298,f}(RuCl^+(aq)) = (\psi - 128.5) \pm 6$ kJ mol^{-1}. Only relative thermodynamic values can presently be assigned for the monobromo and monoiodo complexes for which RuX^{2+}/RuX^+ has E = 0.10 V,[448] since neither RuX^{2+} nor RuX^+ have independent data.

$$RuCl^{2+} = e^- = RuCl^+ \qquad (106)$$

$$Ru^{2+} + Cl^- = RuCl^+ \qquad (107)$$

Table IX summarizes these data for lower valence aqueous ruthenium species.

TABLE IX. Thermodynamic Data for Lower Valence Aqueous Species at 298.15 K

species	$\Delta G°_{298,f}$, kJ mol^{-1}	$\Delta G°_{298,f}$, kJ mol^{-1}
Ru^{2+}(aq)	ψ[a]	150.3 ± 19[b]
Ru^{3+}(aq)	(ψ + 23.1) ± 0.7	173.4 ± 20
$Ru(OH)^{2+}$(aq)	(ψ − 201.3) ± 2.0	−51.0 ± 21
$RuSO_4$(aq)	(ψ − 757.9) ± 0.5	−607.6 ± 19
$RuSO_4{}^+$(aq)	(ψ − 732.5) ± 1.2	−582.2 ± 20
$Ru(SO_4)_2{}^-$(aq)	(ψ − 1483.3) ± 2.1	−1333.0 ± 21
$RuCl^{2+}$(aq)	(ψ − 120.6) ± 0.8	29.7 ± 19
$RuCl_2{}^+$(aq)	(ψ − 260.9) ± 1.0	−110.6 ± 20
$RuCl_3$(aq)	(ψ − 395.3) ± 1.2	−245.0 ± 20
$RuCl_4{}^-$(aq)	(ψ − 525.7) ± 2.0	−375.4 ± 21
$RuCl_5{}^{2-}$(aq)	(ψ − 655.3) ± 4.0	−505.0 ± 23
$RuCl_6{}^{3-}$(aq)	(ψ − 784.3) ± 5.5	−634.0 ± 24
$RuCl^+$(aq)	(ψ − 128.5) ± 6.0	21.8 ± 25

[a] $\psi = \Delta G°_{298,f}(Ru^{2+}(aq))$. [b] Provisional adjustment of ψ based on chemical evidence (see text).

M. Estimation of ψ

It was not possible to assign numerical values for the Gibbs energy of formation of the lower valence aqueous species tabulated in Table IX. However, it is possible to estimate $\psi = \Delta G°_{298,f}(Ru^{2+}(aq))$ from known thermodynamic data for various Ru(III) and Ru(IV) aqueous species and solid compounds. Various one-electron standard state reduction potentials involving Ru(IV) (i.e., $Ru(OH)_2{}^{2+}$(aq), $Ru_4(OH)_{12}{}^{4+}$(aq), and $RuO_2 \cdot 2H_2O$(am)) and Ru(III) (i.e., $Ru(OH)_2{}^+$(aq), $Ru_4(OH)_4{}^{8+}$(aq), and $Ru(OH)_3 \cdot H_2O$(am)) were calculated from the evaluated data, and they fall in the range of 0.45–0.78 V. Then, the standard reduction potential for eq 108

$$Ru(OH)_2{}^{2+} + e^- + H^+ = Ru(OH)^{2+} + H_2O \qquad (108)$$

can be estimated as 0.615 ± 0.165 V. This yields ψ = 157.4 ± 16 kJ mol^{-1}. Similarly, the depolymerization reaction eq 109 is known to occur spontaneously. If the

$$Ru_4(OH)_4{}^{8+} = 4Ru(OH)^{2+} \qquad (109)$$

depolymerization constant falls in the range of 10–10^{10}, then ψ = 145.1 ± 18 kJ mol^{-1}. The hydrolysis constant for eq 110 is unknown. However, as noted earlier, ΔpK

$$Ru(OH)^{2+} + H_2O = Ru(OH)_2{}^+ + H^+ \qquad (110)$$

= 2.5 for $Ru(NO)Cl_3(H_2O)_2$. For the hydrolysis of TcO^{2+}, ΔpK = 1.0.[477,478] Baes and Mesmer[479] give a rule of thumb that $\Delta pK \simeq 1.3$ for the first and second stages of hydrolysis. Then, assuming the average $\Delta pK \simeq 1.6 \pm 0.8$ for Ru^{3+}, ψ = 148.5 ± 22 kJ mol^{-1}. These three estimates of ψ are fairly concordant, and their average of 150.3 ± 19 kJ mol^{-1} is recommended as our provisional value. The Gibbs energies of formation in Table IX have then been adjusted to this value. A direct experimental determination of ψ would be extremely desirable, but owing to chemical problems it is not likely to become available in the foreseeable future.

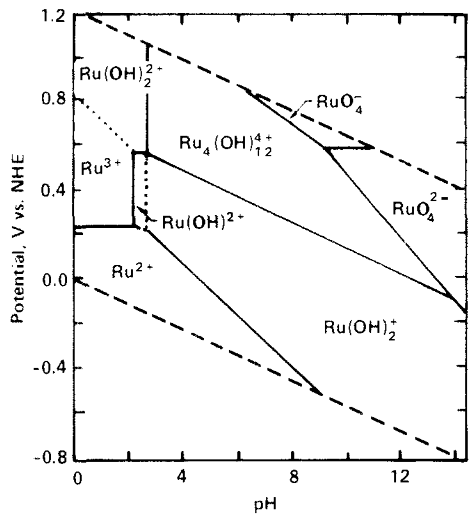

Figure 1. Potential–pH diagram for Ru–H_2O at 298 K and a total Ru concentration of 10^{-6} mol L^{-1}. This calculation is for the aqueous phase only, and no precipitates have been allowed to form. Dashed lines are for the water stability field, and dotted lines indicate regions that are fairly uncertain due to the uncertainty in ψ. Boundary lines between species indicate where concentrations are equal. Redrawn from Isherwood.[480]

If potential-pH diagram calculations are made by using only the data in either Table VIII or Table IX, then the stability regions will be known as accurately as the original input data allow. However, if all the data are used, then boundaries involving species from different tables will have the ≃0.15 V uncertainty present in ψ. Figure 1 shows the potential–pH diagram for the Ru–H_2O system; this is the first "chemically plausible" diagram ever published for it. Dotted lines indicate boundaries whose locations are fairly uncertain owing to the uncertainty in the estimation of ψ (the $Ru(OH)^{2+}(aq)$–$Ru(OH)_2^+(aq)$ boundary may actually occur at higher pH values).

VI. Summary and Recommendations

Chemical and thermodynamic data for ruthenium and many of its inorganic compounds and aqueous solutions have been critically reviewed. Values for thermodynamic properties are recommended when both the chemistry and thermodynamics are sufficiently well characterized to warrant confidence in them. Systems reviewed included metallic Ru, phase diagrams with metals and non-metals, chalcogenides, oxides, halides, oxyhalides, oxysulfur, and oxynitrogen compounds. Aqueous systems considered are aquo ions, hydrolyzed cations, oxyanions, halide complexes, and sulfate complexes. The oxide, halide, oxyhalide, and aqueous systems (both noncomplexing and complexing media) are described in considerable detail because of their great complexity and because of conflicting claims and questionable analyses in some published reports.

Recommendations were made for data that need to be measured or remeasured. These include high-temperature enthalpy data for Ru(c), combustion enthalpy data for $RuCl_3(c)$ and $RuBr_3(c)$, better characterization of solid-state sulfate complexes, better characterization of Ru(IV) aqueous halide and oxyhalide equilibria, redetermination of the Ru(II) and Ru(III) sulfate complex formation constants in nonoxidizing media (i.e., no ClO_4^-), reinvestigation of redox equilibria in the reduction of Ru(IV) tetramers in nonoxidizing media, more accurate determination of the reduction potentials for systems involving $Ru(OH)_3 \cdot H_2O(am)$ and $Ru_2O_5(am)$, and obtaining a reliable value for the $Ru^{2+}(aq)/Ru(c)$ reduction potential. The most important of these is the Ru^{2+}/Ru redox potential since it is needed to calculate more accurate $\Delta G^\circ_{298,f}$ for most lower valence ruthenium aqueous species. Also, there is a need to verify whether both $Ru(OH)^{2+}(aq)$ and $Ru(OH)_2^+(aq)$ actually exist.

