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REDUCTION POTENTIALS INVOLVING INORGANIC FREE RADICALS IN AQUEOUS SOLUTION

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I. Introduction

The two primary reference works on inorganic thermochemistry in aqueous solution are the National Bureau of Standards tables (*323*) and Bard, Parsons, and Jordan's revision (*30*) (referred to herein as *Standard Potentials*) of Latimer's *Oxidation Potentials* (*195*). These two works have rather little to say about free radicals. Most inorganic free radicals are transient species in aqueous solution. Assignment of thermodynamic properties to these species requires, nevertheless, that they have sufficient lifetimes to be vibrationally at equilibrium with the solvent. Such equilibration occurs rapidly enough that, on the time scale at which these species are usually observed (nanoseconds to milliseconds), it is appropriate to discuss their thermodynamics. The field is still in its infancy; of the various thermodynamic parameters, experiments have primarily yielded free energies and reduction potentials. Enthalpies, entropies, molar volumes, and their derivative functions are available if at all in only a very small subset.

This review attempts to provide a critical survey of the literature on the reduction potentials of inorganic free radicals. In certain cases where no published values are available, appropriate estimates are made. The purview is limited to aqueous systems that are strictly inorganic, but excluding the chemistry of the transition and the *f*-orbital elements. An attempt has been made to be comprehensive in coverage of the literature through 1986. Because free radicals are usually transients, knowing their thermodynamic properties is primarily useful in mechanistic studies. Thus the useful redox couples associated with a given free radical correspond to plausible elementary steps in reaction mechanisms. Accordingly, the emphasis is on electron transfer reactions in which no bonds are formed or broken, electron transfer reactions in which concerted electron transfer and bond cleavage could occur, and certain atom transfer reactions. We also tabulate $\Delta_f G^0$ values for all the radicals so that the interested reader can calculate redox potentials that have been omitted.

Table A-I of the Appendix (Section XIII) summarizes the present state of knowledge regarding reduction potentials. All potentials are expressed versus the normal hydrogen electrode (NHE). Apart from the NHE, the standard state for all solutes is the unit molar solution at 25°C. This violates the usual convention for species such as O_2 that occur as gases, but because we are often concerned with the rates of bimolecular reactions in solution the unit molar standard state is most convenient. Because of the importance of the hydrated electron, e^-_{aq}, the reader should bear in mind the distinction between this species and e^-, which designates the NHE. Thermodynamic quantities in the older literature were designated, for example, ΔG^0_f; according to IUPAC convention such quantities are now designated with the subscript preceding the energy term, e.g., $\Delta_f G^0$. In Table A-II of the Appendix are listed the standard Gibbs free energies of formation of the free radicals associated with Table A-I. These are conventional free energies; that is, $\Delta_f G^0 = 0$ for H^+.

This review makes extensive use of ancillary thermodynamic data. The source of such data, if not specified, is the NBS tables (*323*). The potentials in Table A-I, in most cases, have not been measured directly, and so there is considerable uncertainty in their magnitudes. Only in one case, the ClO_2/ClO_2^- system, has the potential been corrected for activity coefficients to obtain a *standard* potential. A common approach in estimating the thermochemistry of aqueous free radicals is to use gas-phase data with appropriate guesses of solvation energies; an important source of data for the gas-phase species is the JANAF tables (*80*).

The difficulty in determining thermochemical parameters for transient free radicals is considerably greater than for more persistent species. Thus the literature contains several reports for free radicals that are far from correct. There are at least two notable reports of techniques that yield potentials that are generally incorrect. In one case a pulse radiolysis/polarography method gave results that are in error (*203*), apparently because the radicals react with the mercury electrode (*159*); in another case E^0 values were obtained by kinetic "titration" curves from pulse radiolysis, but apparently equilibrium conditions were not obtained (*254*). Results from these misleading techniques will not be discussed further. Two other techniques for estimating the potentials yield results that are not especially accurate (*240, 289*). Of these, the method used by Shizuka *et al.* employs the equation $E(\text{ctts}) = 1.35E(X^-/X\cdot) + 3.55$, in which E(ctts) refers to the energy of the lowest charge-transfer-to-solvent band in the UV spectrum. The basis for this equation was not presented, and it does not appear to have any theoretical justification. One might expect an equation of this form for systems in which the reorganizational energies could be neglected, except that the coefficient would be unity rather than 1.35. It must be assumed that the equation is derived empirically from the data for the halides, for which it is a good approximation. The factor of 1.35 thus represents the complex contributions of reorganizational energies as they occur for the halides. With the revised potentials for the halides presented in this review (excluding F^-) the equation is still a very good fit: $E(\mathrm{ctts}) = 1.49E(X^-/X\cdot) + 3.45$. The equation most certainly should not be applied to systems having large internal reorganizational energies such as NO_2^-, and in practice it does not work very well even for SCN^-. Another possible source of errors is this review, because of the large number of calculations performed in its preparation. It appears as though accurate potentials can only be obtained by careful experiments directed at a specific free radical. Advances in the field have come about by the painstaking efforts of many research groups. It is not surprising that some of the values in Table A-I are considerably revised from a similar table published by Endicott in 1975 (*110*); it is certain that the future will lead to further corrections.

II. The Hydrated Electron

The hydrated electron has an extensive chemistry, and it is clear that e_{aq}^- is a thermodynamic entity. Its redox potential is defined by the following cell:

$$e^- \rightleftharpoons e_{aq}^- \tag{1}$$

The potential of this "couple" was first estimated as −2.7 V. Baxendale derived this value by using the following thermochemical cycle (*34*):

$$e_{aq}^- + H_2O \rightleftharpoons H + OH^- \tag{2}$$

$$H \rightleftharpoons H(g) \tag{3}$$

$$H(g) \rightleftharpoons \tfrac{1}{2}H_2(g) \tag{4}$$

$$H^+ + OH^- \rightleftharpoons H_2O \tag{5}$$

$$e_{aq}^- + H^+ \rightleftharpoons \tfrac{1}{2}H_2(g) \tag{6}$$

The equilibrium constant for reaction (2), 3.9×10^{-5} *M*, was obtained from the rates of the forward and reverse reactions. (Note that in many discussions the concentration of water is included in the equilibrium constant.) Thus $\Delta_f G^0$ for e_{aq}^- is 55 kJ/mol greater than for H. Reaction (3) was estimated to have $\Delta G^0 = 0$. The other data are available in standard tabulations. Matheson revised the potential because of improved rate constants for reaction (2) to obtain $E^0 = -2.67$ V (*211*). By using the same approach with very similar data Draganic and Draganic calculated $E^0 = -2.6$ V (*104*). Jortner and Noyes further improved the estimate by assuming ΔG^0 for reaction (3) to be the same as for the helium atom or the hydrogen molecule, -4.5 kcal/mol (*174*); this led to $E^0 = -2.77$ V (*155*). The various other estimates prior to 1970 have been summarized by Pikaev (*243*). Finally, Swallow rectified some elementary arithmetic and thermodynamic errors in the previous treatments (specifically, the factors of 55 representing the concentration of water) to obtain a potential of -2.87 V (*306*), which is the value tabulated by Schwarz (*276*). Swallow's potential leads to $\Delta_f G^0 = 277$ kJ/mol for the hydrated electron.

Another approach to estimating E^0 for the hydrated electron is to use the equilibrium

$$\mathrm{H} + \mathrm{F}^- \rightleftharpoons e_{\mathrm{aq}}^- + \mathrm{HF} \qquad (7)$$

which was reported by Anbar and Neta (*16*). Their equilibrium constant, 2.5×10^{-4}, leads to $\Delta_f G^0$ for e_{aq}^- that is 37 kJ/mol greater than for H. This is substantially different from that calculated from reaction (2), and, in view of the experimental difficulties in measuring reaction (7) (*15*), the result obtained from reaction (2) is preferred.

Initial reports of a second-order decay of e_{aq}^- that leads to the electron dimer, $(e_{\mathrm{aq}}^-)_2$, have been disputed, but there is still evidence that e_{aq}^- forms some other precursor to H_2 (*313*). The proposal for $(e_{\mathrm{aq}}^-)_2$ has recently been revived (*85*).

III. Hydrogen

The potential associated with the H^+/H couple is related to that of the hydrated electron through reaction (2). Latimer recommends $E^0 = -2.1$ V by assuming $\Delta G^0 = 0$ for hydration of the hydrogen atom (*196*), and this is the result reported by Baxendale (*33*). Toffel and Henglein reported $E^0 = -2.3$, obtained by assuming, in analogy with H_2 and He, $\Delta G^0 = 4.4$ kcal/mol for hydration of the hydrogen atom (*317*). Hart and Anbar prefer 4.6 kcal/mol for the hydration energy, and they report $E^0 = -2.31$ V (*155*). Hart and Anbar's potential leads to $\Delta_f G^0 =$ 223 kJ/mol for the hydrogen atom.

The hydride ion, H^-, has been proposed in the base-catalyzed exchange betwen D_2 and H_2O, in the base-catalyzed conversion of *para*-H_2 (*86, 153, 329*), and in certain radiation chemistry systems (*88*). The evidence from base catalysis is uncontested, but, as noted in Czapski's review (*88*), the evidence from radiation chemistry is not compelling. Presumably such a species, if formed, would be difficult to detect because it would be instantly protonated. The free energy of formation of H^- can be estimated by use of lattice energy calculations (*31*). By combining this free energy with $\Delta_f G^0$ for the hydrogen atom, Toffel and Henglein obtained $E^0 = 0.05$ for the H/H^- couple (*317*). Eberson obtained a value of -0.14 V, but the exact nature of his calculation is unclear (*107*). The possibility of using a good reducing agent to reduce the hydrogen atom by an electron transfer mechanism does not appear to have been explored; such a pathway could be difficult to distinguish from hydrogen atom transfer because both mechanisms would yield H_2.

The hydrogen atom hydrolyzes in alkaline solution as in reaction (2). From the data discussed above it is apparent that H is a weak acid with a pK_a of 9.6.

There have been suggestions that in acid solution the molecule H_2^+ can exist as an intermediate. One case was the reaction of H with Fe^{2+}; however, the reaction was shown to proceed via FeH^{2+} rather than H_2^+ (*89*). The other case was based on the acid-catalyzed oxidation of I^- by H atoms; the most recent report on this reaction suggests that here too H_2^+ is not responsible (*163*). The JANAF tables report $\Delta_f G^0 =$ 1484.931 kJ/mol for H_2^+ in the gas phase. Estimation of hydration energies of ions is a difficult problem, but as a rough approximation $\Delta_{hyd} G^0 = -942$ kJ/mol can be obtained by analogy with Li^+. Thus we have $\Delta_f G^0 = 543$ kJ/mol for H_2^+ and $E^0 = 5.45$ V for the H_2^+/H_2 couple. In view of the extraordinary calculated oxidizing power of H_2^+ it is not surprising that its existence is dubious.

IV. Oxygen

Like that of the hydrated electron and the hydrogen atom, the potential of the hydroxyl radical has long been the subject of estimates based on thermochemical cycles involving the free energy of hydration of OH; the results of these calculations appear, for example, in *Standard Potentials* (pp. 59–64). Recently, however, there have been two direct determinations of E^0 for the OH/OH^- couple. In the first, Schwarz and Dodson (*279*) used pulse radiolysis to measure the equilibrium constants for

$$Tl^+ + OH \rightleftharpoons TlOH^+ \qquad (8)$$

and

$$\mathrm{TlOH^+ + H^+ \rightleftharpoons Tl^{2+} + H_2O} \tag{9}$$

The sum of these equilibria relates the potential of the OH/OH^- couple to that of the Tl^{2+}/Tl^+ couple, and, since the latter was already established (see later, Section IX,E, on Tl), the resulting $E^0 = 1.89$ V ensued. In the second determination, Klaning, Sehested, and Holcman used stopped-flow spectrophotometry to measure the forward rate constant for the reaction

$$\mathrm{ClO_2^- + O_3 \rightleftharpoons ClO_2 + O_3^-} \tag{10}$$

and pulse radiolysis to measure the reverse rate constant (*182*). The ratio of the rate constants gave the equilibrium constant for reaction (10), and together with the potential of the ClO_2/ClO_2^- couple this led to 1.01 V as the potential of the O_3/O_3^- couple. Equilibrium constants for the reactions

$$\mathrm{O_3^- \rightleftharpoons O^- + O_2} \tag{11}$$

and

$$\mathrm{O^- + H^+ \rightleftharpoons OH} \tag{12}$$

were also used in the analysis. In the case of reaction (11) the equilibrium constant was obtained from the ratio of the forward and reverse rate contants, both of which were well established results taken from the literature. Reaction (12), also well established, is discussed below. With these data in hand a value of 1.91 V for the potential of the OH/OH^- couple was derived. The agreement between the two independent determinations of E^0 is very good, and the average value is well within the range of the thermochemical estimates. An average value of $E^0 = 1.90 \pm 0.01$ V is recommended, as is the corresponding $\Delta_f G^0 =$ 26 kJ/mol of OH. Interested readers may look to these two papers for references to the thermochemical estimates (*182, 279*); the differences among them are mostly in the estimation of the hydration energy of OH. It is considered that in some reactions OH may abstract H to form H_2O; thus the derived potential of 2.72 V for the $(H^+, OH)/H_2O$ couple is of interest.

The pK_a of OH is well established as 11.9 ± 0.2 (*103, 120*). This result was obtained in a study of the pH dependence of the reaction of OH with

$Fe(CN)_6^{4-}$ (*247*). Confirmation of this result was found in the reaction of OH with CO_3^{2-}, which gave $pK_a = 11.8 \pm 0.2$ (*326*), and in the reaction of OH with SCN^-, which gave $pK_a = 11.9 \pm 0.15$ (*2*). This pK_a, in combination with the above value for $\Delta_f G^0$ for OH, leads to $\Delta_f G^0 =$ 94 kJ/mol for O^- and $E^0 = 1.77$ V for the O^-/OH^- couple.

Oxygen atoms have been generated in aqueous solution both in the ^3P and ^1D states. The ^1D state can be generated, for example, by photolysis of ozone (*309*), but its only reaction in aqueous solution appears to be insertion into H_2O to form H_2O_2. According to the JANAF tables the ^1D state is higher in energy by 190 kJ/mol, so we may infer that its reaction with solvent is too rapid to permit scavenging by other reactants. Because of the high energy of the ^1D state the $\Delta_f G^0$ value of 231.731 kJ/mol reported in the NBS tables for atomic oxygen in the gas phase refers to a population almost entirely in the ^3P state. The assumption of 19 kJ/mol for the hydration free energy of O (taken to be the same as for Ne) yields 251 kJ/mol for the standard free energy of formation of $O(^3P)_{aq}$. Henglein (*160*), using an old value of $\Delta_f G^0 = 103$ kJ/mol for O^- and an estimated hydration free energy of 10 kJ/mol for O, calculated $E^0 = 1.4$ V for the O/O^- couple; with $\Delta_f G^0 = 94$ kJ/mol for O^- and our higher estimate of the hydration energy of O, this potential becomes 1.63 V. A value of 1.61 V calculated by similar methods was reported in *Standard Potentials*. The chemistry of the ^3P state is fairly extensive (*12, 73, 74, 260*). Despite the substantial oxidizing power of $O(^3P)_{aq}$, this species has not been reported to react as a one-electron oxidant; it has, however, been reported to react as a *reducing* agent, e.g., with BrO_3^-, by abstracting an oxygen atom (*184*).

Potentials can now be calculated for the one-electron reductions of H_2O_2 to $OH + OH^-$ and of HO_2^- to $O^- + OH^-$; these are -0.03 and -0.04 V, respectively.

The chemistry of the ozonide radical anion has been discussed in Czapski's review (*88*), but the chemistry is complex, and the interested reader should consult more recent sources (*282*). The potential of the O_3/O_3^- couple has not been the subject of repeated scrutiny. Klaning *et al.* recently measured it by investigating reaction 10 (*182*). Their value of 1.01 V leads to $\Delta_f G^0 = 77$ kJ/mol for O_3^-; these results are probably fairly accurate because they confirm the potential of the OH/OH^- couple. There is considerable uncertainty expressed in Czapski's review concerning the pK_a of HO_3 (*88*); on the basis of chemical analogy he estimated a pK_a of -2. In a recent investigation it was asserted that HO_3 has a pK_a of 6.15, although it splits into OH and oxygen before it has time to dissociate into O_3^- (*60*). Subsequently the pK_a was corrected to 8.2 ± 0.1 (*61*). It is prudent to await confirmation of these results.

Superoxide (O_2^-) and the peroxyl radical (HO_2) have been intensively studied, and a good account of their thermochemistry is presented in *Standard Potentials* (pp. 60–63). They are related by the pK_a of HO_2, which is 4.8 ± 0.1 (*51*). The reduction potential of the O_2/O_2^- couple has been determined by a variety of methods, including, for example, the equilibria with various quinone–semiquinone systems. The value cited, −0.33 V, is taken with respect to a standard state of 1 atm O_2 pressure. When expressed relative to the 1 *M* standard state of O_2, the potential is −0.16 V. Standard NBS data permit calculation of $\Delta_f G^0 = 4.4$ kJ/mol and 31.8 kJ/mol for HO_2 and O_2^-, respectively. Some related potentials include 0.12 V for $(H^+, O_2)/HO_2$, 1.44 V for $(H^+, HO_2)/H_2O_2$, and 0.75 V for HO_2/HO_2^-.

The notion that H_2O^+ can be a significant species in aqueous solution has recently been revived (*258a*). The argument is based on two items of evidence. One is a citation of Spinks and Woods' text (*290a*); the evidence in this text, however, is a citation of Czapski's review (*88*), which states that "there seems to be better evidence against the existence of $H_2O_2^+$...than for the opposite assumption...." The other item is a citation of the acid-catalyzed dismutation of HO_2 below pH 1. Close examination of the data (Fig. 2 of Ref. *51*) shows that the catalysis is inferred from an increase in the dismutation rate constant from 0.9×10^6 to 1.1×10^6 M^{-1} sec^{-1} from pH 1.8 to pH 0.1. In summary, Czapski's negative remarks concerning the existence of this species are still appropriate.

The thermochemistry of singlet dioxygen has been reviewed by Koppenol (*188*). The potentials he cites refer to dioxygen in the gas phase. Improved thermodynamic functions for singlet molecular dioxygen have recently become available (*55*), and from them we calculate $\Delta_f G^0 = 95$ kJ/mol for ${}^1\Delta_g O_2$ in the gas phase. The assumption of a free energy of hydration the same as that for ${}^3O_2$ leads to $\Delta_f G^0 = 112$ kJ/mol for aqueous ${}^1\Delta_g O_2$, and thus E^0 is 0.83 V for the ${}^1O_2/O_2^-$ couple. Thus the observed quantitative yield of ${}^1O_2$ in the oxidation of O_2^- by $[Ru(bpy)_3]^{3+}$ is thermodynamically acceptable (*217*).

Czapski, in his review (*88*), discusses the chemistry of H_2O_3 and H_2O_4. There does not appear to be any evidence in support of the latter species in aqueous solution. H_2O_3, on the other hand, is fairly well characterized. Although its free energy is unknown, its reported pK_a is 9.5. Nangia and Benson have estimated $\Delta_f H^0 = -15.7$ for this species in the gas phase (*224*).

The dioxygenyl cation, O_2^+, exists in various media, but it has not been reported in aqueous solution. The gas-phase species is assigned $\Delta_f G^0 = 1164.315$ kJ/mol in the JANAF tables. As a very rough approximation it may be assumed that O_2^+ has the same free energy of hydration as Na^+, which leads to $\Delta_f G^0 = 330$ kJ/mol for O_2^+, and $E^0 = 3.2$ V for the O_2^+/O_2 couple.

V. The Halogens

A. FLUORINE

Taube and Bray noted in 1940 that the standard potential for the F(g)/F^- couple is 4.04 V (*310*). Berdnikov and Bazhin obtained a solution-phase potential by use of a thermochemical cycle that involves estimating the free energy of hydration of the fluorine atom (*45*); this led to a calculated E° of 3.6 V for the F/F^- couple and a corresponding $\Delta_f G^0$ of 68 kJ/mol for F. The chemistry of F_2 and HOF has been discussed in Thompson's review (*315*), but there is no evidence of fluorine-containing radicals in the reactions of these species. There does not seem to be any reported evidence for the existence of F_2^- in aqueous solution, although the species has been detected in irradiated crystals. In the reversible reaction of H with F^- to give e_{aq}^- and HF, it has been argued that HF^- does not exist as an intermediate but only as a transition state (*16*).