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VIII. References

(1) Griffith, W. P. "The Chemistry of the Rarer Platinum Metals (Os, Ru, Ir and Rh)"; Wiley-Interscience: London, 1967.
(2) Mellor, J. W. "A Comprehensive Treatise on Inorganic and Theoretical Chemistry"; Longmans, Green and Co.: London, 1936; Vol. 15, Chapter 69.
(3) Ginzburg, S. I.; Ezerskaya, N. A.; Prokof'eva, I. V.; Fedorenko, N. V.; Shlenskaya, V. I.; Bel'skii, N. K. "Analytical Chemistry of Platinum Metals"; Wiley: New York, 1975; English translation.
(4) Amundsen, A. R.; Stern, E. W. In "Kirk-Othmer Encyclopedia of Chemical Technology", 3rd ed.; Wiley-Interscience: New York, 1982; Vol. 18, pp 228–277.
(5) Beamish, F. E. "The Analytical Chemistry of the Noble Metals"; Pergamon Press: Oxford, 1966.
(6) Beamish, F. E.; Van Loon, J. C.; Lewis, C. L. "Analysis of Noble Metals"; Academic Press: New York, 1977.
(7) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 2nd ed.; Wiley-Interscience: New York, 1966.
(8) Johnson, B. F. G.; Lewis, Sir J. *Philos. Trans. R. Soc. London, Ser. A* **1982**, *No. A308*, 5.
(9) Gulliver, D. J.; Levason, W. *Coord. Chem. Rev.* **1982**, *46*, 1.
(10) Trasatti, S.; Lodi, G. In "Electrodes of Conductive Metallic Oxides"; Trasatti, S., Ed.; Elsevier: Amsterdam, 1980, 1981; Part A, pp 301–358, Part B, pp 521–626.
(11) Trasatti, S.; O'Grady, W. E. In "Advances in Electrochemistry and Electrochemical Engineering"; Gerischer, H., Tobias, C. W., Eds.; Wiley-Interscience: New York, 1981; pp 177–261.
(12) Heller, A. In "Photoeffects at Semiconductor-Electrolyte Interfaces"; Nozik, A. J., Ed.; American Chemical Society: Washington, DC, 1981; ACS Symp. Ser. No. 146, pp 63–77.
(13) Katcoff, S. *Nucleonics* **1958**, *16*, 78, Data Sheet 24.
(14) Fleishman, M. R.; Pullman, I.; Soodak, H.; Tralli, N. In "Reactor Handbook"; Soodak, H., Ed.; Wiley-Interscience: New York, 1962; Vol. 3, Part A, pp 10–13.
(15) Bramman, J. I.; Sharpe, R. M.; Thom, D.; Yates, G. *J. Nucl. Mater.* **1968**, *25*, 201.
(16) Coles, D. G.; Ramspott, L. D. *Science (Washington, D.C.)* **1982**, *215*, 1235.

(17) Canterford, J. H.; Colton, R. "Halides of the Second and Third Row Transition Metals"; Wiley-Interscience: London, 1968.

(18) Goldberg, R. N.; Hepler, L. G. *Chem. Rev.* **1968**, *68*, 229.

(19) Llopis, J. F.; Tordesillas, I. M. In "Encyclopedia of Electrochemistry of the Elements"; Bard, A. J., Ed.; Marcel Dekker: New York, 1976; Vol. VI, Chapter 8.

(20) Trent, D. E.; Paris, B.; Krause, H. H. *Inorg. Chem.* **1964**, *3*, 1057.

(21) Jangg, G.; Dörtbudak, T. Z. Metallkd. **1973**, *64*, 715.

(22) Jaeger, F. M.; Rosenbohm, E. *Proc. K. Ned. Akad. Wet.* **1931**, *34*, 808; *Recl. Trav. Chim. Pays-Bas* **1932**, *51*, 1.

(23) Campbell, P. F.; Ortner, M. H.; Anderson, C. J. *Anal. Chem.* **1961**, *33*, 58.

(24) Jaeger, F. M.; Rosenbohm, E. *Proc. K. Ned. Akad. Wet.* **1941**, *44*, 144.

(25) Rudnitskii, A. A.; Polyakova, R. S. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1957**, *2* (12), 120.

(26) McCaldin, J. O.; Duwez, P. *J. Met.* **1954**, *6*, 619.

(27) Douglass, R. W.; Adkins, E. F. *Trans. Metall. Soc. AIME* **1961**, *221*, 248.

(28) Owen, E. A.; Roberts, E. W. *Z. Kristallogr., Kristallgeom., Kristallphys., Krystallchem.* **1937**, *96*, 497.

(29) Hellawell, A.; Hume-Rothery, W. *Philos. Mag.* **1954**, [7} *45*, 797.

(30) Hall, E. O.; Crangle, J. *Acta Crystallogr.* **1957**, *10*, 240.

(31) Ross, R. G.; Hume-Rothery, W. *J. Less-Common Met.* **1963**, *5*, 258.

(32) Hurley, G. F.; Brophy. J. H. *J. Less-Common Met.* **1964**, *7*, 267.

(33) Rudy, E.; Kieffer, B.; Fröhlich, H. *Z. Metallkd.* **1962**, *53*, 90.

(34) Anderson, E.; Buckley, R. A.; Hellawell, A.; Hume-Rothery, W. *Nature (London)* **1960**, *188*, 48.

(35) Tylkina, M. A.; Polyakova, V. P.; Savitskii, E. M. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1962**, *7*, 754.

(36) Chekhovskoi, V. Ya.; Berezin, B. Ya. *Tr. Vses. Nauchno-Tekh. Konf. Termodin. Sb. Dokl. Sekts. "Termodin. Iazovykh Perckhodov, Potoka Neobrotimykh Protsessov" "Teplofiz. Svoistva Veshchestv", 3rd, 1968* **1970**, 379; *Chem. Abstr.* **1972**, *76*, 62507*y*.

(37) Kenisarin, M. M.; Berezin, B. Ya.; Gorina, N. B.; Kats, S. A.; Polyakova, V. P.; Savitskii, E. M.; Checkhovskoi, V. Ya. *Teplofiz. Vys. Temp.* **1974**, *12*, 1309; *Chem. Abstr.* **1975**, *82*, 79769*g*.

(38) Waterstrat, R. M.; Manuszewski, R. C. *J. Less-Common Met.* **1976**, *48*, 151.

(39) Rapperport, E. J.; Smith, M. F. *Trans. Metall. Soc. AIME* **1964**, *230*, 6.

(40) Hultgren, R.; Desai, P. D.; Hawkins, D. T.; Gleiser, M.; Kelley, K. K.; Wagman, D. D. "Selected Values of the Thermodynamic Properties of the Elements"; American Society for Metals: Metals Park, OH, 1973.

(41) Stull, D. R.; Sinke, G. C. "Thermodynamic Properties of the Elements"; American Chemical Society: Washington, DC, 1956.

(42) Panish, M. B.; Reif, L. *J. Chem. Phys.* **1962**, *37*, 128.

(43) Paule, R. C.; Margrave, J. L. *J. Phys. Chem.* **1963**, *67*, 1896.

(44) Carrera, N. J.; Walker, R. F.; Plante, E. R. *J. Res. Natl. Bur. Stand., Sect. A* **1964**, *68A*, 325.

(45) Norman, J. H.; Staley, H. G.; Bell, W. E. In "Mass Spectrometry in Inorganic Chemistry"; American Chemical Society: Washington, DC, 1968; Adv. Chem. Ser. No. 72, pp 101–114.

(46) Wolcott, N. M. *Annexe Bull. Inst. Int. Froid.* **1955**, 286; *Chem. Abstr.* **1959**, *53*, 15734*c*.

(47) Clusius, K.; Piesbergen, U. *Z. Naturforsch. A* **1959**, *14A*, 23.

(48) Batt, R. H. Report UCRL-11580; USAEC: Washington, DC, 1964; *Diss. Abstr.* **1965**, *26*, 2491.

(49) Ho, J. C.; Viswanathan, R. *J. Phys. Chem. Solids* **1969**, *30*, 169.

(50) Reese, W.; Johnson, W. L. *Phys. Rev. B: Solid State* **1970**, *2*, 2972.

(51) Holzmann, H. *Siebert Festschr.* **1931**, 147; *Chem. Abstr.* **1932**, *26*, 4223.

(52) Berezin, B. Ya.; Chekhovskoi, V. Ya.; Kats, S. A. *Conf. Int. Thermodyn. Chim., [C. R.], 4th* **1975**, *9*, 74; *Chem. Abstr.* **1976**, *84*, 96272*y*.

(53) Furukawa, G. T.; Reilly, M. L.; Gallagher, J. S. *J. Phys. Chem. Ref. Data* **1974**, *3*, 163.

(54) Fisher, E. S.; Dever, D. *Trans. Metall. Soc. AIME* **1967**, *239*, 48.

(55) Hilsenrath, J.; Messina, C. G.; Evans, W. H. Report TDR-64-44; Air Force Weapons Laboratory: Kirtland Air Force Base, NM, 1964. Also available from NTIS, Report AD 606163: *Chem. Abstr.* **1965**, *62*, 7177*b*.

(56) Krikorian, O. H.; Carpenter, J. H.; Newbury, R. S. *High Temp. Sci.* **1969**, *1*, 313.

(57) Kats, S. A.; Berezin, B. Ya.; Gorina, N. B.; Polyakova, V. P.; Savitskii, E. M.; Chekhovskoi, V. A. *Izv. Akad. Nauk SSSR, Met.* **1974**, 87; *Chem. Abstr.* **1975**, *82*, 65250*u*.

(58) Park, J. J. *J. Res. Natl. Bur. Stand., Sect. A* **1968**, *72A*, 1.

(59) Savitskiy, E. M.; Polyakova, V. P.; Gorina, N. B. *Russ. Metall. (Engl. Transl.)* **1971**, 117.

(60) Eremenko, V. N.; Shteps, T. D.; Khoruzhaya, V. G. *Russ. Metall. (Engl. Transl.)* **1973**, 155.

(61) Allen, B. C. *Trans. Metall. Soc. AIME* **1963**, *227*, 1175.

(62) Müller, E.; Schwabe, K. *Z. Elektrochem.* **1929**, *35*, 165; *Z. Phys. Chem., Abt. A* **1931**, *154*, 143.

(63) Gutbier, A.; Schieferdecker, W. *Z. Anorg. Allg. Chem.* **1929**, 184, 305.

(64) Galaktionowa, N. A. "Hydrogen–Metal Systems Databook"; Ordentlich: Holon, Israel, 1980; English translation.

(65) Stevenson, D. P. *J. Chem. Phys.* **1955**, *23*, 203.

(66) Bouten, P. C. P.; Miedema, A. R. *J. Less-Common Met.* **1980**, *71*, 147.

(67) Fisher, G. B. *Surf. Sci.* **1979**, *87*, 215.

(68) Yartys', V. A.; Burnasheva, V. V.; Semenenko, K. N. *Russ. Chem. Rev. (Engl. Transl.)* **1983**, *52*, 299.

(69) "Gmelins Handbuch der Anorganischen Chemie"; Verlag: Weinheim, Germany, 1970; System No. 63.

(70) Brewer, L.; Wengert, P. R. *Metall. Trans.* **1973**, *4*, 83.

(71) Wijbenga, G. Report ECN-102; Netherlands Energy Research Foundation: Petten, Netherlands, 1981.

(72) Miedema, A. R.; Boom, R.; De Boer, F. R. *J. Less-Common Met.* **1975**, *41*, 283.

(73) (a) Wilkes, P. *J. Nucl. Mater.* **1979**, *83*, 166. (b) Raub, Ch. J. *Platinum Met. Rev.* 1984, *28*, 63.

(74) (a) Savitskii, E. M.; Tylkina, M. A.; Polyakova, V. P. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1962**, *7*, 224; **1963**, *8*, 74. (b) Savitskii, E. M.; Polyakova, V. P.; Roshan, N. R. *Obshch. Zakonomern. Str. Diagramm Sostoyaniya Met. Sist. Vses. Soveshch., 5th, 1971* **1973**, 47; *Chem. Abstr.* **1974**, *81*, 159633*c*.

(75) Paschoal, J. O. A.; Kleykamp, H.; Thümmler, F. *J. Less-Common Met.* **1984**, *98*, 279.

(76) McDaniel, C. L.; Schneider, S. J. *J. Res. Natl. Bur. Stand., Sect. A* **1969**, *73A*, 213.

(77) Abou-Zahra, A. A.; Hammad, F. H. *J. Less-Common Met.* **1976**, *48*, 177.

(78) Coffinberry, A. S.; Schonfeld, F. W.; Waber, J. T.; Kelman, L. R.; Tipton, C. R., Jr. In "Reactor Handbook"; Saller, H. A., Tipton, C. R., Jr., Eds.; Wiley-Interscience: New York, 1960; Vol. 1, Part B, pp 248–290.

(79) Holleck, H.; Kleykamp, H. *J. Nucl. Mater.* **1970**, *35*, 158.

(80) Thomson, J. R. *Nature (London)* **1961**, *189*, 217.

(81) Thomson, J. R. *J. Less-Common Met.* **1963**, *5*, 437.

(82) Palenzona, A. *J. Less-Common Met.* **1979**, *66*, P27.

(83) Gschneidner, K. A., Jr.; Elliott, R. O.; Cromer, D. T. *J. Less-Common Met.* **1965**, *8*, 217.

(84) Dwight, A. E.; Downey, J. W.; Conner, R. A., Jr. *Trans. Metall. Soc. AIME* **1966**, *236*, 1509.

(85) Waterstrat, R. M. *J. Less-Common Met.* **1981**, *80*, P31.

(86) (a) Kubaschewski, O. "Iron-Binary Phase Diagrams"; Springer-Verlag: Berlin, 1982. (b) Swartzendruber, L. J.; Sundman, B. *Bull. Alloy Phase Diagrams* **1983**, *4*, 155.

(87) Anderson, E.; Hume-Rothery, W. *J. Less-Common Met.* **1960**, *2*, 443.

(88) Testardi, L. R.; Royer, W. A.; Bacon, D. D.; Strom, A. R.; Wernick, J. H. *Metall. Trans.* **1973**, *4*, 2195.

(89) Rudnitskii, A. A.; Novikova, O. A. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1959**, *4*, 719, 722.

(90) Schmerling, M. A.; Das, B. K.; Lieberman, D. S. *Metall. Trans.* **1970**, *1*, 3273.

(91) Yatsenko, S. P.; Anikin, Yu. A. *Sov. Mater. Sci. (Engl. Transl.)* **1970**, *6*, 333.

(92) Dieva, E. N. *Tr. Inst. Khim., Ural. Nauchn. Tsentr, Akad. Nauk SSSR* **1974**, *29*, 105; *Chem. Abstr.* **1975**, *83*, 66239*e*.

(93) Obrowski, W. *Metall (Berlin)* **1963**, *17*, 108.

(94) Chernogorenko, V. B.; Lynchak, K. A.; Kulik, L. Ya.; Shkaravskii, Yu. F.; Klochkov, L. A. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1977**, *22*, 639.

(95) Flörke, U.; Jeitschko, W. *J. Less-Common Met.* **1982**, *86*, 247.

(96) Müller, R.; Shelton, R. N.; Richardson, J. W., Jr.; Jacobson, R. A. *J. Less-Common Met.* **1983**, *92*, 177.

(97) Buddery, J. H.; Welch, A. J. E. *Nature (London)* **1951**, *167*, 362.

(98) Aronsson, B. *Acta Chem. Scand.* **1959**, *13*, 109.

(99) Finnie, L. N. *J. Less-Common Met.* **1962**, *4*, 24.

(100) Slaski, M.; Szytula, A. *J. Less-Common Met.* **1982**, *87*, L1.

(101) (a) Scullman, R.; Thelin, B. *Phys. Scr.* **1971**, *3*, 19; **1972**, *5*, 201. (b) McIntyre, N. S.; Vander Auwera-Mahieu, A.; Drowart, J. *Trans. Faraday Soc.* **1968**, *64*, 3006. (c) Vander Auwera-Mahieu, A.; Peeters, R.; McIntyre, N. S.; Drowart, J. *Trans. Faraday Soc.* **1970**, *66*, 809.

(102) Behrens, R. G. *J. Less-Common Met.* **1977**, *56*, 55; **1978**, *58*, 47.

(103) Holleck, H.; Kleykamp, H.; Franco, J. I. *Z. Metallkd.* **1975**, *66*, 298.

(104) Wijbenga, G.; Cordfunke, E. H. P. *J. Chem. Thermodyn.* **1982**, *14*, 409.