B. CHLORINE

There have been several reports on the potential of the Cl/Cl^- couple. The first of these was by Taube and Bray (*310*), in which it was estimated that the potential of the (H^+, OH)/H_2O couple exceeded that of the Cl/Cl^- couple by 0.12 V. Subsequent estimates gave absolute values for the couple; these are collected in Table I. With the exception of Pearson's estimate (*240*), the various thermochemical estimates were based on the standard free energy of formation of the chlorine atom in

TABLE I

REPORTED REDUCTION POTENTIALS FOR THE Cl/Cl^- COUPLE

E^0 (V)	Year	Reference	Author	Technique
2.55	1970	*45*	Berdnikov and Bazhin	Gas-phase thermochemical cycle
2.6	1972	*205*	Malone and Endicott	Gas-phase thermochemical cycle
2.59	1973	*316*	Thornton and Laurence	Gas-phase thermochemical cycle
2.31	1986	*240*	Pearson	Gas-phase thermochemical cycle
2.20	1982	*206*	Martins	Quenching of ^{3}DQ
2.41	1984	*279*	Schwarz and Dodson	Pulse radiolysis

the gas phase; they differ primarily in their assumptions regarding solvation energies. Pearson's result involved an estimate of the pK_a of HCl, and hence it is relatively unreliable. Of the two experimental results, Martins' appears to have been based on the quenching rate of triplet-state duroquinone by Cl^- and certain assumptions regarding LFERs (*206*). The result of Schwarz and Dodson (2.41 V) is based on their potential for the OH/OH^- couple and two previously reported equilibria as follows (*279*):

$$OH + Cl^- \rightleftharpoons ClOH^- \tag{13}$$

$$ClOH^- \rightleftharpoons Cl + OH^- \tag{14}$$

These equilibrium constants have been determined only once (*173*), but they are estimated to lead to an uncertainty in E^0 of ± 0.03 V. The results of Schwarz and Dodson (*279*) also lead to a standard free energy of formation of the aqueous chlorine atom of 101 kJ/mol. Thus the hydration energy of Cl is substantially greater than that of Ar.

As in bromine and iodine systems, chlorine atoms bind chloride as in reaction 15.

$$Cl + Cl^- \rightleftharpoons Cl_2^- \tag{15}$$

The equilibrium constant (1.9×10^5 M^{-1}) was measured by use of pulse radiolysis (*173*). A more recent determination (*335*) of this constant (18 M^{-1}) is clearly in error because of the internal incompatibility of the data, as pointed out in a very recent study of the decay of Cl_2^- (*324*). The analogous values for Br_2^- and I_2^- are discussed below; however, the disagreement in the published results for these systems suggests that the reader should be cautious in accepting the above result for Cl_2^-. Some degree of confirmation of the original Cl_2^- result may be found in a recent measurement (*223*) of the rate constant of association of Cl with Cl^- ($k = 8 \times 10^9$ M^{-1} sec^{-1}) that is close to the value reported by Jayson, Parsons and Swallow (2.8×10^{10} M^{-1} sec^{-1}) (*173*). As reported by Schwarz and Dodson, combining E^0 for Cl/Cl^- with the above equilibrium constant leads to $E^0 = 2.09$ V for the $Cl_2^-/2Cl^-$ couple (*279*). These results also lead to $\Delta_f G^0 = -61$ kJ/mol for Cl_2^- and $E^0 =$ 0.70 V for the Cl_2/Cl_2^- couple.

As noted above, the equilibrium constant for formation of $ClOH^-$ from OH and Cl^- has been determined ($K_{eq} = 0.7$ M^{-1}). This establishes $\Delta_f G^0 = -104$ kJ/mol, and with use of the NBS value of -79.9 kJ/mol for $\Delta_f G^0$ of HOCl these data yield $E^0 = 0.25$ V for the $HOCl/ClOH^-$ couple.

ClO has been reported as an intermediate in various photolytic and radiolytic systems (*72, 73, 184, 186*). No thermochemical data are available on this aqueous species, but the NBS tables give a value of $\Delta_f G^0 = 98.11$ kJ/mol for the gas-phase species, which is probably good within ±2 kJ/mol. If a hydration free energy of 10 kJ/mol is assumed (a subjectively weighted average of the values for O_2, Cl_2, and CO), then an estimate of $\Delta_f G^0 = 108$ kJ/mol is obtained for aqueous ClO. By use of the NBS value of $\Delta_f G^0 = -36.8$ kJ/mol for ClO^- it is found that ClO is a good oxidant, with $E^0 = 1.50$ V for the ClO/ClO^- couple. This potential is consistent with reports that ClO can oxidize O_3^- and ClO_2^- (*184*); it is also consistent with reports that ClO can be generated by the reactions of Cl and OH with ClO^- (*186*). In a very recent study Alfassi *et al.* investigated the reactions of ClO with a variety of inorganic and organic compounds, including ClO_2^- (*9*). On the basis of its reactivity they bracketed its potential between 1.5 and 1.8 V, which is consistent with the above thermochemical estimate.

In contrast with the bromine system discussed below, ClO apparently is not produced upon reduction of ClO_2^- by, for example, e_{aq}^- (*113*). Instead, reaction with e_{aq}^- yields ClO^- and O^- even though this process is thermodynamically less favorable. This seems to imply that ClO_2^{2-} does not have a significant lifetime.

Unlike most of the free radicals discussed in this review, ClO_2 is persistent in aqueous media, and direct measurements of its thermochemical properties have been conducted by several research groups. The most recent of these reports is given by Klaning *et al.* (*182*) in which they obtain $E^0 = 0.934 \pm 0.002$ V for the ClO_2/ClO_2^- couple; note that these authors actually report a standard potential instead of a formal potential. Furthermore, they report the temperature dependence of the potential. They note that their result is in agreement with prior measurements but that it disagrees with that calculated from the NBS tables (1.066 V). The NBS data for aqueous and gaseous ClO_2 agree with the known solubility of ClO_2 (*328*), so the discrepancy (13 kJ/mol) must reflect errors in the NBS data for ClO_2^- or for gaseous ClO_2. According to the JANAF tables (prepared in 1961) $\Delta_f G^0 = 122 \pm 6$ kJ/mol for gaseous ClO_2. Considerably greater uncertainty is expressed in Darwent's tables, where a value of 243 ± 13 kJ/mol is listed for the O–ClO bond dissociation energy at 0 K (*91*). More recently an upper limit of 231 ± 8 kJ/mol was reported for this same dissociation energy (*28*). On the other hand, the work of Clyne *et al.* appears quite reliable (*87*), and, as noted by Schmitz (*267*), it leads to a value for $\Delta_f G^0$ of 119 ± 3 kJ/mol for gaseous ClO_2; this appears to be the result used in the NBS tables. We follow Schmitz in adopting a value of 119 kJ/mol for $\Delta_f G^0$ of aqueous ClO_2 as determined from the gas-phase result and the solubility. A value of 29 kJ/mol is derived for $\Delta_f G^0$ of ClO_2^- from this result and the reduction potential of ClO_2 cited above.

There is no reported evidence of formation of ClO_2^+ by oxidation of ClO_2 or of formation of ClO_3^{2-} by reduction of ClO_3^-. Interconversion of ClO_2 and ClO_3^- thus is contingent upon attachment of an oxygen atom. The above result for ClO_2 and the NBS data for ClO_3^- lead to 1.14 V for the potential of the half-cell

$$ClO_3^- + e^- + 2H^+ \rightleftharpoons ClO_2 + H_2O \tag{16}$$

Chlorine trioxide has been reported in many electron spin resonance (ESR) studies of irradiated crystals of $NaClO_3$ and $Ba(ClO_4)_2$. However, there do not seem to be any reports of its generation in aqueous solution. In the NBS tables is listed a value of 155 kJ/mol for its $\Delta_f H^0$ in the gas phase, but this result does not appear to be very firm. The assumption of a value of $S^0 = 253$ J/K/mol (that of NO_3) and a hydration free energy of -10 kJ/mol leads to $\Delta_f G^0 = 194$ kJ/mol for aqueous ClO_3 and $E^0 = 2.1$ V for the ClO_3/ClO_3^- couple. The reported failure of OH to oxidize ClO_3^- may be taken in support of this calculated potential (*72*).

The radical $ClSCN^-$ has been reported to form during radiolysis of aqueous Cl^-/SCN^- mixtures (*268*). It is formed by the equilibrium

$$SCN + Cl^- \rightleftharpoons ClSCN^- \tag{17}$$

which has an equilibrium constant of 6.6 M^{-1}. By using the value of $\Delta_f G^0$ for SCN discussed below, a value of $\Delta_f G^0 = 114$ kJ/mol for $ClSCN^-$ and a potential of 1.58 V are calculated for the $ClSCN^-/(Cl^-, SCN^-)$ couple.

C. BROMINE

Potentials reported for the Br/Br^- couple are collected in Table II. As with the I/I^- system there have been several estimates of the Br/Br^- potential by use of thermochemical cycles that involve the heat of formation of Br(g) (*235, 308*). These estimates place the potential near 2.0 V. The experimental measurements start with Lilie's pulse radiolysis/polarography report that is obviously misleading (*203*). Laurence and Thornton's measurement of the oxidation of Mn^{2+} by Br_2^- enabled them to calculate E^0 for the $Br_2^-/2\ Br^-$ couple (*197*); the reduction potential for the Br/Br^- couple can thus be obtained by using

TABLE II

REPORTED REDUCTION POTENTIALS FOR THE Br/Br⁻ COUPLE

E^0 (V)	Year	Reference	Author	Technique
1.85	1986	*240*	Pearson	Gas-phase thermochemical cycle
1.96	1980	*235*	Noyes	Gas-phase thermochemical cycle
2.0[a]	1980	*160*	Henglein	Gas-phase thermochemical cycle
2.08	1973	*316*	Thornton and Laurence	Gas-phase thermochemical cycle
2.06	1973	*333*	Woodruff and Margerum	Gas-phase thermochemical cycle
2.2	1972	*205*	Malone and Endicott	Gas-phase thermochemical cycle
2.0	1970	*45*	Berdnikov and Bazhin	Gas-phase thermochemical cycle
1.95	1948	*308*	Taube	Gas-phase thermochemical cycle
1.96	1987		This review	Pulse radiolysis equilibria
1.93	1984	*279*	Schwarz and Dodson	Pulse radiolysis equilibria
1.90	1982	*206*	Martins	Pulse radiolysis equilibria
1.92	1973	*197*	Laurence and Thornton	Pulse radiolysis equilibria

[a] Calculated from Henglein's result for the $Br_2^-/(2Br^-)$ couple with the assumption that $K_{eq} = 1.1 \times 10^5\ M^{-1}$ for association of Br^- with Br.

the formation constant for the reaction

$$\mathrm{Br} + \mathrm{Br}^- \rightleftharpoons \mathrm{Br}_2^- \tag{18}$$

With this formation constant selected as $1.1 \times 10^5\ M^{-1}$ (see below), we obtain $E^0 = 1.92$ V, which is within the range of the thermochemical estimates. Martins (*206*) obtained his result by combining our accepted E^0 for the I/I^- couple with equilibrium constants reported by Schoneshofer (*271, 272*) for the reactions

$$\mathrm{I} + \mathrm{SCN}^- \rightleftharpoons \mathrm{I}^- + \mathrm{SCN} \tag{19}$$

$$\mathrm{Br} + \mathrm{SCN}^- \rightleftharpoons \mathrm{Br}^- + \mathrm{SCN} \tag{20}$$

the latter relying on a previously reported equilibrium constant for reaction (18).

The agreement between the results of Laurence and Thornton (*197*) and of Martins (*206*) is quite satisfactory. Schwarz and Dodson (*279*) arrived at their E^0 by using pulse radiolysis to measure equilibrium constants for the reactions

$$\mathrm{Tl}^+ + \mathrm{OH} \rightleftharpoons \mathrm{TlOH}^+ \tag{21}$$

$$\mathrm{TlOH}^+ + \mathrm{H}^+ \rightleftharpoons \mathrm{Tl}^{2+} + \mathrm{H_2O} \tag{22}$$

They combined these values with the known E^0 for the Tl^{2+}/Tl^+ couple and reported equilibrium constants for reaction (18) and the following reactions:

$$\mathrm{OH + Br^- \rightleftharpoons BrOH^-} \tag{23}$$

$$\mathrm{BrOH^- + Br^- \rightleftharpoons Br_2^- + OH^-} \tag{24}$$

The agreement with the prior experimental results must be considered excellent considering the cumulative errors in such a procedure. The experimental results lead to a recommended E^0 of 1.92 V and $\Delta_f G^0 =$ 81 kJ/mol for Br.

While the consistency between the reported "experimental" E^0 values for the Br/Br^- couple is encouraging, it should be noted that all values rely upon the reported equilibrium constant for reaction (18). As noted in Fornier de Violet's review (*127*), the magnitude of this formation constant is contentious, with reported results ranging from 3.3×10^3 to $2.2 \times 10^5\ M^{-1}$. The most recent value is $1.1 \times 10^5\ M^{-1}$, and it is the value accepted, albeit reluctantly, in this review. An estimate of E^0 can be made that is relatively insensitive to this equilibrium constant by using some recently available data. Klaning and Wolff reported that for

$$\mathrm{Br + OH^- \rightleftharpoons Br^- + OH} \tag{25}$$

the equilibrium constant is 9.6 (*186*). It appears that they obtained this value by measuring the rate of reaction of Br atoms with OH^- and combining this value with the published rate constant for dissociation of $BrOH^-$ to Br + OH^- and the equilibrium constant for dissociation to Br^- + OH. By using the recently reported E^0 for OH (=1.90 V; see above) we obtain $E^0 = 1.96$ V for the Br/Br^- couple. Considering the cumulative errors in this calculation, this result can be taken as support of the other E^0 values reported, as well as of the selected equilibrium constant for reaction (18). The selected equilibrium constant for reaction (18) leads to $\Delta_f G^0 = -52$ kJ/mol for Br_2^-, $E^0 = 1.62$ V for the $Br_2^-/2Br^-$ couple, and $E^0 = 0.58$ V for the Br_2/Br_2^- couple.

It is of some interest to note that Taube in 1948 determined a value of 1.7 V for the $Br_2^-/2Br^-$ couple by a careful analysis of the catalysis by Mn^{2+} of the reaction of Br_2 with oxalic acid (*308*). He also derived a value of $10^4\ M^{-1}$ for the equilibrium constant of reaction (18). In his analysis Taube used a potential of 1.6 V for the Mn^{3+}/Mn^{2+} couple. A value of 1.5 V for the Mn^{3+}/Mn^{2+} couple is presently recommended in *Standard Potentials*; if Taube's data are corrected to this new Mn^{3+}/Mn^{2+} potential, a potential of 1.6 V is derived for the $Br_2^-/2Br^-$ couple, which is essentially the same as the most accurate determinations discussed above. Unfortunately, Taube's contribution seems not to have been recognized by the more recent workers in the field.

IBr^- has been observed in inorganic glasses (*319*), but it has yet to be detected in aqueous solution. Catalysis by Br^- of the oxidation of I^- by $[Fe(phen)_3]^{3+}$ has been attributed to stabilization of nascent I by Br^- (*171*), but the reduction potential of IBr^- is not established.

As required by the above equilibria, hydrolysis of Br occurs in alkaline media according to

$$Br + H_2O \rightleftharpoons HOBr^- + H^+ \tag{26}$$

with an equilibrium constant of 3.1×10^{-11} *M* (*186*). This establishes $\Delta_f G^0 = -96$ kJ/mol, and with NBS data for HOBr, $E^0 = 0.14$ V for the $HOBr/HOBr^-$ couple. Rapid reduction of HOBr by O_2^- has been reported (*305*), and it is consistent with the favorable driving force.

Rapid reduction of BrO^- by the hydrated electron has been reported to yield O^- and Br^- (*67*). The pertinent half-cell is

$$BrO^- + e^- \rightleftharpoons Br^- + O^- \tag{27}$$

which has a calculated potential of -0.24 V. Thus the observed reduction is thermodynamically viable.

In the NBS tables is reported a value for $\Delta_f G^0$ of 108.22 kJ/mol for BrO in the gas phase, and according to Huber and Herzberg this is probably good within ± 1 kJ/mol (*168a*). As a rough estimate, the hydration free energy of BrO may be taken as that of ICl, -12 kJ/mol, which leads to $\Delta_f G^0_{aq} = 96$ kJ/mol. The reduction potential of the OBr/OBr^- couple is calculated as 1.34 V with NBS data for OBr^-. This potential is consistent with the rapid reduction of OBr by O_3^- (*184*) and the rapid oxidation of OBr^- by Br and OH (*186*) and Br_2^- (*67*).

There do not appear to be any reports of oxidation of BrO. One-electron reduction of BrO_2^- has been reported in the diffusion-controlled reaction with e^-_{aq}, and the products are claimed to be BrO and $2OH^-$ (*67*); presumably BrO_2^{2-} is an intermediate. $HBrO_2$ has not been reported to act as a one-electron oxidizing agent, and because of its instability such measurements would be difficult.

Compared to reducing BrO_2^-, oxidizing BrO_2^- to BrO_2 is a relatively common process. NBS data for BrO_2, BrO_2^-, and $HBrO_2$ are lacking. The thermodynamics of these species has been discussed extensively because of their importance in the Belousov–Zhabotinskii reaction. One important result that has been generally accepted is Lee and Lister's value of 27.2 kJ/mol for $\Delta_f G^0$ of BrO_2^- (*198*), which was obtained from direct measurement of the equilibrium constant of the reaction

$$BrO_3^- + Br^- \rightleftharpoons BrO_2^- + BrO^- \qquad (28)$$

This result, however, does not yet appear to have received independent confirmation and it does not appear in the NBS tables.

The reaction

$$BrO_3^- + HBrO_2 + H^+ \rightleftharpoons 2BrO_2 + H_2O \qquad (29)$$

is central to the subsequent discussions. Field, Koros, and Noyes (FKN) originally estimated the equilibrium constant of this reaction ($5 \times 10^{-4}\ M^{-1}$) from the ratio of the forward and reverse rate constants (*123*). The reverse rate constant ($2 \times 10^7\ M^{-1}\ sec^{-1}$) was measured directly by Buxton and Dainton (*67*). The forward rate constant ($1.0 \times 10^4\ M^{-2}\ sec^{-1}$) was obtained by making the risky assumption that it was twice the rate constant for isotope exchange in $BrO_3^-/Br_2/HClO_4$ mixtures, as measured by Betts and MacKenzie (*49*). This isotope exchange rate constant depends in turn upon the assumption that such mixtures are in equilibrium with $HBrO_2$ and that the pK_a of $HBrO_2$ is 2. The value for the pK_a was simply a guess, based on Pauling's empirical rules. From the equilibrium constant and the pK_a they obtained a value of $\Delta_f G^0 = 144$ kJ/mol for BrO_2 and an $E^0 = 1.33$ V for the $BrO_2/HBrO_2$ couple.

In subsequent work it has been shown that the original estimate of the equilibrium constant for reaction (29) was based on erroneous data for the dissociation of Br_2O_4 to $2BrO_2$ and that the correct dissociation constant should be $5.3 \times 10^{-5}\ M$ (*124*); because of compensating effects, however, this does not affect the calculated value of K_{eq} for reaction (29). More recently Tyson (*322*) has shown that the FKN value of $\Delta_f G^0$ for BrO_2 is actually independent of the pK_a of $HBrO_2$. Thus we calculate $E^0 = 1.21$ V for the BrO_2/BrO_2^- couple. Most recently Field and Forsterling obtained $K_{eq} = 0.9 \times 10^{-6}\ M^{-1}$ for reaction (29) by a direct measurement (*122*). That this result is consistent with the FKN value supports the original FKN assumption that the forward rate constant of reaction (29) is twice the isotope exchange rate constant. Field and Forsterling then used this result in combination with the FKN result for BrO_2 to obtain a new pK_a (= 4.9) and $\Delta_f G^0 = -0.4$ kJ/mol for $HBrO_2$. This now establishes $E^0 = 1.50$ V for the $BrO_2/HBrO_2$ couple, which is substantially different from the original FKN result. The discrepancy between the calculated pK_a and the FKN rule-of-thumb estimate has been discussed by Field and Forsterling

(*122*) and by Noyes (*236*). As pointed out by Noyes, additional support for the new pK_a may be gleaned from the fact that HOBr is substantially less acidic than HOCl, so by analogy it might be expected that $HBrO_2$ is less acidic than $HClO_2$.