(105) Cordfunke, E. H. P.; Muis, R. P.; Wijbenga, G.; Burriel, R.; Zainel, H.; To, M.; Westrum, E. F., Jr., manuscript in preparation.
(106) Edwards, J. G.; Starzynski, J. S.; Peterson, D. E. *J. Chem. Phys.* **1980**, *73*, 908.
(107) Kleykamp, H.; Murabayashi, M. *J. Less-Common Met.* **1974**, *35*, 227.
(108) Holleck, H. *J. Nucl. Mater.* **1977**, *66*, 273.
(109) Campbell, G. M.; Mullins, L. J.; Leary, J. A. In "Thermodynamics of Nuclear Materials, 1967"; International Atomic Energy Agency: Vienna, 1968; pp 75–88.
(110) Campbell, G. M. In "Plutonium 1975 and Other Actinides"; North-Holland Publishing Co.: Amsterdam, 1976; pp 95–104.
(111) Peterson, D. E. *J. Nucl. Mater.* **1980**, *91*, 306.
(112) Stepakoff, G. L.; Kaufman, L. *Acta Metall.* **1968**, *16*, 13.
(113) Yamawaki, M.; Nagai, Y.; Kogai, T.; Kanno, M. In "Thermodynamics of Nuclear Materials 1979"; International Atomic Energy Agency: Vienna, 1980; Vol. I, pp 249–261.
(114) (a) Fröhlich, K.; Severin, H. G.; Hempelmann, R.; Wicke, E. *Z. Phys. Chem. (Wiesbaden)* **1980**, *119*, 33. (b) Cubicciotti, D. *J. Phys. Chem.* **1966**, *70*, 2410.
(115) Juza, R.; Meyer, W. *Z. Anorg. Allg. Chem.* **1933**, *213*, 273.
(116) Knop, O. *Can. J. Chem.* **1963**, *41*, 1832.
(117) Passaretti, J. D.; Dwight, K.; Wold, A.; Croft, W. J.; Chianelli, R. R. *Inorg. Chem.* **1981**, *20*, 2631.
(118) De Jong, W. F.; Hoog, A. *Recl. Trav. Chim. Pays-Bas* **1927**, *46*, 173.
(119) Sutarno; Knop, O.; Reid, K. I. G. *Can. J. Chem.* **1967**, *45*, 1391.
(120) Svendsen, S. R. *Acta Chem. Scand., Ser. A* **1979**, *A33*, 601.
(121) Svendsen, S. R. *J. Chem. Thermodyn.* **1977**, *9*, 789.
(122) Zhao, H.; Schils, H. W.; Raub, C. J. *J. Less-Common Met.* **1982**, *86*, L13.
(123) Thomassen, L. *Z. Phys. Chem., Abt. B.* **1929**, *2*, 349.
(124) Groeneveld Meijer, W. O. J. *Am. Mineral.* **1955**, *40*, 646.
(125) Wöhler, L.; Ewald, K.; Krall, H. G. *Ber.* **1933**, *66B*, 1638.
(126) Murray, J. J.; Heyding, R. D. *Can. J. Chem.* **1967**, *45*, 2675.
(127) Raub, C. J.; Compton, V. B.; Geballe, T. H.; Matthias, B. T.; Maita, J. P.; Hull, G. W., Jr. *J. Phys. Chem. Solids* **1965**, *26*, 2051.
(128) Guittard, R.; Heindl, R.; Parsons, R.; Redon, A. M.; Tributsch, H. *J. Electroanal. Chem. Interfacial Electrochem.* **1980**, *111*, 401.
(129) Foise, J.; Kim, K.; Covino, J.; Dwight, K.; Wold, A.; Chianelli, R.; Passaretti, J. *Inorg. Chem.* **1983**, *22*, 61.
(130) Taimni, I. K.; Salaria, G. B. S. *Anal. Chim. Acta* **1954**, *11*, 329.
(131) Taimni, I. K.; Tandon, S. N. *Anal. Chim. Acta* **1960**, *22*, 553.
(132) Taimni, I. K.; Rakshpal, R. *Anal. Chim. Acta* **1961**, *25*, 438.
(133) Rudnev, N. A.; Malofeeva, G. I. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1962**, *7*, 606.
(134) Dehnicke, K.; Loessberg, R.; Pebler, J. *Chem.-Ztg.* **1981**, *105*. 377.
(135) Wöhler, L.; Ewald, K. F. A. *Z. Anorg. Allg. Chem.* **1931**, *199*, 57.
(136) Heyding, R. D.; Calvert, L. D. *Can. J. Chem.* **1961**, *39*, 955.
(137) Zhuravlev, N. N.; Kertes, L. *Zh. Eksp. Teor. Fiz.* **1957**, *32*, 1313; *Chem. Abstr.* **1957**, *51*, 15236*g*.
(138) Kuz'min, R. N.; Zhuravlev, N. N.; Losievskaya, S. A. *Sov. Phys.—Crystallogr. (Engl. Transl.)* **1960**, *4*, 202.
(139) Westrum, E. F., Jr.; Carlson, H. G.; Grønvold, F.; Kjekshus, A. *J. Chem. Phys.* **1961**, *35*, 1670.
(140) Kelley, K. K. "Contributions to the Data on Theoretical Metallurgy, VII.". *Bull.—U.S., Bur. Mines* **1937**, No. 406.
(141) Boerio, J.; Chirico, R.; Galeas, C.; Grøvold, F.; Westrum, E. F., Jr., unpublished data. Cited in: *Bull. Chem. Thermodyn.* **1977**, *20*, 357.
(142) Hepworth, M. A.; Robinson, P. L. *J. Chem. Soc.* **1953**, 3330.
(143) Antony, U.; Lucchesi, A. *Gazz. Chim. Ital.* **1898**, *28* (ii), 139; **1899**, *29* (ii), 314; **1900**, *30* (ii), 71.
(144) Martin, F. S. *J. Chem. Soc.* **1952**, 3055.
(145) Brito, F.; Lewis, D. *Ark. Kemi* **1967**, *26*, 401.
(146) Ginzburg, S. I.; Yuz'ko, M. I.; Fomina, T. A. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1966**, *11*, 1369.
(147) Ginzburg, S. I.; Yuz'ko, M. I.; Fomina, T. A. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1966**, *11*, 1370.
(148) Ginzburg, S. I.; Yuz'ko, M. I.; Fomina, T. A.; Evstaf'eva, O. N. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1975**, *20*, 1082.
(149) Ginzburg, S. I.; Dubrovskaya, G. M. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1971**, *16*, 231.
(150) (a) Orlov, A. M.; Shorikov, Yu. S.; Kunaeva, I. V.; Chalisova, N. N.; Fomina, T. A. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1979**, *24*, 1373. (b) Bernhard, P.; Ludi, A. *Inorg. Chem.* **1984**, *23*, 870.
(151) Remy, H. *Z. Anorg. Allg. Chem.* **1922**, *124*, 248.
(152) Remy, H.; Breimeyer, C. *Z. Anorg. Allg. Chem.* **1923**, *129*, 215.
(153) Gleu, K.; Breuel, W.; Rehm, K. *Z. Anorg. Allg. Chem.* **1938**, *235*, 201, 211.