While the above is logically correct, complete, and involves no dubious estimates, it must be acknowledged that it is very intricate. A direct measure of E^0 of the BrO_2/BrO_2^- couple or of the pK_a of $HBrO_2$ would be quite welcome. In a study of the pH dependence of the decomposition of Br(III) in weakly acidic media Massagli *et al.* inferred that $HBrO_2$ had a pK_a of about 6, which has been taken in support of the new result over the original FKN result (*210*). The uncertainty in the analysis is increased by an assertion that BrO_2 and Br_2O_4 are protonated in acidic media (*259*).

Examples of the one-electron reduction of BrO_3^- to BrO_2 are discussed in Thomspon's review (*315*). The potential for the couple, obtained by using our $\Delta_f G^0$ for BrO_2, is 1.16 V.

It is claimed that BrO_3 is generated in the relatively slow oxidation of BrO_3^- by OH (*11*), but no thermochemical data are available for this radical. Reduction of BrO_4^- by the hydrated electron yields BrO_3^- and O^- (*237*). A potential of 0.06 V can be calculated for the $BrO_4^-/(BrO_3^-, O^-)$ couple.

Another bromine-containing radical is $BrSCN^-$. This species was detected upon radiolysis of Br^-/SCN^- mixtures, and the equilibrium constant for the reaction

$$BrSCN^- \rightleftharpoons Br + SCN^- \qquad (30)$$

was reported as 4.6×10^{-9} *M* (*271*). The associated data are $\Delta_f G^0 = 126$ kJ/mol for $BrSCN^-$ and $E^0 = 1.42$ V for the $BrSCN^-/(Br^-, SCN^-)$ couple.

D. IODINE

In Table III are listed the various reported values for the I/I^- couple. As can be seen from this Table, the potential for this couple has been repeatedly calculated by thermochemical cycles that rely primarily on the heat of formation of the iodine atom in the gas phase (*45, 76, 136, 161, 205, 286, 333*). These authors made additional corrections for entropy effects and for the solvation energy of the iodine atom; it is gratifying to see that the calculations largely agree! How Thornton and Laurence (*316*) and Haim and Taube (*151*) arrived at their estimates is not clear, but presumably they used similar thermochemical cycles. More recently Pearson used a somewhat different thermo-

TABLE III

REPORTED REDUCTION POTENTIALS FOR THE I/I$^-$ COUPLE

E^0 (V)	Year	Reference	Author	Technique
1.33	1986	*277*	Schwarz and Bielski	Pulse radiolysis equilibrium
1.36	1982	*233*	Nord *et al.*	Kinetics and pulse radiolysis
<1.2	1981	*256*	Raycheba and Margerum	Redox kinetics
1.33	1980	*294*	Stanbury *et al.*	Redox kinetics
1.38	1978	*232*	Nord *et al.*	Redox kinetics
1.19	1986	*240*	Pearson	Gas-phase thermochemical cycle
1.235	1982	*136*	Furrow and Noyes	Gas-phase thermochemical cycle
1.30	1980	*161*	Henglein	Gas-phase thermochemical cycle
1.35	1978	*76*	Cannon	Gas-phase thermochemical cycle
1.235	1976	*286*	Sharma and Noyes	Gas-phase thermochemical cycle
1.42	1973	*333*	Woodruff and Margerum	Gas-phase thermochemical cycle
1.31	1973	*316*	Thornton and Laurence	⟨?⟩
1.4	1972	*205*	Malone and Endicott	Gas-phase thermochemical cycle
1.4	1970	*45*	Berdnikov and Bazhin	Gas-phase thermochemical cycle
1.27	1963	*151*	Haim and Taube	⟨?⟩

chemical cycle that uses proton affinities, electron affinities, and an estimate of the pK_a of HI (*240*); that his result is somewhat discordant is to be expected considering the cumulative errors of the method. The outcome of these estimates is that the potential should certainly be in the range of 1.3 ± 0.2 V.

The first reliable experimental measurement of E^0 for I/I$^-$ appeared in 1978; Nord *et al.* extracted their result by a careful analysis of the effect of Os(II) on the kinetics of oxidation of I$^-$ by $[Os(bpy)_3]^{3+}$ (*232*). In 1980 Stanbury *et al.* published the results of a kinetic study of the oxidation of I$^-$ by a variety of substitution-inert coordination complexes (*294*). They found that the rates of these reactions were related to the E^0 values of the complexes by a log/log plot of unit slope with remarkably little scatter. The origin of this LFER was attributed to the rate constants for back electron transfer being diffusion controlled. An estimate of the diffusion-controlled rate constant (1.2×10^{10} M^{-1} sec^{-1}, which is probably good within factor of 2) led to an assignment of the reduction potential for the I/I$^-$ couple of 1.33 V, in good agreement with Nord's result and well within the range of the thermochemical estimates. Concurrently, Raycheba and Margerum reported on the kinetics of oxidation of I$^-$ by some Cu(III) peptide complexes (*256*); they arrived at an upper limit of 1.2 V for the I/I$^-$ couple by imposing the constraint that the reaction of I + Cu(II) must not exceed the limit of diffusion control, which was taken to be 1 × 10^9 M^{-1} $\sec^{-1}$. This low value led to a significant difference in the calculated E^0. In a subsequent paper Nord *et al.* reported measurements by pulse radiolysis of the rates of reaction of I_2^- with $[Os(bpy)_3]^{2+}$ (*233*); on combining this rate constant with the third-order rate constant for oxidation of I^- by $[Os(bpy)_3]^{3+}$ they calculated E^0 for the $I_2^-/2I^-$ couple. This E^0, when combined with the equilibrium constant for the reaction

$$I + I^- \rightleftharpoons I_2^- \tag{31}$$

led to the tabulated value of 1.36 V, which is in excellent agreement with their prior result and the result of Stanbury *et al.* Most recently Schwarz and Bielski, apparently unaware of the prior experimental studies, published another experimental determination of $E^0 = 1.33$ V for the I/I^- couple (*277*). They arrived at their result in a pulse radiolysis study by measuring the equilibrium constant for the reaction

$$HO_2 + I_2 \rightleftharpoons H^+ + O_2 + I_2^- \tag{32}$$

and combining it with known values for the equilibrium constant of reaction (31) and the O_2/HO_2 reduction potential. This final result is in excellent accord with the experimental results of Nord *et al.* and Stanbury *et al.* In summary, the reduction potential of the iodine atom is now fairly well established, despite our inability to measure it by conventional methods. This reduction potential, taken together with standard NBS, leads to 77 kJ/mol, the standard Gibbs free energy of formation of I_{aq}.

Polyhalide radical anions have recently been reviewed; I_4^- and I_6^- have been observed in *tert*-butanol solution, but they are unknown in aqueous solution (*127*). The equilibrium constant for formation of I_2^- [reaction (31)] is the link between the reduction potentials of the iodine atom, the diiodine radical anion, and diiodine. Numerous measurements of this equilibrium constant have been made over the years. There are even two reports of the enthalpy of the reaction, obtained from the temperature dependence of the equilibrium constant (*35*). Published values for the formation constant of I_2^- are listed in Table IV (*32, 36, 128, 129, 149, 314, 318*). As noted in Fornier de Violet's review (*127*) and in Elliot and Sopchyshyn's paper (*109*), there is a systematic discrepancy between the flash photolysis results and the pulse radiolysis results. Fornier de Violet suggested that the pulse radiolysis results might be in error because of unrecognized adduct formation

TABLE IV

REPORTED FORMATION CONSTANTS FOR I_2^-

K_{eq} (M^{-1})	Method	Author	Year	Reference
1.13×10^5	Pulse radiolysis	Baxendale *et al.*	1968	*36*
8.4×10^4	Pulse radiolysis	Thomas	1969	*314*
5×10^4	Pulse radiolysis	Elliot and Sopchyshyn	1984	*109*
1.1×10^5	Pulse radiolysis	Schwarz and Bielski	1986	*277*
$>1.2 \times 10^4$	Flash photolysis	Grossweiner and Matheson	1957	*149*
1.4×10^4	Flash photolysis	Fornier de Violet *et al.*	1973	*128*
1.2×10^4	Flash photolysis	Fornier de Violet *et al.*	1974	*129*
1.1×10^4	Flash photolysis	Barkatt and Ottolenghi	1974	*32*
3×10^3	Flash photolysis	Treinin and Hayon	1975	*318*

between OH and I^-. Elliot and Sopchyshyn, however, were well aware of this potential problem, and they proposed that the flash photolysis results were in error because they relied on kinetic measurements rather than equilibrium measurements (*109*). We tend to favor the result of Schwarz and Bielski (*277*), primarily because it leads to an E^0 for the iodine atom that is consistent with the E^0 values reported by Stanbury *et al.* (*294*) and Nord *et al.* (*233*). Unfortunately, there does not yet seem to be a definitive explanation for the discrepancy between the flash photolysis and pulse radiolysis results.

Having selected a value of 1.1×10^5 M^{-1} for K_{eq} for reaction (31), combination with the E^0 values for the I/I^- couple and the $I_2/2I^-$ couple leads to an E^0 of 1.03 V for the $I_2^-/2I^-$ couple and an E^0 of 0.21 V for the I_2/I_2^- couple. $\Delta_f G^0$ of I_2^- is computed to be -3 kJ/mol.

In alkaline media the iodine atom is reported (*59*) to be hydrolyzed according to

$$I + OH^- \rightleftharpoons IOH^- + H_2O \tag{33}$$

with a pK_a for the iodine atom of 11.7 ± 1.0, which leads to $\Delta_f G^0 = -93 \pm 6$ kJ/mol for IOH^-. This value, when combined with NBS data, leads to an E^0 of 0.03 ± 0.06 V for the HIO/HIO^- redox couple; however, we are not aware of any studies that have implicated a chemical role for this couple.

Hypoiodous acid deprotonates in alkaline solution (pK_a = 11); furthermore, IO is a well-characterized species in the gas phase (*42*), and it has been reported as an intermediate in the radiolysis and photolysis of HIO in aqueous solution (*70*). A value of 149.77 kJ/mol is reported in the NBS tables for the standard free energy of formation of IO in the gas phase, but this is probably accurate only ±20 kJ (*167*). As a rough estimate, the free energy of solution of IO may be taken as that of ICl, -11.64 kJ/mol, which leads to $\Delta_f G^0_{aq} = 138 \pm 20$ kJ/mol. With NBS data for IO^- this result gives $E^0 = 1.8 \pm 0.2$ V for the IO/IO^- couple and $E^0 = 2.5$ V for the $(H^+, IO)/HIO$ couple. Sharma and Noyes (*286*) estimated 2.4 V for the latter couple, presumably by similar methods, although subsequently Furrow and Noyes expressed some doubt about this value (*136*). Apparently the only reports of reactions that involve this couple are the oxidation of IO^- by I_2^- and O^-. However, according to Buxton and Sellers the former reaction proceeds undetectably slowly (*70*); this is supported by the potentials presently estimated, which imply that the oxidation by I_2^- is highly endothermic. Buxton and Sellers also report the oxidation of HIO by I_2^-, but this reaction must also be highly endothermic.

IO_2 has been observed in irradiated crystals by ESR (*75*), but as discussed below recent studies indicate that I(IV) in aqueous solution exists as HIO_3^- and IO_3^{2-}. There is a report of the reaction of IO_2^- with IO^- and I_2OH^- and of the Raman spectrum of IO_2^- in aqueous solutions of decomposing IO^- (*334*). Presumably one-electron oxidation of IO_2^- could lead to IO_2 as an intermediate prior to hydrolysis. There has also been a recent report by Noszticzius *et al.* that demonstrates that it is feasible to conduct experiments with HIO_2 (*234*). By analogy with the chemistry of other halogens, $E^0 = 1.0$ V for the IO_2/HIO_2 couple was estimated by Sharma and Noyes (*286*), but it was subsequently declared unreliable by Furrow and Noyes (*136*).

Klaning *et al.* estimated $\Delta_f G^0 < 190$ kJ/mol for HIO_3^- and $\Delta_f G^0 < -120$ kJ/mol for IO_3^{2-} (*185*). Central to their argument is the assumption that OH reacts with IO_3^- according to

$$OH + IO_3^- \rightleftharpoons HOOIO_2^- \tag{34}$$

with $\Delta G^0 < 0$. The indicated free energy was obtained by the relationship $\Delta_f G^0(HOOIO_2^-) - \Delta_f G^0(HIO_3^-) = \Delta_f G^0(H_2O_2) - \Delta_f G^0(H_2O)$. In a previous study these workers reported that the above reaction yields IO_3 (*183*), but this was revised because it was considered that formation of IO_3 would be too endothermic. The value for IO_3^{2-} was obtained from that for HIO_3^- by using Pauling's rule for estimation of acidity constants ($pK_a = 12.3$). Buxton and Sellers (*70*) subsequently measured the pK_a of HIO_3^- as 13.3, which corrects the upper limit of $\Delta_f G^0$ for IO_3^{2-} to -126 kJ/mol. These results suggest $E^0 > -0.02$ and >0.60 V for the IO_3^-/IO_3^{2-} and HIO_3/HIO_3^- couples, respectively.

The present consensus is that there are several forms of I(VI). As noted above it is now believed that the reaction of OH with IO_3^-

produces a peroxyl species. On the other hand the reaction of O^- with IO_3^- to form IO_4^{2-}, according to Klaning *et al.* (*183*), is reversible, with an equilibrium constant of $10^6\ M^{-1}$. This led them to assign $\Delta_fG^0 = -57$ kJ/mol for IO_4^{2-}. In a rather ambiguous statement Buxton and Sellers (*70*) seem to cast doubt on this result with the observation that hydration of IO_4^{2-} competes very effectively with loss of O^-. Because Klaning *et al.* (*183*) used their result for IO_4^{2-} to derive free energies for several related I(VI) compounds (HIO_4^-, H_2IO_4, $H_5IO_6^-$, $H_4IO_6^{2-}$, $H_2IO_5^{2-}$, HIO_5^{3-}, and IO_3), these latter results are also questionable. Generation of IO_3 by photolysis of IO_4^- is not presently disputed (*183, 325*). I(VI) can also be generated by reduction of periodate; because the composition of periodate is a function of pH, the structure of the I(VI) so generated is also pH dependent, as indicated by the above list of species. The energetics of these species is a matter for further research.

Various mononuclear and binuclear species related to "I(VIII)" have been generated in the radiolysis of I(VII) solutions. The chemistry is complex and still somewhat unsettled; the interested reader should consult the paper by Buxton and Sellers (*70*) and references therein for a discussion of the problems.

Another iodine-containing radical is $ISCN^-$. It was observed in a pulse radiolysis study, and the reaction

$$ISCN^- \rightleftharpoons I + SCN^- \tag{35}$$

was found to have an equilibrium constant of $4.8 \times 10^{-4}\ M$ (*272*). This establishes Δ_fG^0 for $ISCN^-$ as 151 kJ/mol, and $E^0 = 1.14$ for the $ISCN^-/(I^-, SCN^-)$ couple.

E. ASTATINE

The chemistry of astatine is reviewed in *Standard Potentials* and elsewhere (*148*). Because of the short half-life of this element (≈8 hr) not much is known of its chemistry. There are no reports of its free radicals in aqueous solution.

VI. The Heavier Chalcogens

A. SULFUR

Sulfur, in its reduced oxidation states, has a complex chemistry due to the formation of polysulfides and their facile interconversions. Pearson estimated the HS/HS^- potential as 1.08 V by a thermochemical cycle, which leads to $\Delta_f G^0 = 116$ kJ/mol for HS (*240*); this result used the approximation that the hydration free energy of HS is the same as that of CH_3SH, 0.6 kcal/mol. Surdhar and Armstrong performed a similar estimate based upon the approximation that HS had for its hydration free energy the mean of those for H_2S and Ar (1.35 and 3.88 kcal/mol, respectively) (*304*); these authors obtained $E^0 = 1.15$ V, and from this we calculate $\Delta_f G^0 = 123$ kJ/mol. Henglein and Gutierrez estimated an upper limit of the HS/HS^- potential as 1.4 V (*162*); unfortunately, this result was based erroneously on the bond enthalpy of H_2S rather than the bond free energy, which introduced an error of 0.3 V. If the potential of Henglein and Gutierrez is corrected by this amount the resulting value, 1.1 V, is consistent with the other estimates cited above. It is not clear whether Pearson's or Surdhar and Armstrong's results are more accurate, so we have somewhat arbitrarily adopted Pearson's.

Mills *et al.* report considerable uncertainty as to the pK_a of HS, but they suggest it may be less than 7 (*218*). Association as in

$$HS^- + HS \rightleftharpoons H_2S_2^- \tag{36}$$

was reported to have a formation constant of $2.5 \times 10^4\ M^{-1}$ at pH 7, but this is only a conditional value because the pK_a values of both HS and $H_2S_2^-$ are uncertain. It is claimed that in acid solution $H_2SSH_2^+$ is formed by protonation of $H_2S_2^-$, and that the intermediate state of protonation, H_2SSH, is unstable (*81*). Thus the E^0 value calculated by Surdhar and Armstrong for $H_2S_2^-/2HS^-$ (0.90 V) is dubious. There does not seem to be a report concerning the radical chemistry of the higher polysulfides.

From the result of Henglein and Gutierrez (*162*), Mills *et al.* estimated a value of -1.3 V for the S/SH couple, in which "S" apparently refers to dissolved S_8 (*218*). If we use Pearson's result for HS and estimate the hydration free energy of atomic sulfur as 16.4 kJ/mol, the value for Ar, we obtain a potential of 1.44 V for reduction of atomic aqueous sulfur to HS.

At this time little can be said about the oxidation states between atomic sulfur and S(III). There is a report of generation of $S_2O_2^-$ by photolysis of $S_2O_3^{2-}$ (*101*), but the results have been shown to be, at least in part, spurious (*40*).

S(III) is found as dithionite, $S_2O_4^{2-}$, which is in homolytic equilibrium with SO_2^- in aqueous solution as in reaction (37).

$$S_2O_4^{2-} \rightleftharpoons 2SO_2^- \tag{37}$$

The equilibrium constant for this reaction $[(0.6–1.4) \times 10^{-9}\ M]$ was determined from ESR measurements in three laboratories with good agreement (*194*). This establishes $E^0 = -0.26$ V for the SO_2/SO_2^- couple (*293*), and $\Delta_f G^0 = -275$ kJ/mol for SO_2^-. The conditional potential of the SO_2^-/S(IV) system is pH dependent because of formation of HSO_3^-, and this has been treated by Mayhew (*212*). Recently the SO_2/SO_2^- system was investigated by direct cyclic voltammetry studies of acidic SO_2 solutions (*228*). In such measurements the peak potential is related to the half-wave potential by a function that is dependent (among other things) on the scan rate and the recombination rate constant of SO_2^-. The potential so obtained (-0.288 V) differs significantly from that presented above; the origin of this discrepancy is unclear because the SO_2^- dimerization rate constant used in the electrochemical studies was not reported. Reports of this rate constant range from $2k = 1.3 \times 10^9$ to 1×10^{10} M^{-1} s^{-1} (*111, 112, 158*). Furthermore, these authors observed a pH dependence in the cyclic voltammetry which was taken as evidence that SO_2^- can be protonated in acidic media. In view of these uncertainties the results obtained from the ESR measurements are provisionally recommended.