(154) Mingos, D. M. P. *Transition Met. Chem. (Weinheim, Ger.)* **1978**, *3*, 1.
(155) Ryan, R. R.; Kubas, G. J.; Moody, D. C.; Eller, P. G. In "Structure and Bonding"; Clarke, M. J. et al., Eds.; Springer-Verlag: Berlin, 1981; Vol. 46, pp 47–100.
(156) Wöhler, L.; Balz, P. *Z. Anorg. Allg. Chem.* **1924**, *139*, 411.
(157) Hyde, K. R.; Hooper, E. W.; Waters, J.; Fletcher, J. M. *J. Less-Common Met.* **1965**, *8*, 428.
(158) Howe, J. L.; Howe, J. L., Jr.; Ogburn, S. C., Jr. *J. Am. Chem. Soc.* **1924**, *46*, 335.
(159) Remy, H.; Wagner, T. *Z. Anorg. Allg. Chem.* **1926**, *157*, 339.
(160) Krauss, F.; Kükenthal, H. *Z. Anorg. Allg. Chem.* **1924**, *137*, 32, 333.
(161) Berch, M. L.; Davison, A. *J. Inorg. Nucl. Chem.* **1973**, *35*, 3763.
(162) Shchukarev, S. A.; Kolbin, N. I.; Ryabov, A. N. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1958**, *3* (8), 1.
(163) Bell, W. E.; Garrison, M. C.; Merten, U. *J. Phys. Chem.* **1960**, *64*, 145.
(164) Hill, M. A.; Beamish, F. E. *J. Am. Chem. Soc.* **1950**, *72*, 4855.
(165) Fletcher, J. M.; Gardner, W. E.; Hooper, E. W.; Hyde, K. R.; Moore, F. H.; Woodhead, J. L. *Nature (London)* **1963**, *199*, 1089.
(166) Fletcher, J. M.; Gardner, W. E.; Fox, A. C.; Topping, G. *J. Chem. Soc. A* **1967**, 1038.
(167) Ryumin, A. I.; Ivashentsev, Ya. I. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1978**, *23*, 1613.
(168) Shchukarev, S. A.; Kolbin, N. I.; Ryabov, A. N. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1960**, *5*, 923.
(169) Von Schnering, H. G.; Brodersen, K.; Moers, F.; Breitbach, H. K.; Thiele, G. *J. Less-Common Met.* **1966**, *11*, 288.
(170) Shchukarev, S. A.; Kolbin, N. I.; Ryabov, A. N. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1961**, *6*, 517.
(171) Colton, R. *Nature (London)* **1962**, *193*, 872.
(172) Gall, H.; Lehmann, G. *Ber.* **1926**, *59B*, 2856.
(173) Brodersen, K.; Breitbach, H.-K.; Thiele, G. *Z. Anorg. Allg. Chem.* **1968**, *357*, 162.
(174) Clausen, C. A., III; Prados, R. A.; Good, M. L. *Chem. Phys. Lett.* **1971**, *8*, 565.
(175) Remy, H.; Köhn, M. *Z. Anorg. Allg. Chem.* **1924**, *137*, 365.
(176) Bell, W. E.; Garrison, M. C.; Merten, U. *J. Phys. Chem.* **1961**, *65*, 517.
(177) Shchukarev, S. A.; Kolbin, N. I.; Ryabov, A. N. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1959**, *4*, 763.
(178) Kolbin, N. I.; Ryabov, A. N.; Samoilov, V. M. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1963**, *8*, 805.
(179) Ruff, O.; Vidic, E. *Z. Anorg. Allg. Chem.* **1924**, *136*, 49.
(180) Crowell, W. R.; Yost, D. M. *J. Am. Chem. Soc.* **1928**, *50*, 374.
(181) Grube, G.; Nann, H. *Z. Elektrochem.* **1939**, *45*, 871, 874.
(182) Grube, G.; Fromm, G. *Z. Elektrochem.* **1940**, *46*, 661.
(183) Belikin, A. V.; Borisov, V. V.; Sinitsyn, N. M.; Solomonova, A. S. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1979**, *24*, 1693.
(184) Duvigneaud, P. H.; Reinhard-Derie, D. *Thermochim. Acta* **1981**, *51*, 307.
(185) Seddon, K. R. *Coord. Chem. Rev.* **1982**, *41*, 79.
(186) Remy, H.; Lührs, A. *Ber.* **1928**, *61B*, 917.
(187) Ivanter, I. A.; Kubasov, V. L.; Vorob'ev, G. A.; Pechnikova, G. P. *J. Appl. Chem. USSR (Engl. Transl.)* **1977**, *50*, 871.
(188) Woodhead, J. L.; Fletcher, J. M. Report AERE-R4123; U. K. Atomic Energy Research Establishment: Harwell, England, 1962.
(189) Pizzini, S.; Buzzanca, G.; Mari, C.; Rossi, L.; Torchio, S. *Mater. Res. Bull.* **1972**, *7*, 449.
(190) Lodi, G.; Sivieri, E.; de Battisti, A.; Trasatti, S. *J. Appl. Electrochem.* **1978**, *8*, 135.
(191) Iwakura, C.; Tada, H.; Tamura, H. *Electrochim. Acta* **1977**, *22*, 217.
(192) Howe, J. L. *J. Am. Chem. Soc.* **1901**, *23*, 775.
(193) Howe, J. L. *J. Am. Chem. Soc.* **1927**, *49*, 2381.
(194) Griffith, W. P.; Pawson, D. *J. Chem. Soc., Dalton Trans.* **1973**, 1315.
(195) Petrov, K. I.; Kravchenko, V. V.; Sinitsyn, N. M. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1970**, *15*, 1420.
(196) Aoyama, S. *Z. Anorg. Allg. Chem.* **1924**, *138*, 249.
(197) Jaber, M.; Bertin, F.; Thomas-David, G. *C. R. Hebd. Sēances Acad. Sci., Ser. C* **1977**, *285*, 317.
(198) Alimarin, I. P.; Khvostova, V. P.; Pichugina, G. V.; Tikhonov, I. G.; Kuratashvili, Z. A. *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk* **1974**, *No. 2*, 31; *Chem. Abstr.* **1974**, *81*, 17452*u*.
(199) Charonnat, R. *Ann. Chim. (Paris)* **1931**, *16*, 5; *Chem. Abstr.* **1932**, *26*, 1538.
(200) Mathieson, A. McL.; Mellor, D. P.; Stephenson, N. C. *Acta Crystallogr.* **1952**, *5*, 185.
(201) Dunitz, J. D.; Orgel, L. E. *J. Chem. Soc.* **1953**, 2594.
(202) (a) Deloume, J.-P.; Faure, R.; Thomas-David, G. *Acta Crystallogr., Sect. B* **1979**, *B35*, 558. (b) Clark, R. J. H.; Franks, M. L.; Turtle, P. C. *J. Am. Chem. Soc.* **1977**, *99*, 2473.
(203) San Filippo, J., Jr.; Fagan, P. J.; DiSalvo, F. J. *Inorg. Chem.* **1977**, *16*, 1016.