Dithionite apparently can undergo direct one-electron oxidation. $S_2O_4^-$ has not been reported in aqueous solution, but its existence in nonaqueous media is well established (*137*). Thus oxidation of $S_2O_4^{2-}$ presumably leads to $S_2O_4^-$ in aqueous media. Because of the lack of data regarding $S_2O_4^-$ we will simply write

$$SO_2 + SO_2^- + e^- \rightleftharpoons S_2O_4^{2-} \qquad (38)$$

for which the calculated potential is 0.255 V.

The chemistry of SO_3^- has recently been reviewed by Neta and Huie (*226*). This radical decays with second-order kinetics that appear to be pH dependent, as are the relative yields of SO_4^{2-} and $S_2O_6^{2-}$ (*111*). These results seem to suggest that SO_3^- can be protonated near pH 7, but most authors presently indicate the unprotonated form at all values of pH, perhaps because the UV/visible and ESR spectra are pH independent. In a recent study of SO_3^- in strongly acidic media no dependence of the spectrum was found over the range pH 11.3 to 61.2% $HClO_4$ (*93*). The first estimate of the potential of the SO_3^-/SO_3^{2-} couple was made by Anast and Margerum on the basis of the kinetics of oxidation of SO_3^{2-} by a Cu(III) complex (*13*). The obtained $E^0 < 0.89$ V by detecting kinetic inhibition by Cu(II). Subsequently in a study of the quenching of the triplet state of BNFA by various anions an E^0 of 2.15 V was obtained (*207*). This result is clearly inconsistent with the general ease of generation of SO_3^- in chemical oxidations. Finally, a direct determination of the E^0 was obtained by Huie and Neta (*170*).

Their value of 0.63 V was obtained relative to the potentials of phenoxide and chlorpromazine by direct measurement of the equilibria. Their potential is consistent with Anast and Margerum's result. Very recently Merenyi *et al.* (*215a*) have reported a value of 0.76 V for the SO_3^-/SO_3^{2-} couple, i.e., substantially greater than Huie and Neta's value. This recent result is based on an apparent electron transfer equilibrium between SO_3^- and ClO_2^- to form SO_3^{2-} and ClO_2. We question the validity of this method because the reaction of ClO_2 with SO_3^{2-} seems to involve atom transfer (*305a*).

From Huie and Neta's potential of the SO_3^-/SO_3^{2-} couple other results can be derived. Thus $\Delta_f G^0 = -426$ kJ/mol for SO_3^-. From Guthrie's estimate of $\Delta_f G^0 = -402$ kJ/mol for aqueous SO_3 (*150*) we obtain $E^0 = 0.25$ V for the SO_3/SO_3^- couple. Direct measurement of the $SO_3^{2-}/S_2O_6^{2-}$ half-cell potential (0.07 V) by use of a Au(I)-catalyzed electrode (*95*) establishes $\Delta_f G^0 = -960$ kJ/mol for $S_2O_6^{2-}$. Thus the reaction

$$S_2O_6^{2-} \rightleftharpoons 2SO_3^- \tag{39}$$

has an equilibrium constant of 1×10^{-19} *M*, and one-electron reduction of dithionate as in

$$S_2O_6^{2-} + e^- \rightleftharpoons SO_3^- + SO_3^{2-} \tag{40}$$

has $E^0 = -0.49$ V. These two values form the quantitative basis for the general observation that dithionate is quite inert. The substantially weaker bonding in dithionite may be due to the fact that the unpaired electron in SO_3^- resides in a σ orbital whereas in SO_2^- it is in a π orbital.

SO_4^- is a well-established species that is an enormously powerful oxidant. Thus it can even oxidize Cl^-. There is some evidence that it can be protonated in acidic media (*100*), but the pK_a does not appear to be established. In a study of the decomposition of $S_2O_8^{2-}$ Kolthoff and Miller determined the activation energy for a process believed to be homolysis of the peroxide bond (*187*). From this they estimated the energy of the O–O bond as 33.5 kcal/mol. Eberson has estimated the potential for the SO_4^-/SO_4^{2-} couple to lie between 2.52 and 3.08 V (*106*). The lower value derives from an estimate of the O–H bond homolysis energy in HSO_4^-, while the higher value comes from attempts to fit rate constants involving the radical to Marcus theory. Another approach is to use Shizuka's equation (*288*) [$E(\text{ctts}) = 1.35E^0 + 3.55$ in eV units] with $E(\text{ctts}) = 7.08$ eV (*52*). This method yields $E^0 = 2.62$ V, which is consistent with Eberson's estimates. The agreement may be fortuitous because there is little basis for expecting Shizuka's equation to apply to divalent anions.

A firmer estimate can be obtained from the persulfate decomposition data of Kolthoff and Miller (*187*), which can be extrapolated to yield a homolysis rate constant of 1.1×10^{-8} sec^{-1} at 25°C. The recombination rate constant for SO_4^- is $2k = 1.0 \times 10^9\ M^{-1}$ sec^{-1} (*157*). The ratio of these two rate constants yields a value for the homolysis equilibrium constant: i.e., $K_{eq} = 2.3 \times 10^{-17}\ M$ for reaction (41).

$$S_2O_8^{2-} \rightleftharpoons 2SO_4^- \tag{41}$$

The tabulated $\Delta_f G^0$ for $S_2O_8^{2-}$ has changed substantially with the various editions of the NBS tables, but the newest value, -1114.9 kJ/mol, leads to $\Delta_f G^0 = -510$ kJ/mol for SO_4^- and $E^0 = 2.43$ V for the SO_4^-/SO_4^{2-} couple. An additional result is the potential for direct one-electron reduction of persulfate: $E^0 = 1.45$ V for the $S_2O_8^{2-}/(SO_4^-, SO_4^{2-})$ couple.

The weak point in the above argument lies in the assumption that persulfate decomposes via homolysis. One alternative mechanism is

$$S_2O_8^{2-} \rightleftharpoons SO_4^- + HSO_4^- + OH \tag{42}$$

which continues to be defended by Fronaeus (*131*). The relative merits of the various proposals have been discussed in detail by Wilmarth and Haim (*330*). If Froneaus' mechanism is correct then the potential derived above for the SO_4^-/SO_4^{2-} couple is still useful as a lower limit.

Some support for persulfate homolysis results may be obtained from the reaction

$$SO_4^- + H_2O \rightleftharpoons HSO_4^- + OH \tag{43}$$

A forward rate constant of 3×10^3 sec^{-1} has been reported for this reaction, although the authors caution that it may only be an upper limit (*158*). The reverse rate constant, $1.6 \times 10^6\ M^{-1}$ sec^{-1}, is relatively well established (*121*). An equilibrium constant of $K_{eq} < 2 \times 10^{-3}\ M$ is obtained from the ratio of these rate constants, and from NBS data and $\Delta_f G^0$ for OH we derive $\Delta_f G^0 < -517$ kJ/mol for SO_4^- and $E^0 < 2.36$ V for the SO_4^-/SO_4^{2-} couple. The mild disagreement between these results and those obtained from homolysis of persulfate is not understood, but the fact that Cl^- is rapidly oxidized by SO_4^- although its E^0 is 2.41 V favors the homolysis results.

In yet another treatment Furholz and Haim obtain a value of 2.6 V for the SO_4^-/SO_4^{2-} couple (*135*). This result was obtained by using a value of $10^3\ M^{-2}$ for the equilibrium

$$OH + H^+ + SO_4^{2-} \rightleftharpoons SO_4^- + H_2O \tag{44}$$

which was culled from Wilmarth and Haim's review (*330*). The various approximations involved in this estimate, while not highly accurate, are probably essentially correct.

A species believed to be important in the autoxidation of S(IV) is SO_5^-, which is formed in the reaction of SO_3^- with O_2, as well as in the oxidation of HSO_5^- by OH (*208*). The state of protonation and related pK_a of "HSO_5" is unknown, although Huie and Neta propose $pK_a < 2$ (*170*). The fact that the radical is formed in the reaction with O_2 with $k = 1.5 \times 10^9\ M^{-1}\ sec^{-1}$ (*170*) suggests that the Δ_fG^0 for SO_5^- is less than that for SO_3^-, i.e., less than -426 kJ/mol. Recent studies of the chemistry of HSO_5^- have established $E^0 = 1.842 \pm 0.010$ V for the HSO_5^-/HSO_4^- couple (*246*), which gives $\Delta_fG^0 = -638$ kJ/mol for HSO_5^-. Combination of this result with the above limit for SO_5^- (or HSO_5) sets an absolute upper limit of 2.2 V for the HSO_5/HSO_5^- couple. In view of Eberson's success in estimating the SO_4^- potential by using an estimated O–H homolysis energy (*106*), the same approach may be applied to SO_5^-. According to Benson, the peroxidic O–H bond enthalpy is 377 kJ/mol (*44*), while Steele and Appelman report $\Delta_fH^0 = -798$ kJ/mol for aqueous HSO_5^- (*296*). These values lead to $\Delta_fH^0 = -639$ kJ/mol for aqueous SO_5^-, or $\Delta_fH^0 = -661$ kJ/mol for HSO_5 (the assumption being made that SO_5^- and SO_4^{2-} have the same enthalpy of protonation). With the further crude assumption that $S^0 = 188$ J/K/mol for HSO_5 (the same as acetic acid), we obtain $E^0 = 1.70$ V for the HSO_5/HSO_5^- couple. On the basis of studies of the reactions of SO_5^- with I_2^-, ascorbate, and promethazine, Huie and Neta suggest a potential near 1.1 V (*170*). Because of the substantial experimental complications in these experiments the suggested potential should be taken rather tentatively. For the purposes of this review we adopt an E^0 of 1.4 ± 0.3 V for the HSO_5/HSO_5^- couple and $\Delta_fG^0 = -500 \pm 30$ kJ/mol for HSO_5.

Thiosulfate ($S_2O_3^{2-}$) can be oxidized to its radical, $S_2O_3^-$. In a study of the oxidations by coordination complexes, Wilmarth and co-workers assigned a potential of 1.35 V to the $S_2O_3^-/S_2O_3^{2-}$ couple (*331*). Their assignment was derived by combining Schoneshofer's equilibrium constant ($K_{eq} = 2.7 \times 10^4$) (*269*) for the reaction

$$SCN + S_2O_3^{2-} \rightleftharpoons SCN^- + S_2O_3^- \qquad (45)$$

with the potential previously derived for the SCN/SCN^- couple (1.66 V). The derived potential was found to be consistent with the condition that the reverse rate constants of the reactions generating the radical not exceed diffusion control. Martins (*206*) reported essentially the same result by using the same data. As there do not appear to be any other pertinent results in the literature, $E^0 = 1.35$ V for the $S_2O_3^-/S_2O_3^{2-}$ couple and $\Delta_fG^0 = -392$ kJ/mol for $S_2O_3^-$ are tentatively accepted.

In Schoneshofer's study of the $SCN^-/S_2O_3^-$ system the radicals were generated by oxidation of SCN^- with OH (*269*). In another of his studies the reaction of OH with $S_2O_3^{2-}$ was employed (*270*). This study yielded a pK_a of 6.2 for $HS_4O_6^{2-}$ and a value of K_{eq} less than 10^{-6} *M* for the reaction

$$S_4O_6^{3-} \rightleftharpoons S_2O_3^- + S_2O_3^{2-} \tag{46}$$

In a subsequent study Mehnert and co-workers reinvestigated this system and found that $S_2O_3OH^{2-}$ is an intermediate in the reaction and that $S_2O_3^-$ is generated only by decomposition of $S_4O_6^{3-}$ as in reaction 46 with $k = 2.5 \times 10^6$ sec^{-1} (*213*). If we assume a diffusion-controlled rate constant of 2×10^9 M^{-1} sec^{-1} for the reverse process, then a value of 1.3×10^{-3} *M* is obtained for the equilibrium constant, in contrast with Schoneshofer's result. This value of 1.3×10^{-3} *M*, with use of the above value for $\Delta_f G^0$ of $S_2O_3^-$, leads to $\Delta_f G^0 = -931$ V for $S_4O_6^{3-}$ and $E^0 = 1.18$ V for the $S_4O_6^{3-}/2S_2O_3^{2-}$ couple. By using NBS data for $S_4O_6^{2-}$ a potential of -1.13 V can be derived for the $S_4O_6^{2-}/S_4O_6^{3-}$ redox couple.

Sulfur hexafluoride is reported to be reduced to the pentafluoride by the hydrated electron and that SF_5 has a significant lifetime (*29*). A potential for the reaction

$$SF_6 + e^- \rightleftharpoons SF_5 + F^- \tag{47}$$

can be calculated by using the gas-phase thermochemical data for SF_5 tabulated by Herron (*164*) and the assumption of equal hydration free energies for SF_6 and SF_5. The result of these calculations is $E^0 = 0.05$ V and $\Delta_f G^0 = -822$ kJ/mol for aqueous SF_5. It has been proposed (*19*) that SF_5 hydrolyzes as in

$$SF_5 + H_2O \rightleftharpoons SF_4 + OH + F^- + H^+ \tag{48}$$

In a subsequent study (*29*) it was found that SF_5 could account for the oxidizing properties and that there was no need to postulate reaction (48). With Herron's thermochemical data for SF_5 and SF_4 and the assumption of a hydration free energy of SF_4 the same as that of SF_6, we calculate $\Delta G^0 = 105$ kJ/mol for reaction (48), and thus conclude that this process will not occur. The oxidizing power of SF_5 can be represented in reaction (49)

$$SF_5 + e^- \rightleftharpoons SF_4 + F^- \tag{49}$$

for which $E^0 = 1.64$ V can be derived, which is consistent with the observation that SF_5 is indeed a good oxidant.

The oxidizing power of $F_2S_2O_6$ has been demonstrated by its ability to oxidize aqueous iodide. In the gas phase the species undergoes homolysis, and the pertinent thermochemical values have been tabulated by Benson (*44*). If a hydration free energy of 20 kJ/mol (the same as for SF_6) is assumed then a value of $\Delta_f G^0 = -465$ kJ/mol is calculated for aqueous FSO_3. The NBS tables present only $\Delta_f H^0$ for FSO_3^-, but as a rough estimate a value of 140 J/K/mol (that of HSO_3^-) may be assumed for the entropy of FSO_3^-. These calculations lead to $E^0 = 3.09$ V for the FSO_3/FSO_3^- couple. Because of the weak peroxide bond in $F_2S_2O_6$ the potential for direct one-electron reduction of $F_2S_2O_6$ should be only slightly less than for FSO_3. The enormous oxidizing power of these species suggests that their lifetimes in water should be very short. If these species could be generated they would probably produce OH before they could react with other species present in solution.

Radicals derived from SCN^- and CS_2 are discussed in the section on carbon (Section VIII,A), except for the species $XSCN^-$, which are discussed in the relevant halogen sections.

B. SELENIUM

A direct investigation of the radicals derived from HSe^- was conducted in a pulse radiolysis study by Schoneshofer and co-workers (*273*). Among other things, they were able to determine pK_a values for H_2Se_2 and HSe_2^- (1.7 and 9.3), the spectra of HSe and Se^-, and the dissociation constant for $H_2Se_2^-$ with formation of HSe and HSe^- ($K = 6 \times 10^{-5}$ *M*). Pearson estimated $E^0 = 0.62$ V for the HSe/HSe^- couple by using a thermochemical cycle involving gas-phase data (*240*). Corresponding to this potential is $\Delta_f G^0 = 104$ kJ/mol for aqueous HSe. If it is assumed that atomic Se has the same hydration free energy as that of Kr, we obtain $\Delta_f G^0 = 202$ kJ/mol for aqueous Se, and the potential of the $(Se, H^+)/HSe$ couple is 1.02 V. Finally, by incorporating the data of Schoneshofer *et al.* we calculate $\Delta_f G^0 = 124$ kJ/mol for $H_2Se_2^-$ and $E^0 = 0.37$ V for the $H_2Se_2^-/2HSe^-$ couple. Unfortunately, the free energy of formation of H_2Se_2 does not appear in the NBS tables.

SeO_2^- has been generated by reaction of Se(IV) with e_{aq}^-, and dimerization to form $Se_2O_4^{2-}$ has been observed (*307*). The redox properties of these species are unknown; the adventuresome reader may wish to draw analogies with sulfur chemistry.

The chemistry of Se(V) has recently been probed in a pulse radiolysis study by reduction of SeO_4^{2-} and oxidation of SeO_3^{2-} (*181*). Over the pH range of 0.3 to 14, Klaning and Sehested found two species of Se(V): SeO_3^- and $HSeO_4^{2-}$. These are related by the equilibrium

$$OH^- + SeO_3^- \rightleftharpoons HSeO_4^{2-} \qquad (50)$$

with $K_{eq} = 0.78\ M^{-1}$. In a previous report qualitatively different conclusions were arrived at regarding the acid/base chemistry of S(V). Klaning and Sehested also obtained the equilibrium constant for the reaction

$$OH + SeO_3^{2-} \rightleftharpoons HSeO_4^{2-} \qquad (51)$$

by measuring the rates of the forward and reverse rates ($K_{eq} = 4.8 \times 10^3\ M^{-1}$) (*181*). With use of their previously determined value for $\Delta_f G^0$ of OH they derived the following results: $\Delta_f G^0 = -358$ kJ/mol for $HSeO_4^{2-}$, and $\Delta_f G^0 = -202$ kJ/mol for SeO_3^-. The authors noted that these calculations are not consistent with the NBS tables because the NBS data are inconsistent with the measured pK_a of biselenite. From these free energies E^0 values for eight different reactions were derived, but only one of them does not involve concurrent acid/base reactions: $E^0 = 1.68$ V for the SeO_3^-/SeO_3^{2-} couple. From the above results we calculate $E^0 = -0.97$ V for the $HSeO_4^-/HSeO_4^{2-}$ couple. It is notable that Se(V), unlike S(V), does not form an adduct with O_2.

SeO_4^- has been reported in the reactions of OH and CO_3^- with SeO_4^{2-} (*298*). Because CO_3^- is not an especially strong oxidant ($E^0 = 1.5$ V), it may be assumed that SeO_4^- is also not an especially strong oxidant. A potential in the range of 1.4 V for the SeO_4^-/SeO_4^{2-} couple would not be unreasonable. The second-order decay of SeO_4^- is of some interest in that the preparation of $Se_2O_8^{2-}$ has not been reported. A problematic issue is that SeO_4^- was reported to decay by pseudo-first-order kinetics in alkaline media; if this process involves generation of OH as suggested, then it is difficult to understand how CO_3^- could oxidize SeO_4^{2-}.

Species analogous to those found in sulfur chemistry, such as $SeO_2(O_2)^{2-}$, SO_3Se^{2-}, SeO_3S^{2-}, and $Se_xS_yO_6^{2-}$, have been described, but the chemistry of their related radicals appears to be unexplored. Selenocyanate and its radicals are discussed in Section VIII,A.

In a fascinating recent development Dimitrijevic has found it possible to assign a redox potential to a colloid (*96*). The report deals with the redox potential of small colloids of $(CdSe)_n/(CdSe)_n^-$ in acetonitrile, and it seems likely that the concept soon will be applied to aqueous systems as well.

C. TELLURIUM

The free-radical chemistry of tellurium is not extensively documented. The UV/visible spectrum of TeO_3^- and the rate constant for generation of this species by reaction of OH with TeO_3^{2-} have been reported (*3, 4*). Some information about Te(III) and Te(V) may also be gleaned from two γ-radiolysis studies (*90, 152*). Leipoldt and co-workers report that in the absence of Os(VIII) catalysis, TeO_3^{2-} is not oxidized by $Mo(CN)_8^{3-}$ (*200*), which implies that TeO_3^- is a strong oxidant. This is in keeping with the trend established by the analogous S(V) and Se(V) couples.

D. POLONIUM

The chemistry of polonium was recently reviewed by Bagnall (*23*). Regarding free radicals this review cites a calculation of the bond length of PoH (*245*) and some electrochemical evidence of Po(III) as an intermediate in the oxidation of Po(II) to Po(IV) in aqueous hydrochloric acid (*24*).