(204) Glowiak, T.; Sabat, M.; Jėzowska-Trzebiatowska, B. *Acta Crystallogr., Sect. B* **1975**, *B31*, 1783.
(205) Deloume, J.-P.; Duc, G.; Thomas-David, G. *Bull. Soc. Chim. Fr.* **1981**, I-129.
(206) Crisp, R. I.; Seddon, K. R. *Inorg. Chim. Acta* **1980**, *44*, L133.
(207) Phenitsyn, N. K.; Ginzburg, S. I. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1957**, *2* (1), 172.
(208) Briggs, S. H. C. *J. Chem. Soc.* **1925**, *127*, 1042.
(209) Dehand, J.; Rosé, J. *J. Chem. Res., Synop.* **1979**, 155; *J. Chem. Res., Miniprint* **1979**, 2167.
(210) Dehand, J.; Rosé, J. *Inorg. Chim. Acta* **1979**, *37*, 249.
(211) Fergusson, J. E.; Greenaway, A. M. *Aust. J. Chem.* **1978**, *31*, 497.
(212) Adams, C. S.; Mellor, D. P. *Aust. J. Sci. Res., Ser. A* **1952**, *5A*, 577.
(213) Forcheri, S.; Lungagnani, V.; Martini, S.; Scibona, G. *Energ. Nucl. (Milan)* **1960**, *7*, 537.
(214) Gutbier, A.; Krauss, F. *J. Prakt. Chem.* **1915**, *91*, 103.
(215) Kukushkin, Yu. N.; Maslov, E. I.; Ryabkova, T. P.; Lobadyuk, V. I. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1982**, *27*, 1470.
(216) Adams, D. M.; Gebbie, H. A. *Spectrochim. Acta* **1963**, *19*, 925.
(217) Earnshaw, A.; Figgis, B. N.; Lewis, J.; Peacock, R. D. *J. Chem. Soc.* **1961**, 3132.
(218) Rössler, K.; Winter, J. *Chem. Phys. Lett.* **1977**, *46*, 566.
(219) Sinitsyn, N. M.; Kozlov, A. S.; Borisov, V. V. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1982**, *27*, 1617.
(220) Khodashova, T. S. *J. Struct. Chem. (Engl. Transl.)* **1960**, *1*, 308.
(221) Hopkins, T. E.; Zalkin, A.; Templeton, D. H.; Adamson, M. G. *Inorg. Chem.* **1966**, *5*, 1431.
(222) Earnshaw, A.; Figgis, B. N.; Lewis, J.; Nyholm, R. S. *Nature (London)* **1957**, *179*, 1121.
(223) Hartmann, H.; Buschbeck, C. *Z. Phys. Chem. (Wiesbaden)* **1957**, *11*, 120.
(224) Buividaite, M. *Z. Anorg. Allg. Chem.* **1935**, *222*, 279; **1937**, *230*, 286.
(225) Drew, M. G. B.; Rice, D. A.; Timewell, C. W. *Inorg. Nucl. Chem. Lett.* **1971**, *7*, 59.
(226) Gaylor, J. R.; Senoff, C. V. *Inorg. Chem.* **1972**, *11*, 2551.
(227) Danilov, M. P.; Nazarov, Yu. N.; Plotnikov, K. A. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1982**, *27*, 1503.
(228) Hopkins, T. E.; Zalkin, A.; Templeton, D. H.; Adamson, M. G. *Inorg. Chem.* **1969**, *8*, 2421.
(229) Ijdo, D. J. W. Ph.D. Dissertation, University of Leiden, Leiden, Netherlands, 1960. Cited in ref 211.
(230) Darriet, J. *Rev. Chim. Miner.* **1981**, *18*, 27.
(231) Ivanova, S. N.; Gindin, L. M.; Mironova, L. Ya. *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk.* **1967**, *No. 1*, 97; *Chem. Abstr.* **1967**, *67*, 68134*k*.
(232) Bursten, B. E.; Cotton, F. A.; Fang, A. *Inorg. Chem.* **1983**, *22*, 2127.
(233) Rose, D.; Wilkinson, G. *J. Chem. Soc. A* **1970**, 1791.
(234) Mercer, E. E.; Dumas, P. E. *Inorg. Chem.* **1971**, *10*, 2755.
(235) Remy, H. *Z. Anorg. Allg. Chem.* **1920**, *113*, 229.
(236) Bino, A.; Cotton, F. A. *J. Am. Chem. Soc.* **1980**, *102*, 608.
(237) Barton, J. K.; Szalda, D. J.; Rabinowitz, H. N.; Waszczak, J. V.; Lippard, S. J. *J. Am. Chem. Soc.* **1979**, *101*, 1434.
(238) Bernhard, P.; Bürgi, H.-B.; Hauser, J.; Lehmann, H.; Ludi, A. *Inorg. Chem.* **1982**, *21*, 3936.
(239) Rechnitz, G. A.; Catherino, H. A. *Inorg. Chem.* **1965**, *4*, 112.
(240) Dumas, P. E.; Mercer, E. E. *Inorg. Chem.* **1972**, *11*, 531.
(241) Evans, I. P.; Spencer, A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1973**, 204.
(242) Mercer, A.; Trotter, J. *J. Chem. Soc., Dalton Trans.* **1975**, 2480.
(243) Allen, A. D.; Senoff, C. V. *Can. J. Chem.* **1967**, *45*, 1337.
(244) Young, J. F.; Gillard, R. D.; Wilkinson, G. *J. Chem. Soc.* **1964**, 5176.
(245) Farrugia, L. J.; James, B. R.; Lassigne, C. R.; Wells, E. J. *Can. J. Chem.* **1982**, *60*, 1304.
(246) DeFord, D. D.; Davidson, A. W. *J. Am. Chem. Soc.* **1951**, *73*, 1469.
(247) Rajan, K. P.; Neff, V. D. *J. Phys. Chem.* **1982**, *86*, 4361.
(248) Howe, J. L. *J. Am. Chem. Soc.* **1901**, *23*, 781.
(249) Adamson, M. G. *Aust. J. Chem.* **1967**, *20*, 2517.
(250) Key, D. L.; Larkworthy, L. F.; Salmon, J. E. *J. Chem. Soc. A* **1971**, 2583.
(251) Kubaschewski, O.; Alcock, C. B. "Metallurgical Thermochemistry", 5th ed.; Pergamon Press: Oxford, 1979.
(252) Myers, C. E.; Graves, D. T. *J. Chem. Eng. Data* **1977**, *22*, 440.
(253) Fletcher, J. M.; Woodhead, J. L. *J. Inorg. Nucl. Chem.* **1965**, *27*, 1517.
(254) Maya, L. *J. Inorg. Nucl. Chem.* **1979**, *41*, 67.
(255) Bottomley, F. *Coord. Chem. Rev.* **1978**, *26*, 7.
(256) Pandey, K. K.; Ahuja, S. R.; Poonia, N. S.; Bharti, S. *J. Chem. Soc., Chem. Commun.* **1982**, 1268.
(257) Fletcher, J. M.; Jenkins, I. L.; Lever, F. M.; Martin, F. S.; Powell, A. R.; Todd, R. *J. Inorg. Nucl. Chem.* **1955**, *1*, 378.
(258) Nikol'skii, V. D.; Shmidt, V. S. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1957**, *2* (12), 97; **1958**, *3* (11), 50.
(259) Fletcher, J. M. *J. Inorg. Nucl. Chem.* **1958**, *8*, 277.
(260) Fletcher, J. M.; Brown, P. G. M.; Gardner, E. R.; Hardy, C. J.; Wain, A. G.; Woodhead, J. L. *J. Inorg. Nucl. Chem.* **1959**, *12*, 154.
(261) Brown, P. G. M. *J. Inorg. Nucl. Chem.* **1960**, *13*, 73.
(262) Scargill, D.; Lyon, C. E.; Large, N. R.; Fletcher, J. M. *J. Inorg. Nucl. Chem.* **1965**, *27*, 161.
(263) Simonsen, S. H.; Mueller, M. H. *J. Inorg. Nucl. Chem.* **1965**, *27*, 309.
(264) Boswell, G. G. J.; Soentono, S. *J. Inorg. Nucl. Chem.* **1981**, *43*, 1625.
(265) Blasius, E.; Glatz, J.-P.; Neumann, W. *Radiochim. Acta* **1981**, *29*, 159.
(266) Nikol'skii, B. P.; Il'enko, E. I. *Sov. Radiochem. (Engl. Transl.)* **1966**, *8*, 175.
(267) Mercer, E. E.; McAllister, W. A.; Durig, J. R. *Inorg. Chem.* **1966**, *5*, 1881.
(268) Mercer, E. E.; Campbell, W. M., Jr.; Wallace, R. M. *Inorg. Chem.* **1964**, *3*, 1018.
(269) Gans, P.; Sabatini, A.; Sacconi, L. *Inorg. Chem.* **1966**, *5*, 1877.
(270) Polak, P. *Radiochim. Acta* **1977**, *24*, 193.
(271) Zvyagintsev, O. E.; Starostin, S. M. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1961**, *6*, 658.
(272) Sinitsyn, N. M.; Kokunova, V. N.; Svetlov, A. A. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1982**, *27*, 1317.
(273) Al Omer, S. S.; Askar, K. A.; Habboush, D. A. *Thermochim. Acta* **1981**, *45*, 1.
(274) Wehner, P.; Hindman, J. C. *J. Am. Chem. Soc.* **1950**, *72*, 3911.
(275) Niedrach, L. W.; Tevebaugh, A. D. *J. Am. Chem. Soc.* **1951**, *73*, 2835.
(276) Gortsema, F. P.; Cobble, J. W. *J. Am. Chem. Soc.* **1961**, *83*, 4317.
(277) Vdovenko, V. M.; Lazarev, L. N.; Khvorostin, Ya. S. *Sov. Radiochem. (Engl. Transl.)* **1965**, *7*, 228.
(278) Wallace, R. M.; Propst, R. C. *J. Am. Chem. Soc.* **1969**, *91*, 3779.
(279) Brémard, C.; Nowogrocki, G.; Tridot, G. *Bull. Soc. Chim. Fr.* **1974**, 392.
(280) Wilson, A. S. *J. Inorg. Nucl. Chem.* **1958**, *7*, 149.
(281) VanHoudt, H. E. *J. Inorg. Nucl. Chem.* **1981**, *43*, 1603.
(282) Anderson, J. S.; McConnell, J. D. M. *J. Inorg. Nucl. Chem.* **1955**, *1*, 371.
(283) Brémard, C.; Nowogrocki, G.; Tridot, G. *Bull. Soc. Chim. Fr.* **1968**, 1961.
(284) Wöhler, L.; Balz, P.; Metz, L. *Z. Anorg. Allg. Chem.* **1924**, *139*, 205.
(285) Lunde, C. *Z. Anorg. Allg. Chem.* **1927**, *163*, 345.
(286) Wilson, A. S. *J. Chem. Eng. Data* **1960**, *5*, 521.
(287) Koda, Y. *J. Inorg. Nucl. Chem.* **1963**, *25*, 314.
(288) Remy, H. *Z. Anorg. Allg. Chem.* **1923**, *126*, 185.
(289) Bell, W. E.; Tagami, M. *J. Phys. Chem.* **1963**, *67*, 2432.
(290) Prosychev, I. I.; Shaplygin, I. S. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1981**, *26*, 1677.
(291) Tagirov, V. K.; Chizhikov, D. M.; Kazenas, E. K.; Shubochkin, L. K. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1975**, *20*, 1133.
(292) Battaglin, C.; Carnera, A.; Mazzoldi, P.; Lodi, G.; Bonora, P.; Daghetti, A.; Trasatti, S. *J. Electroanal. Chem. Interfacial Electrochem.* **1982**, *135*, 313.
(293) Kim, K. S.; Winograd, N. *J. Catal.* **1974**, *35*, 66.
(294) Augustynski, J.; Balsenc, L.; Hinden, J. *J. Electrochem. Soc.* **1978**, *125*, 1093.
(295) Schäfer, H.; Gerhardt, W.; Tebben, A. *Angew. Chem.* **1961**, *73*, 27.
(296) Schäfer, H.; Schneidereit, G.; Gerhardt, W. *Z. Anorg. Allg. Chem.* **1963**, *319*, 327.
(297) Butler, S. R.; Gillson, J. L. *Mater. Res. Bull.* **1971**, *6*, 81.
(298) Huang, Y. S.; Park, H. L.; Pollak, F. H. *Mater. Res. Bull.* **1982**, *17*, 1305.
(299) Cotton, F. A.; Mague, J. T. *Inorg. Chem.* **1966**, *5*, 317.
(300) Rogers, D. B.; Shannon, R. D.; Sleight, A. W.; Gillson, J. L. *Inorg. Chem.* **1969**, *8*, 841.
(301) Fredrickson, D. R.; Chasanov, M. G. *J. Chem. Eng. Data* **1972**, *17*, 21.
(302) Mattheiss, L. F. *Phys. Rev. B: Solid State* **1976**, *13*, 2433.
(303) Sasaki, T. A.; Soga, T. *Physica B+C (Amsterdam)* **1981**, *111B+C*, 304.
(304) Krishna Rao, K. V.; Iyengar, L. *Acta Crystallogr., Sect. A* **1969**, *A25*, 302.
(305) Boman, C.-E. *Acta Chem. Scand.* **1970**, *24*, 116.
(306) Bayer, G.; Wiedemann, H. G. *Thermochim. Acta* **1975**, *11*, 79.
(307) Schäfer, H.; Tebben, A.; Gerhardt, W. *Z. Anorg. Allg. Chem.* **1963**, *321*, 41.
(308) Alcock, C. B.; Hooper, G. W. *Proc. R. Soc. London, Ser. A* **1960**, *254*, 551.
(309) Raziunas, V.; Macur, G.; Katz, S. *J. Chem. Phys.* **1965**, *43*, 1010.

(310) Scullman, R.; Thelin, B. *J. Mol. Spectrosc.* **1975**, *56*, 64.
(311) Dillard, J. G.; Kiser, R. W. *J. Phys. Chem.* **1965**, *69*, 3893.
(312) Vadimsky, R. G.; Frankenthal, R. P.; Thompson, D. E. *J. Electrochem. Soc.* **1979**, *126*, 2017.
(313) Sharma, S. P.; Hines, L. L. *IEEE Trans. CHMT* **1983**, *CHMT-6*, 89.
(314) Llopis, J.; Vâzquez, M. *Electrochim. Acta* **1966**, *11*, 633.
(315) Burke, L. D.; Murphy, O. J.; O'Neill, J. F.; Venkatesan, S. *J. Chem. Soc., Faraday Trans. 1* **1977**, *73*, 1659.
(316) Iwakura, C.; Hirao, K.; Tamura, H. *Electrochim. Acta* **1977**, *22*, 329.
(317) Horkans, J.; Shafer, M. W. *J. Electrochem. Soc.* **1977**, *124*, 1202.
(318) Lam, K. W.; Johnson, K. E.; Lee, D. G. *J. Electrochem. Soc.* **1978**, *125*, 1069.
(319) Burke, L. D.; Whelan, D. P. *J. Electroanal. Chem. Interfacial Electrochem.* **1979**, *103*, 179.
(320) Krauss, F.; Kükenthal, H. *Z. Anorg. Allg. Chem.* **1924**, *136*, 62.
(321) Nikol'skii, A. B. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1963**, *8*, 541.
(322) Krauss, F. *Z. Anorg. Allg. Chem.* **1923**, *131*, 348.
(323) Remy, H. *Angew. Chem.* **1926**, *39*, 1061.
(324) Nikol'skii, A. B. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1963**, *8*, 668.
(325) Němec, I.; Berka, A.; Zýka, J. *Microchem. J.* **1962**, *6*, 525.
(326) Nikol'skii, A. B.; Ryabov, A. N. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1964**, *9*, 3.
(327) Nisel'son, L. A.; Sokolova, T. D.; Orlov, A. M.; Shorikov, Yu. S. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1981**, *26*, 412.
(328) Nisel'son, L. A.; Sokolova, T. D.; Shorikov, Yu. S.; Orlov, A. M. *Russ. J. Inorg. Chem.* (*English Transl.*) **1981**, *26*, 1788.
(329) Martin, F. S. *J. Chem. Soc.* **1954**, 2564.
(330) Shiloh, M.; Givon, M.; Spiegler, K. S. *J. Inorg. Nucl. Chem.* **1963**, *25*, 103.
(331) Dodd, R. E. *Trans. Faraday Soc.* **1959**, *55*, 1480.
(332) Ortner, M. H. *J. Chem. Phys.* **1961**, *34*, 556.
(333) Barton, G. B. *Spectrochim. Acta* **1963**, *19*, 1619.
(334) Levin, I. W.; Abramowitz, S. *J. Chem. Phys.* **1969**, *50*, 4860.
(335) Levin, I. W. *Inorg. Chem.* **1969**, *8*, 1018.
(336) Königer, F.; Müller, A. *J. Mol. Spectrosc.* **1977**, *65*, 339.
(337) Brevard, C.; Granger, P. *J. Chem. Phys.* **1981**, *75*, 4175.
(338) Schäfer, L.; Seip, H. M. *Acta Chem. Scand.* **1967**, *21*, 737.
(339) Trehoux, J.; Thomas, D.; Nowogrocki, G.; Tridot, G. *C. R. Hebd. Séances Acad. Sci., Ser. C* **1969**, *268*, 246.
(340) Krebs, B.; Hasse, K.-D. *Acta Crystallogr., Sect. B* **1976**, *B32*, 1334.
(341) Passenheim, B. C.; McCollum, D. C. *J. Chem. Phys.* **1969**, *51*, 320.
(342) Ryden, W. D.; Lawson, A. W.; Sartain, C. C. *Phys. Lett. A* **1968**, *A26*, 209.
(343) Shchukarev, S. A.; Ryabov, A. N. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1960**, *5*, 941.
(344) Kleykamp, H. *Z. Phys. Chem.* (*Wiesbaden*) **1969**, *66*, 131.
(345) Pizzini, S.; Rossi, L. *Z. Naturforsch., A* **1971**, *26A*, 177.
(346) Chatterji, D.; Vest, R. W. *J. Am. Ceram. Soc.* **1971**, *54*, 73.
(347) (a) Ortner, M. H.; Anderson, C. J.; Campbell, P. F. Report IDO-14504; USAEC: Idaho Operations, May 19, 1961. (b) Brewer, L.; Rosenblatt, G. M. *Adv. High Temp. Chem.* **1969**, *2*, 1. (c) Pedley, J. B.; Marshall, E. M. *J. Phys. Chem. Ref. Data* **1983**, *12*, 967.
(348) Mercer, E. E.; Farrar, D. T. *Can. J. Chem.* **1969**, *47*, 581.
(349) Myuller, R. L.; Nikol'skii, A. B. *Sov. Radiochem.* (*Engl. Transl.*) **1962**, *4*, 321.
(350) Nikol'skii, A. B. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1964**, *9*, 1356.
(351) Silverman, M. D.; Levy, H. A. Report ORNL-746; Oak Ridge National Laboratory: Oak Ridge, TN, Nov 13, 1950.
(352) Nowogrocki, G.; Tridot, G. *Bull. Soc. Chim. Fr.* **1965**, 688.
(353) Silverman, M. D.; Levy, H. A. *J. Am. Chem. Soc.* **1954**, *76*, 3319.
(354) Silverman, M. D.; Levy, H. A. *J. Am. Chem. Soc.* **1954**, *76*, 3317.
(355) Krauss, F. *Z. Anorg. Allg. Chem.* **1924**, *132*, 301.
(356) Popova, T. L.; Kisel', N. G.; Karlov, V. P.; Krivobok, V. I. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1981**, *26*, 1613.
(357) Nowogrocki, G.; Abraham, F.; Trêhoux, J.; Thomas, D. *Acta Crystallogr., Sect. B* **1976**, *B32*, 2413.
(358) Carrington, A.; Symons, M. C. R. *J. Chem. Soc.* **1960**, 284.
(359) Hauck, J. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1969**, *B24*, 1067.
(360) Darriet, J.; Drillon, M.; Villeneuve, G.; Hagenmuller, P. *J. Solid State Chem.* **1976**, *19*, 213.
(361) Gibb, T. C.; Greatrex, R.; Greenwood, N. N. *J. Solid State Chem.* **1980**, *31*, 153.
(362) Hayashi, K.; Demazeau, G.; Pouchard, M. *C. R. Hebd. Séances Acad. Sci., Ser. II* **1981**, *292*, 1433.
(363) Greatrex, R.; Greenwood, N. N.; Lal, M.; Fernandez, I. *J. Solid State Chem.* **1979**, *30*, 137.
(364) Popova, T. L.; Kisel', N. G.; Karlov, V. P.; Bezrukov, V. I.; Krivobok, V. I. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1980**, *25*, 898.
(365) Donohue, P. C.; Katz, L.; Ward, R. *Inorg. Chem.* **1965**, *4*, 306.
(366) Drillon, M.; Padel, L.; Bernier, J.-C. *J. Chem. Soc., Faraday Trans. 2* **1979**, *75*, 1193.
(367) Kochergina, L. L.; Kondratov, O. I.; Shorikov, Yu. S.; Fomichev, V. V.; Petrov, K. I. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1982**, *27*, 638.
(368) Blacklock, K.; White, H. W.; Gürmen, E. *J. Chem. Phys.* **1980**, *73*, 1966.
(369) Komarov, V. P.; Shaplygin, I. S. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1982**, *27*, 164.
(370) Shaplygin, I. S.; Lazarev, V. B. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1980**, *25*, 1837.
(371) Popova, T. L.; Kisel', N. G.; Krivobok, V. I.; Karlov, V. P. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1981**, *26*, 1610.
(372) Wilhelm, M.; Hoppe, R. *Z. Anorg. Allg. Chem.* **1978**, *438*, 90.
(373) Drillon, M.; Darriet, J.; Hagenmuller, P.; Georges, R. *J. Phys. Chem. Solids* **1980**, *41*, 507.
(374) Blanquet, P. R. *Histochemistry* **1976**, *47*, 63.
(375) de C. T. Carrondo, M. A. A. F.; Griffith, W. P.; Hall, J. P.; Skapski, A. C. *Biochim. Biophys. Acta* **1980**, *627*, 332.
(376) Fletcher, J. M.; Greenfield, B. F.; Hardy, C. J.; Scargill, D.; Woodhead, J. L. *J. Chem. Soc.* **1961**, 2000.
(377) Campbell, J. R.; Clark, R. J. H.; Griffith, W. P.; Hall, J. P. *J. Chem. Soc., Dalton Trans.* **1980**, 2228.
(378) Morgan, G. T.; Burstall, F. H. *J. Chem. Soc.* **1936**, 41.
(379) Sterling, C. *Am. J. Bot.* **1970**, *57*, 172.
(380) Larsen, R. P.; Ross, L. E. *Anal. Chem.* **1959**, *31*, 176.
(381) Marczenko, Z.; Balcerzak, M.; Kuś, S. *Talanta* **1980**, *27*, 1087.
(382) Luoma, E. V.; Brubaker, C. H., Jr. *Inorg. Chem.* **1966**, *5*, 1618.
(383) Haissinsky, M.; Dran, J.-C. *J. Chim. Phys. Phys.-Chim. Biol.* **1968**, *65*, 321.
(384) Viste, A.; Gray, H. B. *Inorg. Chem.* **1964**, *3*, 1113.
(385) Jørgensen, C. K. *Prog. Inorg. Chem.* **1970**, *12*, 101–158.
(386) Santos, P. S.; Temperini, M. L. A.; Sala, O. *J. Mol. Struct.* **1979**, *53*, 31; *56*, 310 (errata).
(387) Eichner, P. *Bull. Soc. Chim. Fr.* **1967**, 2051.
(388) Connick, R. E.; Hurley, C. R. *J. Phys. Chem.* **1957**, *61*, 1018.
(389) Connick, R. E.; Hurley, C. R. *J. Am. Chem. Soc.* **1952**, *74*, 5012.
(390) Luoma, E. V.; Brubaker, C. H., Jr. *Inorg. Chem.* **1966**, *5*, 1637.
(391) Carrington, A.; Symons, M. C. R. *J. Chem. Soc.* **1956**, 3373.
(392) Avdeev, D. K.; Seregin, V. I.; Tekster, E. N. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1971**, *16*, 399.
(393) (a) Nowogrocki, G.; Tridot, G. *Bull. Soc. Chim. Fr.* **1965**, 684. (b) Nikitina, G. P.; Ivanov; Yu. E.; Egorova, V. P.; Pushlenkov, M. F.; Shumkov, V. G. *Kinet. Catal.* (*Engl. Transl.*) **1973**, *14*, 1271.
(394) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Halow, I.; Bailey, S. M.; Schumm, R. H. Technical Note 270-4; NBS: Washington, DC, May 1969.
(395) Fletcher, J. M.; Gardner, W. E.; Greenfield, B. F.; Holdoway, M. J.; Rand, M. H. *J. Chem. Soc. A* **1968**, 653.
(396) Keattch, C. J.; Redfern, J. P. *J. Less-Common Met.* **1962**, *4*, 460.
(397) Bardin, M. B.; Tkhan, N. P. *Russ. J. Anal. Chem.* (*Engl. Transl.*) **1975**, *30*, 464.
(398) Trojánek, A. *J. Electroanal. Chem. Interfacial Electrochem.* **1977**, *81*, 189.
(399) Khain, V. S.; Volkov, A. A. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1978**, *23*, 1631.
(400) Avdeev, D. K.; Seregin, V. I.; Tekster, E. N. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1971**, *16*, 592.
(401) El Guebely, M. A.; Haissinsky, M. *J. Chim. Phys. Phys.-Chim. Biol.* **1954**, *51*, 290.
(402) Doblhofer, K.; Metikoš, M.; Ogumi, Z.; Gerischer, H. *Ber. Bunsenges Phys. Chem.* **1978**, *82*, 1046.
(403) Hadži-Jordanov, S.; Angerstein-Kozlowska, H.; Vukovič, M.; Conway, B. E. *J. Electrochem. Soc.* **1978**, *125*, 1471.
(404) (a) Galizzioli, D.; Tantardini, F.; Trasatti, S. *J. Appl. Electrochem.* **1974**, *4*, 57. (b) Cady, H. H. Ph.D. Dissertation, University of California, Berkeley, CA, 1957; UCRL-3757. (c) Michell, D.; Rand, D. A. J.; Woods, R. *J. Electroanal. Chem. Interfacial Electrochem.* **1978**, *89*, 11. (d) Lenza, R. O.; De Tacconi, N. R.; Arvia, A. J. *J. Electroanal. Chem. Interfacial Electrochem.* **1983**, *151*, 193.
(405) Atwood, D. K.; De Vries, T. *J. Am. Chem. Soc.* **1962**, *84*, 2659.
(406) Gortsema, F. P.; Cobble, J. W. *J. Am. Chem. Soc.* **1959**, *81*, 5516.
(407) Brito, F.; Lewis, D. *Ark. Kemi* **1967**, *26*, 391.
(408) Wallace, R. M. *J. Phys. Chem.* **1964**, *68*, 2418.
(409) Brito, F. *U.S. Dep. Commer. Off. Tech. Serv., AD* **1961**, *267432*, 28 pp; *Chem. Abstr.* **1963**, *58*, 6425*e*.
(410) Atwood, D. K.; De Vries, T. *J. Am. Chem. Soc.* **1961**, *83*, 1509.
(411) Brandštetr, J.; Křivánek, M.; Vřeštál, J. *Collect. Czech. Chem. Commun.* **1961**, *26*, 2596.
(412) Böttcher, W.; Brown G. M.; Sutin, N. *Inorg. Chem.* **1979**, *18*, 1447.