VII. Group V

A. NITROGEN

The chemistry of atomic nitrogen, $N(^4S)$, in aqueous solution has been investigated by bubbling a stream of active nitrogen into water (*83*). It was found that $N(^4S)$ reacts with alcohols, and the reaction was proposed to proceed by insertion into a C–H bond. The water was found to be rather unreactive. Further work in this area would be facilitated by an *in situ* source of $N(^4S)$.

NH_3^+ is often generated by reduction of NH_2OH with Ti(III) (*140*), and it can be deprotonated to form NH_2. The associated pK_a has been reported variously as 3.65, 6.7 ± 0.2, and 2.3. The value of 6.7 has been widely cited (*290*), but it appears that the value of 2.3 is more likely correct (*165*). Endicott estimated a potential of 2.7 V for the NH_3^+/NH_3 couple, but the basis of this estimate is unclear (*110*). Pearson estimated a value of 1.61 V from gas-phase thermochemical data (*240*); unfortunately, this calculation also relied on the pK_a of NH_3^+, for which the incorrect value of 6.7 was used. Another estimate of $E^0 = 1.9$ V was also based on $pK_a = 6.7$ (*230*). An estimate of E^0 may be derived by using the value of $\Delta_f G^0 = 199.8$ kJ/mol for NH_2 in the gas phase, as listed in the JANAF tables. The assumption of a hydration free energy of -8 kJ/mol for NH_2 (a subjectively weighted average of $\Delta_{hyd}\, G^0$ for H_2S, NH_3, and half of N_2H_4) leads to $\Delta_f G^0 = 192$ kJ/mol for aqueous NH_2 and, making use of $pK_a = 2.3$ for NH_3^+, to $\Delta_f G^0 = 179$ kJ/mol for aqueous NH_3^+ and $E^0 = 2.13$ V for the NH_3^+/NH_3 couple.

It has been argued that NH_2 acts as an oxidizing agent by undergoing simple electron transfer (*229*). On the basis of reactivity trends, an E^0 of 0.7–0.8 was estimated for the NH_2 radical. The identity of the associated reaction was not specified (*10*), but it may reasonably be assumed to be NH_2/NH_2^-. An estimate of the $E^0 = 0.25$ V for this couple may be obtained from the above $\Delta_f G^0$ for NH_2 and $\Delta_f G^0 = 168$ kJ/mol for NH_2^- [derived from Pearson's estimate (*240*) of $pK_a = 34$ for NH_3]. From a similar calculation Pearson obtained $E^0 = 0.22$ V (*240*). These latter estimates appear too low in view of the reactivity of NH_2 relative to other free radicals. The disagreement may be due, perhaps, to the estimated pK_a of NH_3.

As noted above, reduction of hydroxylamine leads to formation of NH_2. No evidence has been presented in support of NH_2OH^- as an intermediate. The appropriate standard potential thus refers to the half-cell

$$e^- + NH_2OH \rightleftharpoons NH_2 + OH^- \tag{52}$$

No value of $\Delta_f G^0$ for NH_2OH is given in the NBS tables, but a value of 23.4 kJ/mol is cited in *Standard Potentials*. Thus $E^0 = -0.12$ V can be calculated for the $NH_2OH/(NH_2, OH^-)$ couple. In the case of NH_3OH^+ it is reported that reaction with the hydrated electron yields OH and NH_3. By use of thermochemical data from *Standard Potentials*, E^0 for the $NH_3OH^+/(NH_3, OH)$ couple is calculated as -0.58 V.

Nitrene, NH, has been suggested as an intermediate in the photolysis of aqueous hydrazoic acid (*285*). The only detected reaction of this proposed species was insertion into water to form NH_2OH.

Oxidation of hydroxylamine by OH leads to NHOH (or its tautomer NH_2O), which can be protonated; the pK_a of NH_2OH^+ is reported as 4.2 ± 0.1 (*290*). On the basis of its UV spectrum Simic and Hayon argued that NHOH was the predominant tautomer. There do not seem to be any estimates of E^0 for the NH_2OH^+/NH_2OH couple in the literature. There is a report (*283*) of the oxidation of hydroxylamine by $IrCl_6^{2-}$ in acidic solution for which the rate law is

$$-d[IrCl_6^{2-}]/dt = k[IrCl_6^{2-}][NH_3OH^+]/[H^+] \tag{53}$$

If it is assumed that this reflects a mechanism in which NH_2OH is oxidized, then the rate constant for electron transfer is 7.3×10^3 M^{-1} sec^{-1}. An upper limit of 1×10^{10} M^{-1} sec^{-1} for the reverse reaction establishes $E^0 \leq 1.26$ V for the NH_2OH^+/NH_2OH couple. This result should be accepted with some caution because unpublished experiments by the present author indicate that the reaction is catalyzed by adventitious copper (*291*), as was the case in the oxidation by $Fe(CN)_6^{3-}$ (*58*).

Several important redox couples are related to HNO, which is a transient species, although not a free radical. The JANAF tables report data for HNO in the gas phase, but these rely on the H–NO bond dissociation enthalpy for which only an upper limit was available. Recently a dissociation enthalpy of 196.8 ± 0.1 kJ/mol has been determined by consideration of the predissociation mechanism of HNO (*97*). If we apply a rough correction to 298 K and use the entropy data in the JANAF tables a value of 123 kJ/mol is calculated for $\Delta_f G^0$ of HNO in the gas phase. Finally, on estimating a free energy of hydration as −14 kJ/mol (that of HClO), we calculate $\Delta_f G^0 = 109$ kJ/mol for aqueous HNO. The triplet excited state has the form NOH. It is presumed that in solution the ground state is HNO. In the gas phase NO^- has a triplet ground state, and the singlet state is 6050 cm^{-1} (72 kJ/mol) higher in energy (*168*). It is argued that both singlet and triplet states of HNO (NOH) and of NO^- can be generated in aqueous solution (*102*). A pK_a of 4.7 was reported for "HNO" in a pulse radiolysis study in which NO^- was generated by reaction of e_{aq}^- with NO and "HNO" was generated by reaction of H with NO (*147*). It is unclear what electronic states are involved in this pK_a measurement, although Donald *et al.* suggest that it refers to the singlet molecules (*102*); they also suggest that the triplet system will be more acidic. The adoption of this suggestion leads to $\Delta_f G^0 = 136$ kJ/mol for aqueous singlet NO^-. If equal hydration energies for $^1NO^-$ and $^3NO^-$ are assumed and entropy effects are neglected, $\Delta_f G^0$ for aqueous $^3NO^-$ is calculated as 64 kJ/mol.

The NBS tables give $\Delta_f G^0 = 86.55$ kJ/mol for NO in the gas phase. Because NO is a persistent species in solution, an accurate value of its solubility of 1.9×10^{-3} *M*/atm has been determined (*274*), so a value of $\Delta_f G^0 = 102$ kJ/mol can be calculated for aqueous NO. From the above results for NO^- it is now possible to calculate $E^0 = -0.35$ V for the $NO/^1NO^-$ couple and $E^0 = 0.39$ V for the $NO/^3NO^-$ couple. This latter result is consistent with the suggestion that $[Ru(NH_3)_6]^{2+}$ is capable of reducing NO to NO^- (*5*).

Equilibrium constants have been reported for the association of NO with NO^- and the association of the resulting $N_2O_2^-$ with H^+ (*281*). In principle it would be possible to calculate redox potentials involving $N_2O_2^-$ and HN_2O_2, but because of the current uncertainty in the electronic state of NO^- in these reactions such a calculation is reserved for the future.

A hydrolyzed form of NO, H_2NO_2, has been detected in the reaction of e_{aq}^- with NO_2^-, and pK_a values have been determined for both deprotonation steps (*144*). HNO_2^- is also implicated in certain chemical reductions of HNO_2 (*251*). All of these species appear to be unstable with respect to NO, but values $\Delta_f G^0$ for them are not available.

In strongly acidic media nitrous acid is in equilibrium with NO^+, and one pathway for reduction of nitrous acid is reduction of NO^+ to NO. Likewise, NO is oxidized via NO^+ in certain cases (*252*). The calculated potential of the NO^+/NO couple is dependent on $\Delta_f G^0$ of HNO_2 and the equilibrium constant for production of NO^+; both of these parameters are somewhat uncertain. An early value of 1.45 V was reported in an electrochemical study of the NO/HNO_2 equilibrium (*266*); an assumed value for the formation constant of NO^+ was employed. A value of 1.21 V can be calculated from the substantially revised thermodynamic parameters selected by Ram and Stanbury (*252*). This latter value is preferred because of the numerous cross-checks described in the paper.

Wishart *et al.* (*332*) have recently determined the enthalpy change ($\Delta H^0 = -44 \pm 2$ kJ/mol) for hydrolysis of NO^+ as given by the reaction

$$NO^+ + H_2O \rightleftharpoons 2H^+ + NO_2^- \qquad (54)$$

We have combined this result with data from the NBS tables to derive a value of 177 kJ/mol for the standard enthalpy of formation of NO^+. A value for $\Delta_f H^0$ of 78 kJ/mol for aqueous NO can be derived from $\Delta_f H^0$ of gaseous NO and its heat of hydration (*328*). These data lead to a value of -99 kJ/mol for the standard enthalpy change of the NO^+/NO half-cell.

Direct oxidation of NO_2^- can yield NO_2, and NO_2 derived from various sources is often reduced to NO_2^-. Rapid bimolecular disproportionation of NO_2 in solution vitiates a simple electrochemical measurement of the potential for the NO_2/NO_2^- couple, but estimates have been reported on numerous occasions. Endicott (*110*) cited a value of 1.13 V for the $(H^+, NO_2)/HNO_2$ couple, apparently taken from the data in Latimer (*195*). Berdnikov and Bazhin estimated a value of 1.0 ± 0.1 V for the NO_2/NO_2^- couple by use of an estimated hydration energy of NO_2 (*45*). Koppenol derived a value of 0.91 V, but the details of the calculation are not obvious (*189*). By employing several approximations Pearson obtained a value of 0.89 V (*240*). Wilmarth *et al.* reported a value of 1.03 ± 0.04 V, which was based on an estimate of the solubility of NO_2 (*331*). A value of 0.993 V estimated by Ram and Stanbury (*251*) was based on a measurement of the solubility of NO_2. This value was revised to 1.045 V by using revised data for NO_2^- (*252*). Finally, an experimental value of 1.04 V was obtained by measuring the forward and reverse rates of the reaction

$$NO_2^- + [Fe(TMP)_3]^{3+} \rightleftharpoons NO_2 + [Fe(TMP)_3]^{3+} \qquad (55)$$

and using the known potential of the Fe(III)/Fe(II) couple (*252*). These results bear out the conclusions in Schwartz and White's exhaustive review of the solubility of NO_2 (*275*), and they lead to $\Delta_f G^0 = 63$ kJ/mol for aqueous NO_2.

Bontempelli *et al.* studied the NO_2^+/NO_2 couple in acetonitrile (*54*). A potential of 1.51 V can be derived for this couple in aqueous solution from the equilibrium fraction of NO_2^+ present in dilute solutions of nitric acid in 68.3% sulfuric acid, the acidity function of that solvent, and the pK_a of aqueous HNO_3. The reactivity of this couple has been discussed by Eberson and Radner (*108*).

As with NO, Gratzel *et al.* have reported hydrolyzed forms of NO_2, i.e., H_2NO_3, HNO_3^-, and NO_3^{2-}, and the pK_a values that interrelate them: 4.8 and 7.5 (*145*). Because H_2NO_3 and the others are unstable with respect to NO_2, we calculate $\Delta_f G^0 > -104$ kJ/mol for NO_3^{2-}. Thus NO_3^{2-} is a reducing agent, with $E^0 < -0.05$ V for the NO_3^-/NO_3^{2-} couple. Consistent with this estimate is the report that NO_3^{2-} rapidly reduces O_2, benzoquinone, and methyl viologen (*126*). Because methyl viologen has an $E^0 = -0.44$ V and the rate of electron transfer is $3.3 \times 10^9\ M^{-1}\ sec^{-1}$, a potential less than -0.4 V may be inferred for the NO_3^-/NO_3^{2-} couple on the basis that the reverse reaction can hardly be much faster. Thus $\Delta_f G^0 > -70$ kJ/mol for NO_3^{2-}.

NO_3 is generated with difficulty in aqueous solution, the primary technique being radiolysis of concentrated nitric acid or nitrate-containing solutions. Its chemistry has recently been reviewed by Neta and Huie (*227*). Berdnikov and Bazhin gave the first estimate of E^0 for the NO_3/NO_3^- couple as 2.3 ± 0.1 V (*45*). This was obtained from gas-phase data and estimated hydration energies. A recent direct measurement of the equilibrium constant for the $NO_2 + NO_3 \rightleftarrows N_2O_3$ reaction in the gas phase (*321*) allows us to calculate a value of $\Delta_f G^0 = 123$ kJ/mol for NO_3 in the gas phase. By using the same estimate of the hydration free energy as was used by Berdnikov and Bazhin (*45*), we obtain $\Delta_f G^0 = 131$ kJ/mol for aqueous NO_3 and $E^0 = 2.49$ V for the NO_3/NO_3^- couple. Pearson estimated a value of 2.28 V by a related calculation (*240*). Endicott reported an approximate value of 1.9 V, but the details of the calculation were not presented (*110*). On the basis of rate constants of reactions of NO_3, Neta and Huie estimated the potential to lie in the range 2.3–2.6 V (*227*). In summary, E^0 for the NO_3/NO_3^- couple is not well established. A tentative value of 2.5 V is recommended along with the corresponding $\Delta_f G^0 = 131$ kJ/mol for NO_3.

Both N_2O_3 and $N_2O_3^{2-}$ are well-established species in aqueous solution (*146*). Akhtar *et al.* (*5*) have found that $N_2O_3^{2-}$ is rapidly oxidized by $[Ru(NH_3)_6]^{3+}$, which suggests that $N_2O_3^-$ may be a significant intermediate. Further studies on this possibility would be of interest.

The cation radical of hydrazine, $N_2H_4^+$, can be generated chemically and pulse radiolytically. An upper limit of 0.94 V was calculated by Stanbury on the assumption that $Fe(CN)_6^{3-}$ oxidized N_2H_4 via $N_2H_4^+$ and that the reverse reaction could not exceed diffusion control (*292*). Because the reverse reaction in a pulse radiolysis study could not be detected, an upper limit to the rate constant of 3×10^6 M^{-1} sec^{-1} was deduced, and this set an upper limit 0.73 V for the $N_2H_4^+/N_2H_4$ couple. Pearson estimated a potential for this couple of 0.65 V; an essential component of this estimate is the ionization potential of hydrazine, which was taken as 8.74 eV (*240*). An adiabatic ionization potential of 8.1 ± 0.15 eV has recently been reported (*215*), which corrects Pearson's value to 0.01 V. This last result is unexpectedly low, but it is the best available at this time. The corresponding result is $\Delta_f G^0 = 129$ kJ/mol for $N_2H_4^+$. Hayon and Simic reported that $N_2H_4^+$ has a pK_a of 7.1 ± 0.1 (*157a*); accordingly $\Delta_f G^0 = 170$ kJ/mol for N_2H_3.

The major route to the azidyl radical, N_3, is through oxidation of azide. The potential of the N_3/N_3^- couple has an extended history that is summarized in the recent papers of Ram and Stanbury (*253*) and of Alfassi *et al.* (*7*). In the first estimate, a potential of 1.9 V was deduced from the photoredox chemistry of $[Co(NH_3)_5N_3]^{2+}$. An estimate of 1.87 V was derived from the ctts spectrum of N_3, but this was shown subsequently to be based on an erroneous assignment of the UV spectrum. An estimate of 1.37 ± 0.22 V was obtained from the gas-phase proton affinity of N_3^-; a recent redetermination of the electron affinity of N_3 supports the value of $\Delta_f H^0$ used in this calculation (*172*). In yet another estimate, based on the relative reactivity of N_3 and other radicals, an E^0 of 2.0 V was reported (*189a*). In the recent experimental studies cited above reliable results were obtained, with Ram and Stanbury finding $E^0 = 1.33 \pm 0.02$ V by measuring the forward and reverse rates for the oxidation of N_3^- by $IrCl_6^{2-}$ (*253*); Alfassi *et al.* obtained values of 1.35 and 1.32 V (*7*). The first of the results by Alfassi *et al.* was obtained in a pulse radiolysis study by measuring the electron transfer equilibrium between N_3 and Br^-, while the second was obtained electrochemically, with the assumption that the electrochemically produced N_3 decayed by a second-order homogeneous process. Further confirmation of these results is reported in a mechanistic study of the reaction of $Br_2 + N_3^-$, in which the potential was assigned an upper limit of 1.365 V (*6*). Thus recommended values are $E^0 = 1.33$ V for the N_3/N_3^- couple and $\Delta_f G^0 = 477$ kJ/mol for aqueous N_3.

Unlike the halogens, N_3 forms an adduct with its parent anion only weakly. The formation constant of N_6^- is reported as 0.33 M^{-1} (*65*), which leads to $\Delta_f G^0 = 828$ kJ/mol. It is conceivable that N_6^- could be oxidized to N_6, but it is not yet certain whether N_6 is a bound state in aqueous solution (*261*). There is evidence that HN_3^- can be formed, for example, by the reaction of H with N_3^- (*336*). This species is unstable with respect to formation of N_3 and H_2 by reaction with acids, but its energetics is unknown.

In the gas phase the equilibrium between N_2F_4 and NF_2 is well documented. Presumably this equilibrium occurs in aqueous solution also, and since N_2F_4 is hydrolyzed only slowly (*94*) NF_2 should be another of the very few free radicals that can have appreciable concentrations in aqueous solution. A value for $\Delta_f G^0$ of 57.8 kJ/mol for NF_2 in the gas phase is listed in the NBS tables. If we use 10 kJ/mol as a guess for the hydration free energy of NF_2 (based on the value for NO_2), then we obtain $\Delta_f G^0 = 68$ kJ/mol for aqueous NF_2. HNF_2 is also hydrolyzed only slowly and is only a weak acid ($pK_a > 15$) (*201*). Its enthalpy is given as -15.6 kcal/mol (*239*), and its entropy as 59.5 eu (*17*), which establishes $\Delta_f G^0 = -31.0$ kJ/mol for HNF_2 in the gas phase. If it is assumed that HNF_2 and NF_2 have the same free energies of hydration, then the half-cell

$$NF_2 + e^- + H^+ \rightleftharpoons HNF_2 \qquad (56)$$

has a potential of 0.91 V. Thus NF_2 is predicted to be a good oxidant but not strong enough to decompose water.

Fremy's salt, $ON(SO_3)_2^{2-}$ is the last of the stable free radicals in aqueous solution to be described in this review. Quantitative studies of its chemistry are rare, and the reader is referred to a recent paper by Balasubramanian and Gould for details (*26*). According to these workers the protonated radical has a pK_a less than 5.6. They cite a potential of -0.350 V for the $ON(SO_3)_2^{2-}/ON(SO_3)_2^{3-}$ couple in alkaline media. This potential was derived from potentiometric titrations of this electrochemically reversible couple by Aoyagui and Kato, who also noted that for $HON(SO_3)_2^{2-}$ the $pK_a = 12.0$ (*20*). These results have been confirmed in a voltammetric investigation (*255*).

B. PHOSPHORUS

HPO_2^- is the lowest oxidation state known for inorganic free radicals of phosphorus in aqueous solution. Not much is known of this species except that it is formed in the reactions of OH and SO_4^- with $H_2PO_2^-$, that it exhibits an ESR spectrum, and that it undergoes a second-order decay (*41*). $H_2PO_2^-$ is oxidized slowly by $Fe(CN)_3^{3-}$ with a rate law $k[H_2PO_2^-][Fe(CN)_6^{3-}][OH^-]$ (*220*); presumably HPO_2^- is an intermediate, but it is difficult to guess its reduction potential. The species has also been implicated as an intermediate in the oxidation of $H_2PO_2^-$ by a complex of Cr(V) (*138*).