(413) Harzion, Z.; Navon, G. *Inorg. Chem.* **1980**, *19*, 2236.
(414) Brĕmard, C.; Tridot, G. *C. R. Hebd. Sĕances Acad. Sci., Ser. C* **1974**, *278*, 1413.
(415) Wan, B.-Z.; Lunsford, J. H. *Inorg. Chim. Acta* **1982**, *65*, L29.
(416) Starik, I. E. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1958**, *3* (1), 5.
(417) Starik, I. E.; Kositsyn, A. V. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1957**, *2* (2), 332.
(418) Davydov, Yu. P. *Sov. Radiochem.* (*Engl. Transl.*) **1967**, *9*, 89.
(419) Starik, I. E.; Ampelogova, N. I.; Barbanel', Yu. A.; Ginzburg, F. L.; Il'menkova, L. I.; Grozovskaya, N. G.; Skul'skii, I. A.; Sheidina, L. D. *Sov. Radiochem.* (*Engl. Transl.*) **1967**, *9*, 99.
(420) Davies, C. W. "Ion Association"; Butterworths: London, 1962; Chapter 3.
(421) (a) Pshenitsyn, N. K.; Ginzburg, S. I. *Izv. Sekt. Platiny Drugikh Blagorodn. Met., Inst. Obshch. Neorg. Khim., Akad. Nauk SSSR* **1949**, *24*, 100; *Chem. Abstr.* **1951**, *45*, 2811*c–e*. (b) Pshenitsyn, N. K.; Ginzburg, S. I. *Izv. Sekt. Platiny Drugikh Blagorodn. Met., Inst. Obshch. Neorg. Khim., Akad. Nauk SSSR* **1954**, *28*, 213; *Chem. Abstr.* **1956**, *50*, 722*b*.
(422) Varshal, G. M.; Koshcheeva, I. Ya.; Akhmanova, M. V.; Dorofeeva, V. A. *J. Anal. Chem. USSR* (*Engl. Transl.*) **1983**, *38*, 1395.
(423) Koch, H.; Bruchertseifer, H. *Radiochim. Acta* **1965**, *4*, 82.
(424) (a) Lazarev, L. N.; Khvorostin, Ya. S. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1968**, *13*, 1297. (b) Schauwers, J.; Meuris, F.; Heerman, L.; D'Olieslager, W. *Electrochim. Acta* **1981**, *26*, 1065. (c) D'Olieslager, W.; Heerman, L.; Clarysse, M. *Polyhedron* **1983**, *2*, 1107.
(425) Vdovenko, V. M.; Lazarev, L. N.; Khvorostin, Ya. S. *Sov. Radiochem.* (*Engl. Transl.*) **1967**, *9*, 449.
(426) Jorgensen, C. K. *Mol. Phys.* **1959**, *2*, 309.
(427) Broszkiewicz, R. K. *Radiat. Phys. Chem.* **1980**, *15*, 133.
(428) Maslov, E. I.; Goncharov, A. V.; Kukushkin, Yu. N. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1976**, *21*, 1576.
(429) Paramonova, V. I.; Latyshev, Ye. F. *Sov. Radiochem.* (*Engl. Transl.*) **1959**, *4*, 219.
(430) Rysev, A. P.; Zhitenko, L. P.; Alekseeva, I. I. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1977**, *22*, 1340.
(431) Bol'shakov, K. A.; Sinitsyn, N. M.; Borisov, V. V. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1972**, *17*, 1731.
(432) Shlenskaya, V. I.; Biryukov, A. A.; Kadomtseva, V. M. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1972**, *17*, 572.
(433) Wehner, P.; Hindman, J. C. *J. Phys. Chem.* **1952**, *56*, 10.
(434) Ohyoshi, A.; Ohyoshi, E.; Senoo, M.; Shinagawa, M. *J. Nucl. Sci. Technol.* **1966**, *3*, 237.
(435) Biryukov, A. A.; Shlenskaya, V. I.; Rabinovich, B. S. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1969**, *14*, 413.
(436) Pilipenko, A. T.; Sereda, I. P.; Semchinskaya, Z. A. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1971**, *16*, 1349.
(437) Ohyoshi, E.; Ohyoshi, A.; Shinagawa, M. *Radiochim. Acta* **1970**, *13*, 10.
(438) Alimarin, I. P.; Shlenskaya, V. I.; Biryukov, A. A.; Khvostova, V. P.; Efremenko, O. A.; Shumkova, N. G. *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk* **1970**, *No. 4*, 3; *Chem. Abstr.* **1971**, *74*, 71100*w*.
(439) Pshenitsyn, N. K.; Ezerskaya, N. A. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1960**, *5*, 513; **1961**, *6*, 312.
(440) Alimarin, I. P.; Shlenskaya, V. I.; Kuratashvili, Z. A. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1973**, *18*, 250.
(441) Bol'shakov, K. A.; Sinitsyn, N. M.; Borisov, V. V.; Borbat, V. F. *Dokl. Chem.* (*Engl. Transl.*) **1969**, *188*, 791.
(442) Potts, L. W.; Swofford, H. S., Jr. *Anal. Chem.* **1975**, *47*, 131.
(443) Grube, G.; Fromm, G. *Z. Elektrochem.* **1941**, *47*, 208.
(444) Backhouse, J. R.; Dwyer, F. P. *Proc. R. Soc. N. S. W.* **1949**, *83*, 138, 146.
(445) Mercer, E. E.; Buckley, R. R. *Inorg. Chem.* **1965**, *4*, 1692.
(446) Vdovenko, V. M.; Lazarev, L. N.; Khvorostin, Ya. S. *Sov. Radiochem.* (*Engl. Transl.*) **1966**, *8*, 613; **1967**, *9*, 445.
(447) (a) Buckley, R. R.; Mercer, E. E. *J. Phys. Chem.* **1966**, *70*, 3103. (b) Bernhard, P.; Helm, L.; Rapaport, I.; Ludi, A.; Merbach, A. E. *J. Chem. Soc., Chem. Commun.* **1984**, 302.
(448) Kallen, T. W.; Earley, J. E. *Inorg. Chem.* **1971**, *10*, 1149.
(449) Weaver, M. J. *J. Phys. Chem.* **1980**, *84*, 568.
(450) Bernhard, P.; Lehmann, H.; Ludi, A. *J. Chem. Soc., Chem. Commun.* **1981**, 1216.
(451) Kallen, T. W.; Earley, J. E. *Inorg. Chem.* **1971**, *10*, 1152.
(452) Broomhead, J. A.; Basolo, F.; Pearson, R. G. *Inorg. Chem.* **1964**, *3*, 826.
(453) Eliades, T.; Harris, R. O.; Reinsalu, P. *Can. J. Chem.* **1969**, *47*, 3823.
(454) Lazarev, L. N.; Khvorostin, Ya. S. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1968**, *13*, 311.
(455) Shanker, R.; Venkateswarlu, K. S.; Shankar, J. *J. Less-Common Met.* **1968**, *15*, 75.
(456) Garif'yanov, N. S.; Luchkina, S. A. *Russ. J. Inorg. Chem.* (*Engl. Trans.*) **1969**, *14*, 1107.
(457) Fine, D. A. Ph.D. Dissertation, University of California, Berkeley, CA, 1960; UCRL-9059.
(458) Starik, I. E.; Barbanel', Yu. A. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1961**, *6*, 109.
(459) Zintl, E.; Zaimis, P. *Ber.* **1927**, *60B*, 842.
(460) Remy, H.; Wagner, T. *Z. Anorg. Allg. Chem.* **1927**, *168*, 1.
(461) Remy, H.; Wagner, T. *Ber.* **1927**, *60B*, 493; **1928**, *61B*, 151.
(462) Manchot, W.; Schmid, H. *Ber.* **1931**, *64B*, 2672.
(463) Manchot, W.; Düsing, J. *Z. Anorg. Allg. Chem.* **1933**, *212*, 21.
(464) Sawyer, D. T.; George, R. S.; Bagger, J. B. *J. Am. Chem. Soc.* **1959**, *81*, 5893.
(465) Rechnitz, G. A. *Inorg. Chem.* **1962**, *1*, 953.
(466) Radhakrishnamurti, P. S.; Janardhana, C.; Mohanty, G. K. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 3617.
(467) Pantini, F. *J. Less-Common Met.* **1962**, *4*, 116.
(468) Shukla, S. K. *J. Chromatogr.* **1962**, *8*, 96.
(469) Hrabikova, J.; Dolezal, J.; Zyka, J. *Anal. Lett.* **1974**, *7*, 819.
(470) Cady, H. H.; Connick, R. E. *J. Am. Chem. Soc.* **1958**, *80*, 2646.
(471) Connick, R. E.; Fine, D. A. *J. Am. Chem. Soc.* **1960**, *82*, 4187.
(472) Connick, R. E.; Fine, D. A. *J. Am. Chem. Soc.* **1961**, *83*, 3414.
(473) Connick, R. E. In "Advances in the Chemistry of the Coordination Compounds"; Kirschner, S., Ed.; Macmillan: New York, 1961; pp 15–20.
(474) Mercer, E. E.; McAllister, W. A. *Inorg. Chem.* **1965**, *4*, 1414.
(475) Adamson, M. G. *J. Chem. Soc. A* **1968**, 1370.
(476) Marques, B. E.; Simões, M. de L. S. *Rev. Port. Quim.* **1964**, *6*, 29.
(477) Gorski, B.; Koch, H. *J. Inorg. Nucl. Chem.* **1969**, *31*, 3565.
(478) Sundrehagen, E. *Int. J. Appl. Radiat. Isot.* **1979**, *30*, 739.
(479) Baes, C. F.; Mesmer, R. E. "The Hydrolysis of Cations"; Wiley-Interscience: New York, 1976.
(480) Isherwood, D. Report UCRL-53594; Lawrence Livermore National Laboratory: Livermore, CA, in press.