HPO_3^- and PO_3^{2-} are relatively well understood. The pK_a of HPO_3^- was determined by Behar and Fessenden (*41*), and its value was refined to 5.75 by Schafer and Asmus (*262*). By working in strongly acidic media Davis *et al.* used ESR measurements to assign pK_a values of -1.7 and 0.0 to $H_3PO_3^+$ and H_2PO_3, respectively (*93*). Schafer and Asmus (*263*) obtained a value of 800 for the equilibrium constant of the reaction

$$PO_3^{2-} + CH_3CH_2SH \rightleftharpoons CH_3CH_2S + HPO_3^{2-} \tag{57}$$

From theoretical considerations and gas-phase data, Surdhar and Armstrong have obtained $E^0 = 1.44$ V for the CH_3CH_2S/CH_3CH_2SH couple (*304*). Thus Schafer and Asmus' result is important in that it allows us to calculate the potential of the PO_3^{2-}/HPO_3^{2-} couple as 1.61 V. A value for $\Delta_f G^0$ of -810 kJ/mol for HPO_3^{2-} is cited in *Standard Potentials* (apparently Latimer's estimate), which leads to a value of $\Delta_f G^0 = -655$ kJ/mol for PO_3^{2-}. From the pK_a of HPO_3^- we calculate $\Delta_f G^0 = -688$ kJ/mol for HPO_3^- and $E^0 = 1.26$ V for the HPO_3^-/HPO_3^{2-} couple. HPO_3^{2-} is protonated on P, but according to Gilbert *et al.* HPO_3^- is protonated on O (*139*), so the potential of 1.26 V does not correspond to a simple electron transfer.

The phosphate radical, PO_4^{2-}, which can be generated by photolysis or reduction of $P_2O_8^{4-}$, has been shown to engage in acid/base equilibria: thus $pK_a = 5.7$ for H_2PO_4 and $pK_a = 8.9$ for HPO_4^- (*209*). No estimate seems to have been reported for the E^0 of these radicals, but in view of the similar reactivity of H_2PO_4 and SO_4^-, H_2PO_4 clearly is a strongly oxidizing species, with a potential near 2.4 ± 0.2 V.

PO_5^{2-} can be generated by reaction of PO_3^{2-} with O_2 (*262*) or by oxidation of HPO_5^{2-} with OH (*208*). Schafer and Asmus determined a pK_a of 3.4 for HPO_5^- (*262*). Maruthamuthu and Neta reported that PO_5^{2-} oxidized OH^- with a rate constant of $6.2 \times 10^5\ M^{-1}\ \mathrm{sec}^{-1}$ (*208*). This observation is of interest in that it suggests that the reaction

$$PO_5^{2-} + OH^- \rightleftharpoons PO_5^{3-} + OH \tag{58}$$

is reversible. If so, then the potential of the PO_5^{2-}/PO_5^{3-} couple is near 1.9 V.

C. ARSENIC

Some confusion in the literature on arsenite is due to uncertainty as to the identity of the species in solution. It is now recognized that the predominant species is $H_2AsO_3^-$ rather than AsO_2^- (*180*). The redox chemistry of As(III) is summarized by Kirschenbaum and Rush in their study of its reaction with Ag(III) (*180*). By reaction of OH with As(III), Adams *et al.* obtained a UV/visible spectrum of As(IV) (*4a*), and ESR spectra of the spin adducts with various spin traps have been reported (*257*). The composition of As(IV) has not yet been established. Oxidation of As(III) by $Mo(CN)_8^{3-}$ proceeds near pH 9 with rate $= k[Mo(CN)_8^{3-}][As(OH)_3][OH^-]$ with $k = 1.5 \times 10^5\ M^{-2}\ sec^{-1}$; the reaction was also found to be catalyzed by alkali metal ions (*199*). If it is assumed that the reaction occurs via $H_2AsO_3^-$ (pK_a for $As(OH)_3 = 9.2$), then the second-order rate constant for this species is 3 $M^{-1}\ sec^{-1}$. If it is further assumed that the reaction generates H_2AsO_3 and that the reverse reaction cannot exceed diffusion control, then $E^0 < 1.31$ V for the $H_2AsO_3/H_2AsO_3^-$ couple. Unfortunately, nothing is known of the pK_a values for As(IV).

As(VI) tentatively has been reported in a spin-trapping study of the reaction of SO_4^- with As(V) (*257*).

D. ANTIMONY

That various forms of Sb(IV) must be considered can be inferred from the observation that Ce(IV) oxidizes Sb(III) directly and in Cl^--catalyzed paths (*219*), that the oxidation by $Fe(CN)_6^{3-}$ is second order in [Sb(III)] (*176*), and that reduction of $SbCl_6^-$ by Fe^{2+} and $Fe(CN)_6^{4-}$ occurs with Fe(III) inhibition (*25*). The thermochemistry of these free radicals is unknown.

E. BISMUTH

Very little is known of the redox chemistry of bismuth. Ford-Smith and Habeeb found that Bi(V) oxidized a variety of substrates, including $IrCl_6^{3-}$, with a rate law that is independent of the identity or concentration of the substrate (*125*). It is not clear that the reactions involve Bi(IV).

In a pulse radiolysis study of hydrochloric acid solutions of Bi(III), the species Bi(II) and Bi(IV) were observed (*116*). The exact compositions of these species were not determined, nor were their redox properties.

VIII. Group IV

A. CARBON

The selection of molecules and of depth of coverage appropriate in a discussion of the "inorganic" chemistry of carbon is a debatable issue. The present review takes the middle ground, with C—H and C—C bonds usually being inadmissible.

Reduction of CO by the hydrated electron might be expected to yield CO^- or HCO. However, by the use of pulse radiolysis Raef and Swallow demonstrated that the first detectable species is $HC(OH)_2$ (*250*). Presumably CO^- undergoes very rapid hydrolysis. It is difficult to estimate accurately the energetics of the CO/CO^- couple, but the CO/HCO couple is more easily discussed. The JANAF tables indicate a value of $\Delta_f G^0 = 28.3 \pm 8$ kJ/mol for HCO in the gas phase. By neglecting the hydration free energy a value of -1.54 V is calculated for E^0 for the CO/HCO couple. The chemistry of $HC(OH)_2$ is beyond the scope of this review.

The reduction potential of the CO_2/CO_2^- couple was dealt with in a recent review by Koppenol and Rush (*190*), where original sources were cited. It was concluded that the most probable value is $E^0 = -1.8$ V; corresponding to this was $\Delta_f G^0 = -208 \pm 21$ kJ/mol for CO_2^-. Since HCO_2 has a pK_a of 1.4 it is found that $\Delta_f G^0$ for HCO_2 is -216 kJ/mol. Note that a different value appears in Koppenol and Rush's review because of the reference state of pH 7. The potential of the HCO_2/HCO_2^- couple is calculated as 1.36 V, but the mechanistic significance of this result is unclear because the site of protonation in HCO_2 is not known.

The carbonate radical is generated by the reaction of OH or SO_4^- with CO_3^{2-}. In an early study Chen *et al.* generated the radical by flash photolysis of $[Co(NH_3)_4CO_3]^+$ (*84*). Over the pH range 7–13 the ensuing reaction of the radical with indole-3-propionic acid varied by about a factor of two in rate, and from these data a pK_a of 9.6 ± 0.3 for HCO_3 was derived. In a recent study Eriksen and co-workers examined the pH dependence of the UV/visible spectrum of the radical, and from this study they revised the value of the pK_a, concluding that it lies between 7.0 and 8.2 (*114*). An early estimate of $E^0 = 1.85$ V for the CO_3^-/CO_3^{2-} couple was presented without a clear basis (*265*). Henglein estimated the potential of the CO_3^-/CO_3^{2-} couple as 1.5 V on the basis that Br_2^- does not completely oxidize CO_3^{2-} while CO_3^- does oxidize I^- (*160*). The data for these reactions have not yet been published. In a flash photolysis study of the quenching of 2-nitrothiophen by various anions, Martins estimated $E^0 = 2.15$ V, apparently on the basis of Marcus theory (*206*). In his review Eberson calculated $E^0 = 2.14$ V on thermochemical grounds by estimating the bond energy of the O—H bond in HCO_3^- (*106*). With a potential this high, Br_2^- certainly would not oxidize CO_3^{2-} very quickly. A recent study showed that the reaction

$$SeO_3^- + CO_3^{2-} \rightleftharpoons SeO_3^{2-} + CO_3^- \qquad (59)$$

proceeds with a rate constant of $6.2 \times 10^6\ M^{-1}\ sec^{-1}$ (*181*). If it is assumed that the reaction as written may be uphill and that it is driven by other reactions of CO_3^-, then an upper limit to the reverse rate constant of 10^{10} M^{-1} sec^{-1} is imposed by diffusion control. With the known E^0 for the SeO_3^-/SeO_3^{2-} couple these calculations establish an upper limit of 1.87 V for the CO_3^-/CO_3^{2-} couple. Most likely the reverse rate constant is substantially less than 10^{10} M^{-1} sec^{-1}, which would place the potential in the range of Henglein's estimate. It is evident that the thermochemistry of the carbonate radical is not yet on very firm ground. An E^0 of 1.5 V for the CO_3^-/CO_3^{2-} couple is tentatively recommended, as is a pK_a of 7.6 for HCO_3. These results lead to $\Delta_f G^0 =$ -383 kJ/mol for CO_3^- and -426 kJ/mol for HCO_3.

There is an intriguing report that CO_3^- can be oxidized to CO_3 by triplet-state duroquinone in micellar solutions (*264*). From Benson's data we calculate $\Delta_f G^0 = -171 \pm 16$ kJ/mol for CO_3 in the gas phase (*43*). By applying a correction of 10 kJ/mol for hydration of CO_3 we obtain $E^0 = 2.3 \pm 0.2$ V for the CO_3/CO_3^- couple, which shows that CO_3 is indeed a viable intermediate in the triplet duroquinone system.

One-electron reduction of perhalomethanes generally leads to formation of the corresponding trihalomethyl radical and halide. CF_4 appears to be unreactive, even with e_{aq}^-, but CF_3Cl, CF_3Br, and CF_3I are reduced to CF_3 (*27, 62, 204*). The redox potentials associated with these couples do not appear to have been reported, but rough estimates of them can easily be made. In the estimations, NBS free energies are used for all species in the gas phase except, of course, the halide ions. The rough approximation is adopted that the hydration free energies will be the same for the perhalomethanes as for CF_3. These calculations lead to $E^0 = -1.45$, -0.67, -0.58, and -0.65 V for the CF_4/(CF_3, F^-), CF_3Cl/(CF_3, Cl^-), CF_3Br/(CF_3, Br^-), and CF_3I/(CF_3, I^-) couples, respectively. The calculated potential for CF_4 indicates that e_{aq}^- should be capable of reducing CF_4. However, the kinetic barrier imposed by bond cleavage may be enough to make the reaction undetectably slow. It is clear that the other trifluoromethanes should be much more easily reduced. By way of comparison, the facile reductive cleavage of SF_6 by e_{aq}^- is clearly attributable to the enormous driving force for the reaction.

CCl_3 is generated by reduction of CCl_4 (*191, 202*). The NBS tables do not supply a value of $\Delta_f G^0$ for CCl_3, but the JANAF tables cite 92 ± 8 kJ/mol for this species. With the same approximations as above for the CF_3 systems, we calculate $E^0 = -0.23$ V for the CCl_4/(CCl_3, Cl^-) couple. Despite the apparent ease of reduction of CCl_4, Koster and Asmus reported that it was not reduced by CO_2^- (*191*).

The chemistry of CBr_3 has not been explored as extensively as that of its lighter congeners, but it is claimed to be formed in the reaction of e_{aq}^- with CBr_4 (*169*). There has been substantial disagreement regarding $\Delta_f H^0$ for CBr_4 in the gas phase; the most recent value is 83.9 ±

3.4 kJ/mol (*50*). A value of 56.2 ± 1.8 kcal/mol has been reported for the CBr_3–Br bond dissociation enthalpy (*179*). By using the NBS value of 358 J/K/mol for the entropy of CBr_4, estimating an entropy of 324 J/K/mol for CBr_3 by analogy with BBr_3, and assuming equal hydration free energies for CBr_4 and CBr_3, we derive a value of $E^0 = -0.07$ V for the $CBr_4/(CBr_3, Br^-)$ couple.

The mixed halomethyl radicals CF_2Cl and $CFCl_2$ were reported to be generated in the reductions of CF_2Cl_2 and $CFCl_3$ (*27*). The Δ_fG^0 values for CF_2Cl_2 differ significantly as given in the NBS and the JANAF tables. We adopt the JANAF value of −452 kJ/mol because its origin is discussed. A value of $\Delta_fH^0 = -665$ kcal/mol for CF_2Cl has been estimated (*192*). By estimating the entropy of CF_2Cl as 272 J/K/mol in analogy with BF_2Cl, and assuming equal hydration free energies for CF_2Cl_2 and CF_2Cl, we find $E^0 = -0.59$ V for the $CF_2Cl_2/(CF_2Cl, Cl^-)$ couple. A similar calculation makes use of $\Delta_fH^0 = -21.3$ kcal/mol for $CFCl_2$ (*320*), $S^0 = 272$ J/K/mol (by analogy with $BFCl_2$), and $\Delta_fG^0 = -249$ kJ/mol for $CFCl_3$ (from the JANAF tables). The result is $E^0 = -0.44$ V for the $CFCl_3/(CFCl_2, Cl^-)$ couple.

A series of peroxyl radicals can be generated by reaction of O_2 with various trihalomethyl radicals (*169*). The most widely known of these is CCl_3O_2, but CF_3O_2 and CBr_3O_2 have also been reported. They are generally regarded as good one-electron oxidants, being reduced to the corresponding peroxide, but no redox potentials have yet been assigned.

In a pulse radiolysis study of CS_2 Roebke and co-workers identified several derivative species (*258*). SC(OH)S, its conjugate base, and the pK_a (4.4) that relates them were determined from the reaction of CS_2 with OH. SCSH and its pK_a (1.6) were determined by the reactions of e^-_{aq} and H with CS_2. The redox characteristics of these species remain unexplored. A subsequent pulse radiolysis study has not contributed any additional thermochemical information (*56a*).

The existence of the cyanogen free radical (CN) in aqueous solution has not been extensively demonstrated. Oxidation of CN^- by OH yields an adduct (*39*), and photolysis of $Mo(CN)_8{}^{3-}$, which was proposed to yield CN (*295*), has now been shown not to do so (*66*). The sole report that seems to stand is an ESR study in which CN, generated by reaction of $SO_4{}^-$ with CN^-, was detected as a spin adduct of $CH_2{=}NO_2{}^-$ (*82*).

An estimate of $E^0 = 1.9 \pm 0.3$ V for the CN/CN^- couple was obtained by Berdnikov and Bazhin by using a thermochemical cycle (*45*). Endicott obtained a value of ≈2.8 V for the CN/HCN couple, presumably by a similar method (*110*). When this is corrected by the pK_a of HCN a value of 2.26 V for the CN/CN^- couple obtains. By interpolating a nonlinear free-energy relationship for the quenching of triplet *N*-(*n*-butyl)-5-nitro-2-furamide, Martins and Kemp (*207*) estimated $E^0 = 2.15$ V for the

CN/CN^- couple. Pearson obtained a value of 2.52 V by using his unusual thermochemical cycle (*240*). Substantial uncertainty in the thermochemical cycle methods lies in the data regarding CN in the gas phase. As discussed in the JANAF tables, and more recently in Ref. (*48*), the best estimate of $\Delta_f H^0$ for CN in the gas phase is 435 ± 10 kJ/mol, which differs significantly from the value of 368 kJ/mol used by Berdnikov and Bazhin. Correction of their result by this amount yields $E^0 = 2.59$ V for the CN/CN^- couple, which we believe to be the best current estimate. The corresponding value is $\Delta_f G^0 = 422$ kJ/mol for CN. In view of the very high potential of CN it is not surprising that it is so poorly characterized.

A species identified as $(CN)_2^-$ was reported in study of the reaction of e_{aq}^- with $(CN)_2$ (*105*). Its reactivity is essentially unknown. Various species have been suggested in the reaction of OH with CN^- and HCN and of O^- with CN^-, but their chemistry is beyond the scope of this review.

The cyanate radical, OCN, has not been detected in aqueous solution. However, on the basis of the rate constant of quenching of triplet *N*-(*n*-butyl)-5-nitro-2-furamide by OCN^-, Martins and Kemp estimated $E^0 = 2.15$ V for the OCN/OCN^- couple (*207*). Although this method gave an unreasonably high value for the SO_3^-/SO_3^{2-} couple, the high potential reported for the OCN/OCN^- couple is consistent with the very high energy of the ctts absorption of OCN^-. An alternative approach is to use the JANAF value of $\Delta_f G^0 = 151 \pm 10$ kJ/mol for OCN in the gas phase and to assume a hydration free energy of 8 kJ/mol (that of CO_2). This leads to $\Delta_f G^0 = 159$ kJ/mol for aqueous OCN and $E^0 = 2.66 \pm 0.10$ V for the OCN/OCN^- couple. As discussed in a recent paper by Alfassi *et al.* the hydroxyl radical adds to OCN^-, from which a variety of radicals are derived (*8*); however, the properties of these species lie beyond the scope of this review.

Tetranitromethane is frequently used in inorganic systems, for example, as a scavenger of superoxide. Upon one-electron reduction the immediate products are $C(NO_2)_3^-$ and NO_2 (*248*). An estimate of E^0 for this couple can be made by using published values of $\Delta_f H^0$ for $C(NO_2)_4$ and $HC(NO_2)_3$ in the gas phase: 82.0 and −0.2 kJ/mol, respectively (*241*). The calculation also uses $\Delta_f G^0$ from this review for aqueous NO_2, entropies from the NBS tables, and $pK_a = 0.06$ for $HC(NO_2)_3$ (*284*). It is assumed that $HC(NO_2)_3$ and $C(NO_2)_4$ have identical heats of hydration and identical partial molar entropies. The outcome is $E^0 = 0.93$ V for the $C(NO_2)_4/(C(NO_2)_3^-, NO_2)$ couple. Berdnikov *et al.* performed a similar calculation and obtained $E^0 = 0.9$ V (*47*). These workers used different sources of data and made more refined estimates of the entropies and hydration energies; the agreement is gratifying.

Despite the good oxidizing power of $C(NO_2)_4$ it reacts with $Fe(CN)_6^{4-}$ with a rate constant of only $3 \times 10^2\ M^{-1}\ sec^{-1}$ (*222*), presumably because of the constraints imposed by bond cleavage.

One-electron oxidation of SCN^-, by coordination complexes, for example, can lead directly to SCN, although oxidation by OH gives $SCNOH^-$ first. Several equilibrium constants involving this radical have been determined, so that it is an important species in the thermochemistry of inorganic free radicals. The various reports of E^0 for the SCN/SCN^- couple are given in Table V.

The first estimate of E^0 for the SCN/SCN^- couple was performed by Shizuka and co-workers (*289*); their result was based on an equation (of unclear provenance) that relates the energy of the ctts band of the anion and its E^0. Such an approach cannot be expected to yield exact results. The remaining estimates were determined in two ways. One involved measuring the rate of oxidation of SCN^- by an outer-sphere oxidant such as $[Fe(bpy)_3]^{3+}$ and then assuming a rate constant for back-electron transfer that was diffusion controlled. The other method was to use an established E^0 for the I/I^- couple and then to derive the SCN/SCN^- potential by using the equilibrium constants reported by Schoneshofer (*272*) for the following reactions:

$$SCN + I^- \rightleftharpoons ISCN^- \tag{60}$$

$$ISCN^- \rightleftharpoons SCN^- + I \tag{61}$$

Fluctuations in the results by this latter method are presumably due to variable assumed potentials for the I/I^- couple. In any event, the agreement between the two methods may be taken in support of the various assumptions involved. For the purposes of this review a value of $E^0 = 1.63$ V for the SCN/SCN^- couple is adopted, with a corresponding value of $\Delta_f G^0 = 250$ kJ/mol for aqueous SCN.

TABLE V

E^0 VALUES FOR THE SCN/SCN^- REDOX COUPLE

E^0 (V)	Year	Reference	Author	Technique
1.50	1978	*289*	Shizuka *et al.*	Calculated from ctts[a] energy
1.62	1978	*232*	Nord *et al.*	Kinetics, $SCN^- + [Fe(bpy)_3]^{3+}$
1.68	1978	*232*	Nord *et al.*	Kinetics, $SCN^- + [Fe(bpy)_3]^{3+}$
1.66	1980	*294*	Stanbury *et al.*	Kinetics, relative to I
1.60	1982	*206*	Martins	Kinetics, relative to I
1.62	1986	*277*	Schwarz and Bielski	Relative to I

[a] ctts, Charge-transfer-to-solvent band.

Association of SCN with SCN^- to form $(SCN)_2^-$ yields a species having a S–S bond (*327*). Baxendale *et al.* (*36*) first reported a value for the association constant of $2 \times 10^5\ M^{-1}$. This result was confirmed by Behar and co-workers (*39a*). In a recent study Elliot and Sopchyshyn obtained a value of $1.1 \times 10^5\ M^{-1}$, as well as a value for the enthalpy of the reaction (*109*). The discrepancy of a factor of two is unexplained but is not a severe problem compared to the discrepancies reported for the analogous halide systems. A value of $K_{eq} = 1.6 \times 10^5\ M^{-1}$ is adopted in this review, which establishes $\Delta_f G^0 = 313$ kJ/mol for $(SCN)_2^-$.

The above free energy for $(SCN)_2^-$ leads to $E^0 = 1.32$ V for the $(SCN)_2^-/2SCN^-$ couple. Similar values were reported in the papers cited above regarding E^0 for SCN; furthermore, a value of 1.33 V was determined by Nord *et al.* (*232*) by measuring the forward and reverse rate constants for the third-order oxidation of SCN^- by $[Os(bpy)_3]^{3+}$. An anomalous value of 1.25 V was calculated by Butler *et al.* on the basis of an old potential for I/I^- (*64*).

Thiocyanogen is troublesome because of its instability. A potential of 0.54 V for the $(SCN)_2/(SCN)_2^-$ couple was calculated by Nord *et al.* (*232*) by applying Marcus theory to the oxidation of $(SCN)_2^-$ by $[Os(bpy)_3]^{3+}$. In a subsequent publication [Ref. *20* in the paper of Nord *et al.* (*233*)] this result was withdrawn, and a new value was cited: $E^0_{(SCN)_2/(SCN)_2^-} \approx E^0_{I_2/I_2^-}$. Thus $E^0 = 0.21$ V for the $(SCN)_2/(SCN)_2^-$ couple.

The species $SCNOH^-$ is formed in the association of SCN with OH^- (*39a*). The association constant is $31\ M^{-1}$, which yields $\Delta_f G^0 = 84$ kJ/mol for $SCNOH^-$.

Another species, $SCNS_2O_3^{2-}$, was detected by Schoneshofer (*269*), and the equilibrium constant for its dissociation to SCN and $S_2O_3^{2-}$ was measured as $3.1 \times 10^{-8}\ M$. By use of our selected $\Delta_f G^0$ for SCN a value of -315 kJ/mol is calculated for $\Delta_f G^0$ of $SCNS_2O_3^{2-}$. Furthermore, $E^0 = 1.19$ V is calculated for the $SCNS_2O_3^{2-}/(SCN^-, S_2O_3^{2-})$ couple.

Selenocyanate has been investigated by pulse radiolysis (*21*). These studies showed that OH reacts with $SeCN^-$ to yield a transient which was identified as $(SeCN)_2^-$. A potential of 0.9–1.0 V was estimated for the $(SeCN)_2^-/(2SeCN^-)$ couple by use of an empirical relationship between the one-electron and two-electron reduction potentials for I^-, Br^-, Cl^-, and SCN^-; in applying the method, 0.42 V was adopted for the $(SeCN)_2/(2SeCN^-)$, a value which was published in the work of another group (*56*). However, this latter paper does not indicate the source of the potential, so the reported potential of the $(SeCN)_2^-/(2SeCN^-)$ couple is not well supported. An estimate of the potential of the $SeCN/SeCN^-$ couple of 1.27 V was reported by Abdullah and Kemp (*1*). This result was based on Shizuka's equation that relates ctts energies and E^0 values, and in view of the inaccurate result this method yields for SCN^-, the present result for $SeCN^-$ should be regarded only as approximate.

Free radicals derived from thiourea have been proposed as intermediates in several oxidations of thiourea. However, the reactions have not yielded much information regarding the identity or thermochemistry of the species implicated. For example, oxidation by $IrCl_6{}^{2-}$ occurs with a second-order dependence on [thiourea], a complex pH dependence, and hints of copper catalysis (*244*). Oxidation by Cu(me_2-phen)$^{2+}$ is suggested to be an inner-sphere mechanism (*92*). At this time it is difficult even to guess at the redox potential of the thiourea radical.

B. SILICON

The free-radical chemistry of silicon is extremely limited. The only report appears to be a study of $SiO_3{}^-$ generated by a reaction of $SO_4{}^-$ (*193*). It was proposed that the species acted as an oxidant toward various organic species by undergoing H-atom transfer rather than electron transfer.

C. GERMANIUM

There do not appear to be any reports concerning free radicals of germanium in aqueous solution.

D. TIN

The existence of Sn(I) may be inferred from reports of the reactions of H and e_{aq}^- with $SnO_2{}^{2-}$, $SnF_3{}^-$, and certain complexes of Sn(II) (*14a, 14b*). However, rather little is known of these species. The chemistry of Sn(III) is better documented. As summarized by Cannon, this oxidation state is frequently found for intermediates in reactions of Sn(II) with one-electron oxidants (*77*). Asmus *et al.* generated Sn(III) in a pulse radiolysis study by reaction of OH with Sn(II) in an unspecified medium (*18*). By conductivity measurements over the range pH 3–2.5 they obtained data which were interpreted as hydrolysis according to

$$Sn(OH)_3 + H^+ \rightleftharpoons Sn(OH)_2{}^+ + H_2O \tag{62}$$

with $pK \approx 2.9 \pm 0.3$. Shinohara *et al.* recently reported that UV photolysis of Sn(IV) in chloride media generated Sn(III) by elimination of Cl, and under similar conditions Sn(II) photoreduced H^+ to generate Sn(III) (*287*). They found that the Sn(III) so generated reduced O_2 to

HO_2, which indicates the substantial reducing power of Sn(III). In an early report a value of 0.7 V was cited for the Sn(III)/Sn(II) couple, but no reference of basis for the value was provided (*46*).

E. LEAD

Baxendale and Dixon estimated $E^0 = -(1.1\text{–}1.5)$ V for the Pb^{2+}/Pb^+ couple by estimating the hydration free energy of Pb^+ (*37*). Breitenkamp *et al.* estimate $E^0 = -1.0$ V on the basis that reduction of Pb^{2+} by CH_2OH is fairly slow (*57*). From this they deduced a potential of ≈ -0.9 V for reduction of Pb^+ to atomic Pb. These latter potentials imply that the disproportionation of Pb^+ is not strongly driven. Nevertheless, Breitenkamp *et al.* reported a rate constant of $1.7 \times 10^8\ M^{-1}\ \mathrm{sec}^{-1}$ for the second-order decay of Pb^+. The potential of -1.0 V for the Pb^{2+}/Pb^+ couple leads to $\Delta_f G^0 = 72$ kJ/mol for Pb^+.

In alkaline media Pb(II) is reduced to a hydrolyzed Pb(I) species, and in nonalkaline media at high Pb^{2+} concentrations, Pb^+ reacts to form $Pb_2{}^{3+}$ (*300*). By investigating the pulse radiolysis of Pb(II) in concentrated chloride solutions Sukhov and Ershov were able to identify PbCl and to set an upper limit to the association constant of 0.5 M^{-1} (*302*).

Lead (III) has been generated by oxidation of Pb(II) with OH (*300*). On the basis that Pb^{2+} is oxidized by OH but not by HO_2 it was suggested that the Pb^{3+}/Pb^{2+} potential lies between 1.5 and 2.6 V. Ershov also used an empirical trend in potential across the periodic table to estimate $E^0 = 1.8 \pm 0.3$ V for the Pb^{4+}/Pb^{3+} couple, and from the known Pb^{4+}/Pb^{2+} potential he derived $E^0 = 1.6 \pm 0.3$ V for the Pb^{3+}/Pb^{2+} couple (*115*). Sukhov and Ershov (*302*) cite their prior paper (*300*) as the source of the value for $pK_a \approx 4$ for Pb^{3+}; however, the cited paper does not report the pK_a.

From experiments in chloride-containing media Sukhov and Ershov (*302*) found evidence for $PbCl^{2+}$, which is formed with an association constant of $4 \times 10^2\ M^{-1}$. Gogolev and co-workers also investigated Pb(III) in hydrochloric acid solutions (*141, 143*). They found evidence for at least two chloro complexes, and noted that the Pb(IV)/Pb(III) couple is strong enough to oxidize Cl_2^-; i.e., $E^0 > 0.7$ V.

IX. Group III

A. BORON

Borohydride is rapidly oxidized by N_3, Br_2^-, and $(SCN)_2^-$ (*166*). A UV/visible spectrum of the intermediate was obtained and attributed to BH_4. It is not obvious to this writer that the species observed could not be BH_3^-. The weaker oxidant, $Fe(CN)_6^{3-}$, does not oxidize BH_4^-, but rather its hydrolysis product, BH_3OH^- (*178*). Presumably, free radicals are generated in this reaction, but their identities are not established, not to mention their thermochemistry.

B. Aluminum

The free-radical chemistry of aluminum has been discussed in Buxton and Sellers' review (*69*). The only species mentioned is Al^{2+}, and its only reported reaction is the dehalogenation of chloroethanol and bromoacetate.

C. Gallium

Standard Potentials gives an approximate values of -0.67 and -0.45 V for the Ga^{3+}/Ga^{2+} and Ga^{2+}/Ga couples, respectively. These results were obtained from a prior review (*245a*), which, in turn, cites a paper that does not bear on the issue. The correct source of these results is Latimer's *Oxidation Potentials* (*195*). Latimer estimated these potentials on the basis of the chemical behavior of "$GaCl_2$" in aqueous solution. It is now known that the compound under investigation was $Ga^I[GA^{III}Cl_4]$, so little faith can be placed on the above potentials. The bona fide chemistry of aqueous Ga(II) is discussed in Buxton and Sellers' review (*69*) and in recent papers by Sukhov and co-workers (*299, 303*). The latter authors reported that Ga(II) is generated by reduction of Ga(III) with e^-_{aq}, and that Ga^{2+} is hydrolyzed with $pK_a > 3.3$. They also identified $Ga(OH)_6^{4-}$ in alkaline media. On the basis of the reactivity of Ga^{2+} with organic radicals they suggested that Ga(II) is a reasonably good oxidant.

D. Indium

In^+ is a species of limited stability, but, as discussed in *Standard Potentials*, there is a fairly reliable value of -0.126 V for the In^+/In couple, where In is in the bulk state. The assumption of a hydration free energy of 13 kJ/mol for atomic indium leads to $\Delta_f G^0 = 222$ kJ/mol for aqueous In and $E^0 = -2.43$ V for the In^+/In couple. To our knowledge homogeneous reduction of In^+ has not yet been reported.

Latimer's discussion of In^{2+} (*195*), like that of Ga^{2+}, is unreliable because it was based on the incorrect belief that $InCl_2$ is a compound of In(II). In their study of the chemistry of aqueous In^+, Taylor and Sykes found that In^+ does not reduce Cr^{3+}, and thus they estimated $E^0 > -0.41$ V for the In^{2+}/In^+ couple (*311*). On the other hand, they found that In^+ reacts with O_2 with a rate constant of 1.7×10^3 M^{-1} sec^{-1} and with $FeOH^{2+}$ with $k = 1.1 \times 10^3$ M^{-1} sec^{-1} (*312*). These observations suggest that E^0 is probably less than 0.4 V for the In^{2+}/In^+ couple, and thus $\Delta_f G^0$ for In^{2+} is bracketed between -50 and $+26$ kJ/mol. Likewise, E^0 for the In^{3+}/In^{2+} couple must lie between -0.50 and -1.30 V. Sukhov and Ershov reported that In^{3+} reacted indetectably slowly with CO_2^- and H (*301*), which suggests that the potential of the In^{3+}/In^{2+} couple may be closer to the value of -1.30 V. In the first of two pulse radiolysis studies of In^{3+} it was reported that In^{2+} has a $pK_a > 5.0$ (*301*); in the second study it was reported that $pK_a = 4.5 \pm 0.2$, the conclusion being based on the pH dependence of the UV/visible spectrum (*280*). The disagreement may be attributable to the fact that the first group did not correct for scattered light.

E. THALLIUM

As discussed in *Standard Potentials*, the Tl^+/Tl potential is -0.3363 V, in which Tl refers to the bulk metal. If the hydration free energy of atomic thallium is taken as that of xenon, we calculate $\Delta_f G^0 =$ 161 kJ/mol for aqueous Tl, and $E^0 = -2.00$ V for the Tl^+/Tl couple. Thus it is quite reasonable that Tl^+ is reported to be reduced by e_{aq}^- and H. Butler and Henglein estimated a potential of -1.9 V by similar methods, but they neglected the hydration energy of atomic thallium (*63*).

Cercek and co-workers reported that atomic thallium combines with Tl^+ to form Tl_2^+ with an association constant of 2.3×10^3 M^{-1} (*79*). Schwarz and Dodson (*279*) recently cited unpublished data that suggest a value of 160 M^{-1}. By using the result of Cercek *et al.* we calculate $\Delta_f G^0 = 109$ kJ/mol for Tl_2^+, and $E^0 = -1.80$ V for the $2\,Tl^+/Tl_2^+$ couple. Likewise, Butler and Henglein calculated $E^0 = -1.7$ V (*63*). Froben *et al.* found that in the gas phase diatomic thallium is weakly bound with bond enthalpy of 41 kJ/mol at 0 K (*130*). These workers measured the Raman spectrum of Tl_2 in an Ar matrix and used the result to correct a prior determination of the bond enthalpy. The application of conventional statistical mechanical methods to their data yields $\Delta_f G^0 = 251$ kJ/mol for Tl_2 in the gas phase, and the assumption of a free energy of hydration of -3 kJ/mol (that of I_2) leads to $\Delta_f G^0 =$ 248 kJ/mol for aqueous Tl_2. Thus $E^0 = -1.44$ V for the Tl_2^+/Tl_2 couple. The value of $E^0 = -1.5$ V reported by Butler and Henglein (*63*) rests upon an older value for the dissociation energy of Tl_2.

Experimental determinations of the redox potentials involving Tl^{2+} were reported in two concurrent independent publications in 1974. In one of them, by Falcinella *et al.*, Tl^{2+} was generated by flash photolysis of Tl(III) (*118*). These workers measured the rate of reduction of Tl^{2+} by Co^{2+}. By combining this rate with the known rate for the reverse reaction to obtain the electron transfer equilibrium constant and then using the reduction potential for Co^{3+}, they obtained $E^0 = 2.22 \pm 0.05$ V for the Tl^{2+}/Tl^+ couple. They also measured the rate of oxidation of Tl^{2+} by Fe^{3+} and by similar a argument derived $E^0 = 0.33 \pm 0.05$ V for the Tl^{3+}/Tl^{2+} couple. From these two potentials they derived the potential of the Tl^{3+}/Tl^+ couple as 1.28 V, which is in excellent agreement with the known potential of this system (1.25 V). In the other paper on the subject, Schwarz *et al.* used pulse radiolysis to generate Tl^{2+} (*278*). They measured the rate of reduction of Tl^{2+} by Fe^{2+}. They also repeated prior studies of the oxidation of Fe^{2+} by Tl^{3+} under conditions appropriate to the pulse radiolysis work (1 *M* $HClO_4$). This reaction has the mechanism

$$Fe^{2+} + Tl^{3+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Fe^{3+} + Tl^{2+} \qquad (63)$$

$$Fe^{2+} + Tl^{2+} \xrightarrow{k_2} Fe^{3+} + Tl^+ \qquad (64)$$

and from the kinetics, values of k_1 and k_{-1}/k_2 are obtained. Thus the pulse radiolysis study gives k_2, from which k_{-1} is obtained. The ratio of k_1 and k_{-1} gives the equilibrium constant, which yields $E^0 = 0.30$ V for the Tl^{3+}/Tl^{2+} couple. Combination of this result with the standard potential for the Tl^{3+}/Tl^+ couple then gives $E^0 = 2.22$ V. The results are in excellent agreement with those determined in the flash photolysis study.

In a subsequent study Dodson reported results on the Fe^{2+}-induced exchange between Tl^{3+} and Tl^+ (*98*). He measured $k_2/(k_1 k_{III})$ and k_1/k_{III}, where k_{III} is the rate constant of electron exchange between Tl^{3+} and Tl^{2+}. He then used independently determined values of k_1 and k_{III} to determine k_2, and from the independently determined ratio k_{-1}/k_2 he obtained k_{-1}. Finally, by using the ratio of k_1/k_{-1} he obtained $E^0 = 0.32$ V for the Tl^{3+}/Tl^{2+} couple, and with the Tl^{3+}/Tl^+ potential he obtained $E^0 = 2.20$ V for the Tl^{2+}/Tl^+ couple. Excellent agreement with the prior reports is to be noted.

At about the time of the above reports, research in other laboratories was yielding information on the hydrolysis of Tl^{2+}. In the first report a pK_a of 4.6 ± 0.2 was determined for Tl^{2+} (*238*). In the second report the first was confirmed, with $pK_a = 4.65$; in addition, the pK_a ($= 7.7 \pm 0.2$) of $TlOH^+$ was determined (*53*). In view of these developments Nord reanalyzed the above determinations of the redox potentials (*231*). The outcome was $E^0 = 0.30$ V for the Tl^{3+}/Tl^{2+} couple; i.e., not significantly different. Schwarz and Dodson (*279*) recently pointed out that Tl^{2+} is in equilibrium with OH + Tl^+; correcting for this effect leads to $pK_a = 4.72$ for Tl^{2+}.

In conclusion, the following values are recommended: $E^0 = 0.30$ V for the Tl^{3+}/Tl^{2+} couple, $E^0 = 2.22$ V for the Tl^{2+}/Tl^+ couple, $pK_a = 4.72$ for Tl^{2+}, and $pK_a = 7.7$ for $TlOH^+$. From these results the following values can be derived: $\Delta_f G^0 = 186$ kJ/mol for Tl^{2+}, -24.6 kJ/mol for $TlOH^+$, and -218 kJ/mol for $Tl(OH)_2$. These results, when combined with NBS data for hydrolyzed Tl(III), give $E^0 = 0.09$ V for the $TlOH^{2+}/TlOH^+$ couple and $E^0 = -0.28$ V for the $Tl(OH)_2^+/Tl(OH)_2$ couple. Thus Tl(II) becomes a better reducing agent with increasing pH. With NBS data for TlOH and the data selected by Baes and Mesmer (*22*) for $Tl(OH)_2^-$ we calculate $E^0 = 1.76$ V for the $TlOH^+/TlOH$ couple and $E^0 = 1.29$ V for the $Tl(OH)_2/Tl(OH)_2^-$ couple. Tl(II) becomes a weaker oxidizing agent with increasing pH. These trends are qualitatively consistent with reactivity studies of these species (*53*).

Association of Tl(II) with chloride has been studied by Dodson and Schwarz (*99*). They determined stability constants of 6.2×10^4, 1.9×10^3, and 13 M^{-1} for $TlCl^+$, $TlCl_2$, and $TlCl_3^-$, respectively. The corresponding free energies of formation are 27, -123, and -260 kJ/mol. NBS data for the Tl(III) chlorides permit calculation of $E^0 = 0.14$ V for the $TlCl^{2+}/TlCl^+$ couple, $E^0 = 0.00$ V for the $TlCl_2^+/TlCl_2$ couple, and $E^0 = -0.15$ V for the $TlCl_3/TlCl_3^-$ couple. Finally, by using NBS data for the Tl(I) chlorides we calculate $E^0 = 2.01$ V for the $TlCl^+/TlCl$ couple and $E^0 = 1.79$ V for the $TlCl_2/TlCl_2^-$ couple.

X. Group II

A. ZINC, CADMIUM, AND MERCURY

Zn^+ is a recognized species in aqueous solution (*69*). The only known method to generate it is by reduction of Zn^{2+} with e^-_{aq}. The first estimate of the Zn^{2+}/Zn^+ potential was performed by Baxendale and Dixon (*37*) by use of thermochemical cycles. This involved an estimate of the hydration energy of Zn^+, which was in turn dependent on an estimate of its ionic radius. Because of the considerable uncertainties involved they cited a value of $-(2.5-3.2)$ V. The more negative value is based on the assumption that the radius of Zn^+ is the same as that of Zn^{2+}, which is quite unreasonable considering that the electron is being placed into a previously unoccupied *s* orbital. For the less negative value the radius was assumed to be the same as that of Cu^+, which is also probably too small for the same reason. Anbar estimated $E^0 = -1.0$ V by applying Marcus theory to the rate of reaction of e^-_{aq} with Zn^{2+} (*14*). In view of the general failure of e_{aq}^- to react according to this theory, this value is unreliable. Navon and Meyerstein estimated $E^0 = -2.0 \pm 0.4$ V by applying Marcus theory to the reaction of Zn^+ with $[Co(NH_3)_6]^{3+}$ (*225*). In this calculation it was assumed that the self-exchange rate constant of the Zn^{2+}/Zn^+ couple was somewhere between 10^0 and 10^9 M^{-1} sec^{-1}, which accounts for the large uncertainty on E^0. Since the time of that publication the self-exchange rate constant of the $[Co(NH_3)_6]^{3+/2+}$ has been revised from 3×10^{-12} to 8×10^{-6} M^{-1} sec^{-1} (40°C) (*154*), which would shift the potential to -1.6 ± 0.4 V. It is clear that the potential is not known with great certainty. Because e_{aq}^- does reduce Zn^+, the potential must be greater than -2.87 V, and because Zn^+ reduces $[Ru(bpy)_3]^{2+}$, E^0 must be less than -1.3 V (*214*). A provisional value of -1.6 V is recommended for the Zn^{2+}/Zn^+ couple, and, correspondingly, $\Delta_f G^0 = 7$ kJ/mol for Zn^+. If it is assumed that the neutral zinc atom has a hydration free energy of 10 kJ/mol, then $\Delta_f G^0$ is 105 kJ/mol for atomic zinc, and E^0 for the Zn^+/Zn couple is -1.01 V. Thus Zn^+ is expected to disproportionate, as it does ($k = 3.5 \times 10^8$ M^{-1} sec^{-1}) (*249*).

In alkaline media it is reported that the reaction of e_{aq}^- with Zn(II) is reversible and that the Zn(I) is hydrolyzed (*142*). Unfortunately, because of uncertainty regarding the degree of hydrolysis in both oxidation states, no thermochemical data could be derived. Ershov and Sukhov used periodicity arguments to estimate $pK_a = 7$–9 for Zn^+ (*117*).

Cd^+ is generally regarded as a weaker reducing agent than Zn^+. Baxendale and Dixon estimated the Cd^{2+}/Cd^+ potential as $-(1.1$–$1.5)$ V with arguments similar to those for the analogous zinc system (*37*). Anbar estimated E^0 as -0.5 V from Marcus theory applied to reactions of e_{aq}^- (*14*), and Navon and Meyerstein obtained $E^0 = -1.8 \pm 0.4$ V by applying Marcus theory to the reaction of Cd^+ with $[Co(NH_3)_6]^{3+}$ (*225*). Again, a correction of this last calculation, because of the revised Co self-exchange rate, gives $E^0 = -1.4 \pm 0.4$ V. This latter potential seems plausible in view of the reported slow reduction of Cd^{2+} by CO_2^- (*68*) and the rapid reduction of $[Ru(bpy)_3]^{2+}$ by Cd^+ (*214*). A tentatively recommended value of E^0 is -1.4 V for the Cd^{2+}/Cd^+ couple, and thus $\Delta_f G^0 = 58$ kJ/mol for Cd^+. The assumption of a hydration free energy of 10 kJ for the cadmium atom gives $\Delta_f G^0 = 87$ kJ/mol for aqueous Cd and hence $E^0 = -0.31$ V for the Cd^+/Cd couple. A value of 0.6 V was reported by Breitenkamp *et al.* for this later couple (*57*), but their calculation was based upon Navon's uncorrected potential for Cd^{2+}/Cd^+ and it also had an arithmetic error.

Our recommended values place Cd^+ as a weaker reducing agent than Zn^+, in accord with common sentiment. It is expected that both species should be quite reactive and that Zn^+ should easily reduce Cd^+. This process was reported by Baxendale *et al.* (*38*), but Meyerstein and Mulac subsequently reported that the reaction could not be detected (*216*). The discrepancy is a continuing mystery.

Unlike Zn^+ but like Hg^+, Cd^+ rapidly dimerizes to from Cd_2^{2+} (*177*). Almost nothing is known of the reactivity of this unstable species except that it reduces the *t*-butanol radical.

According to Buxton *et al.*, Cd^+ and Zn^+ react with N_2O to form CdO^+ and ZnO^+, respectively (*71*). These species are reported to oxidize Br^- and I^- to Br_2^- and I_2^-, but Cl^- is unreactive. From this we may infer that these species are good oxidants with $E^0 > 1.9$ V.

There is some evidence that Cd(I) is hydrolyzed in alkaline media (*142*), and a pK_a of 7–9 for Cd^+ was estimated on the basis of periodicity (*117*).

Unlike zinc(I) and cadmium(I), mercury(I) is stable and exists as Hg_2^{2+}. In a very early report, Cartledge calculated the dissociation constant to form Hg^+ as 10^{-31} *M* by estimating the hydration energy of Hg^+ (*78*). This has some measure of support in Moser and Voigt's experimental determination that the dissociation constant is less than 10^{-7} *M* (*221*). Cartledge also calculated the potential of the Hg^{2+}/Hg^+ couple as 0.00 V. From his calculations we find $\Delta_f G^0 = 165$ kJ/mol for Hg^+. Ershov, in his review (*115*), estimated $E^0 = -1.4 \pm 0.3$ V for the Hg^{2+}/Hg^+ couple by use of an empirical trend in E^0 values across the periodic table; the enormous discrepancy with Cartledge's estimate probably signals the breakdown of the empirical trend. The potential of the related couple $(Hg^+, Hg^{2+})/Hg_2^{2+}$ is 1.83 V. Mercury is slightly soluble in water, and in solution it presumably exists as the atomic species, as it does in the gas phase. Thus the potential of the Hg^+/Hg couple is 1.33 V, and it is -0.50 V for the $Hg_2^{2+}/(Hg, Hg^+)$ couple. Fujita *et al.* reported in a pulse radiolysis study of HgO that the pK_a of Hg^+ is 5.1 (*132*). Thus $\Delta_f G^0 = -43$ kJ/mol for HgOH, and $E^0 = -0.09$ V for the $HgOH^+/HgOH$ couple. It would be good to have experimental confirmation of these calculations. Qualitatively, the high potential of the $(Hg^{2+}, Hg^+)/Hg_2^{2+}$ couple is consistent with the slow kinetics of oxidation of Hg_2^{2+} by $[Ru(bpy)_3]^{3+}$ and related complexes (*156*).

There is a disagreement regarding the mechanism of decay of Hg^+. Faraggi and Amozig claim that Hg^+ undergoes a bimolecular recombination to give Hg_2^{2+} (*119*), while Fujita *et al.* claim that disproportionation occurs to give Hg and Hg^{2+}, which then combine to form Hg_2^{2+} (*134*). From the above thermochemical data it can be seen that the disproportionation mechanism would have a driving force of 1.33 V in the first step. With such a favorable driving force it is quite conceivable that disproportionation could occur more rapidly than dimerization by substitution of the coordinated water. Furthermore, because Hg(I) is acidic, its decay should be pH dependent.

The species HgCl, HgBr, HgI, HgSCN, and HgCN have been generated by reaction of e_{aq}^- with HgX_2. The identity of these species is somewhat clouded by the suggestion that they are formed in a long-lived excited state (*133*). They are reported to reduce $C(NO_2)_4$ and *p*-benzoquinone, which implies that they are good reducing agents, and they form adducts with O_2 (*175*).

B. THE ALKALI EARTHS

The alkali earths are somewhat problematic. As discussed in *Standard Potentials*, the experimental evidence in favor of Be(I) is substantial. There is some evidence that the species is Be_2^{2+}, but no estimates of the E^0 are available. In Buxton and Sellers' review (*69*), the experimental evidence cited for the monovalent cations is limited to Mg^+, and the existence of even this species appears dubious. Perrault cites three estimates of E^0 for the Mg/Mg^+ potential (-2.657, -3, and -1.2 V) (*242*). He selects the value of -2.657 V and $\Delta_f H^0 = -230$ kJ/mol for aqueous Mg^+ in *Standard Potentials*; this requires a potential of -2.054 V for the Mg^{2+}/Mg^+ couple. Such a potential might well be taken in support of the existence of Mg^+. We note, however that the cited $\Delta_f H^0$ requires a hydration enthalpy of Mg^+ some 150 kJ more exothermic than that of Li^+! A more reasonable although rough estimate of E^0 for the Mg^{2+}/Mg^+ couple was obtained by Baxendale and Dixon by using NBS data for the enthalpy of Mg^+ in the gas phase and assuming an entropy and a hydration enthalpy the same as that of Na^+ (*37*). This leads to $E^0 = -4.87$ V for the Mg^{2+}/Mg^+ couple, which is much more negative than the hydrated electron. Similar calculations for the other alkaline earths lead to potentials that are even more negative.

XI. The Alkali Metals

A casual look at *Standard Potentials* shows that the alkali metals are strong reducing agents. The weakest of these is Na with $E^0 = -2.713$ V. The hydrated electron is a stronger reducing agent than this, which might suggest that it could reduce Na^+. However, the tabulated potentials refer to the bulk metal. When the potentials are corrected to the atomic species (with a minor correction for the hydration energy), all the alkali metals are found to have potentials less than -3.5 V (*37*). Such species would be unstable with respect to emission of an electron. Experimental evidence in support of $M^+-e_{aq}^-$ adducts has been reviewed by Buxton and Sellers (*69*).

XII. The Rare Gases

The thermochemistry of the rare gases and their compounds is discussed in *Standard Potentials*. The only aqueous free radical mentioned in that account is XeF, which is assigned a value of 46.0 kJ/mol for its standard free energy of formation. The associated redox couples are $XeF_2/(XeF, F^-)$ and $XeF/(Xe, F^-)$, which are assigned potentials of 0.9 and 3.37 V, respectively. These results were calculated by using a thermochemical cycle; the actual evidence for aqueous XeF is only inferential, being based on the observation that oxidation of Ti^{3+} by XeF_2 induces vinyl polymerization.

In an extensive study of the radiolysis and photolysis of XeO_3, $HXeO_4^-$, and $HXeO_6^{3-}$, Klaning *et al.* identified a number of free radicals (*185*). Reaction of XeO_3 with e_{aq}^- is claimed to give $HXeO_3$, although a rationale for this composition rather than XeO_3^- was not presented. It is suggested that OH adds to XeO_3 to form $HOOXeO_2$, and that, because the reaction proceeds, $\Delta_f G^0 < 550$ kJ/mol for $HOOXeO_2$. From the relationship $\Delta_f G^0(HOOXeO_2) - \Delta_f G^0(HXeO_3) = \Delta_f G^0(H_2O_2) - \Delta_f G^0(H_2O)$ they derive $\Delta_f G^0 < 450$ kJ/mol for $HXeO_3$, and hence we find $E^0 > 0.67$ V for the $XeO_3/HXeO_3$ couple. On the other hand, XeO_3 cannot be a very powerful one-electron oxidant in view of its slow oxidations of Pu^{3+} and Mn^{2+}.

Klaning *et al.* (*185*) suggest that there are two forms of Xe(VII). One, $HXeO_5^{2-}$, is formed by addition of OH and O^- to $HXeO_4^-$ (the species formed from XeO_3 in base); the other, $H_3XeO_6^{2-}$, arises from e_{aq}^- reacting with $HXeO_6^{3-}$. The two species seem to be chemically indistinguishable. They were able to determine forward and reverse rate constants for the reaction

$$HXeO_4^- + O^- \rightleftharpoons HXeO_5^{2-} \tag{65}$$

from which they derive $K_{eq} \approx 5 \times 10^4\ M^{-1}$ and hence $\Delta_f G^0 = 420$ kJ/mol for $HXeO_5^{2-}$. On the weakly supported assumption that the two forms of Xe(VII) are related by a hydration reaction having an equilibrium constant of unity, they derive $\Delta_f G^0 = 180$ kJ/mol for $H_3XeO_6^{2-}$. The pK_a values for various degrees of protonation of the two Xe(VII) states were estimated by chemical analogy. Finally, for the reaction

$$H_3XeO_6^{2-} + HXeO_6^{3-} \rightleftharpoons [Xe(VII)Xe(VIII)] \tag{66}$$

they determined $K_{eq} = 1600\ M^{-1}$. Because the state of hydration of the mixed-valence species is unknown, no free energy could be assigned.

Formal oxidation of $HXeO_6^{3-}$ by OH was proposed to occur by addition to form $HOOXe(OH)_2O_3^{2-}$. By use of the relationship $\Delta_f G^0$-$[HOOXe(OH)_2O_3^{2-}] - \Delta_f G^0(HXeO_5^{2-}) = \Delta_f G^0(H_2O_2) - \Delta_f G^0(H_2O)$, they derived $\Delta_f G^0 = 280$ kJ/mol for $HOOXe(OH)_2O_3^{2-}$. It was found that association occurred as in

$$HOOXe(OH)_2O_3^{2-} + HXeO_6^{3-} \rightleftharpoons \text{intermediate} \tag{67}$$

and the forward rate constant was measured. If we take the ratio of the forward rate constant and their upper limit of the reverse rate constant as the equilibrium constant, then a value of $K_{eq} > 1 \times 10^3\ M^{-1}$ is derived. It is clear that the chemistry of these radicals is complex; confirmation of the above results will be valuable.

In closing it should be mentioned that Xe_2^+, which is isoelectronic with the well-known species I_2^-, has been generated in superacid media (*297*).

XIII. Appendix

TABLE A-I

PROVISIONAL FREE-RADICAL REDUCTION POTENTIALS[a]

Redox Couple	E^0 (V)	Redox Couple	E^0 (V)
e^-_{aq}	−2.87	ClO_2/ClO_2^-	0.934
H/H^-	0.05	$(2H^+, ClO_3^-)/(ClO_2, H_2O)$	1.14
H^+/H	−2.31	ClO_3/ClO_3^-	2.1
H_2^+/H_2	5.45	$ClSCN^-/(Cl^-, SCN^-)$	1.58
OH/OH^-	1.90	Br/Br^-	1.92
$(H^+, OH)/H_2O$	2.72	$Br_2^-/2\,Br^-$	1.62
$(H^+, O^-)/OH^-$	1.77	Br_2/Br_2^-	0.58
O/O^-	1.63	$HOBr/HOBr^-$	0.14
$H_2O_2/(OH, OH^-)$	−0.03	OBr/OBr^-	1.34
$HO_2^-/(OH, O^-)$	−0.04	$BrO^-/(Br^-, O^-)$	−0.24
O_2/O_2^-	−0.16	BrO_2/BrO_2^-	1.21
$(H^+, O_2)/HO_2$	0.12	$(H^+, BrO_2)/HBrO_2$	1.50
$(H^+, HO_2)/H_2O_2$	1.44	$(2H^+, BrO_3^-)/(BrO_2, H_2O)$	1.16
HO_2/HO_2^-	0.75	$BrO_4^-/(BrO_3^-, O^-)$	0.06
$^1O_2/O_2^-$	0.83	$BrSCN^-/(Br^-, SCN^-)$	1.42
O_3/O_3^-	1.01	I/I^-	1.33
O_2^+/O_2	3.2	$I_2^-/2\,I^-$	1.03
F/F^-	3.6	I_2/I_2^-	0.21
Cl/Cl^-	2.41	HIO/HIO^-	0.03
$Cl_2^-/2\,Cl^-$	2.09	IO/IO^-	1.8
Cl_2/Cl_2^-	0.70	IO_3^-/IO_3^{2-}	> -0.02
$HOCl/ClOH^-$	0.25	HIO_3/HIO_3^-	>0.60
ClO/ClO^-	1.50	$ISCN^-/(I^-, SCN^-)$	1.14

(*continued*)

TABLE A-I (*continued*)

Redox Couple	E^0 (V)	Redox Couple	E^0 (V)
HS/HS^-	1.08	$CF_3Cl/(CF_3, Cl^-)$	-0.67
$(S, H^+)/HS$	1.44	$CF_3Br/(CF_3, Br^-)$	-0.58
SO_2/SO_2^-	-0.26	$CF_3I/(CF_3, I^-)$	-0.65
$(SO_2, SO_2^-)/S_2O_4^{2-}$	0.255	$CCl_4/(CCl_3, Cl^-)$	-0.23
SO_3^-/SO_3^{2-}	0.63	$CBr_4/(CBr_3, Br^-)$	-0.07
SO_3/SO_3^-	0.25	$CF_2Cl_2/(CF_2Cl, Cl^-)$	-0.59
$S_2O_6^{2-}/(SO_3^-, SO_3^{2-})$	-0.49	$CFCl_3/(CFCl_2, Cl^-)$	-0.44
SO_4^-/SO_4^{2-}	2.43	CN/CN^-	2.59
$S_2O_8^{2-}/(SO_4^{2-}, SO_4^-)$	1.45	OCN/OCN^-	2.66
HSO_5/HSO_5^-	1.4	$C(NO_2)_4/[C(NO_2)_3^-, NO_2]$	0.93
$S_2O_3^-/S_2O_3^{2-}$	1.35	SCN/SCN^-	1.63
$S_4O_6^-/2\,S_2O_3^{2-}$	1.18	$(SCN)_2^-/2\,SCN^-$	1.32
$S_4O_6^{2-}/S_4O_6^{3-}$	-1.13	$(SCN)_2/(SCN)_2^-$	0.21
$SF_6/(SF_5, F^-)$	0.05	$SCNS_2O_3^{2-}/(SCN^-, S_2O_3^{2-})$	1.19
$SF_5/(SF_4, F^-)$	1.64	$SeCN/SeCN^-$	1.27
FSO_3/FSO_3^-	3.09	$(SeCN)_2^-/2\,SeCN^-$	0.95
HSe/HSe^-	0.62	Pb^+/Pb	-0.9
$(Se, H^+)/HSe$	1.02	Pb^{2+}/Pb^+	-1.0
$H_2Se_2^-/2\,HSe^-$	0.37	Pb^{3+}/Pb^{2+}	1.6
SeO_3^-/SeO_3^{2-}	1.68	Pb^{4+}/Pb^{3+}	1.8
$HSeO_4^-/HSeO_4^{2-}$	-0.97	In^+/In	-2.43
NH_3^+/NH_3	2.13	Tl^+/Tl	-2.00
NH_2/NH_2^-	0.7	$2\,Tl^+/Tl_2^+$	-1.80
$NH_2OH/(NH_2, OH^-)$	-0.12	Tl_2^+/Tl_2	-1.44
$NH_3OH^+/(NH_3, OH)$	-0.58	Tl^{2+}/Tl^+	2.22
NH_2OH^+/NH_2OH	≤ 1.26	Tl^{3+}/Tl^{2+}	0.30
$NO/{}^1NO^-$	-0.35	$TlOH^{2+}/TlOH^+$	0.09
$NO/{}^3NO^-$	0.39	$Tl(OH)_2^+/Tl(OH)_2$	-0.28
NO^+/NO	1.21	$TlOH^+/TlOH$	1.76
NO_2/NO_2^-	1.04	$Tl(OH)_2/Tl(OH)_2^-$	1.29
NO_2^+/NO_2	1.51	$TlCl^{2+}/TlCl^+$	0.14
NO_3^-/NO_3^{2-}	< -0.40	$TlCl_2^+/TlCl_2$	0.00
NO_3/NO_3^-	2.5	$TlCl_3/TlCl_3^-$	-0.15
$N_2H_4^+/N_2H_4$	0.01	$TlCl^+/TlCl$	2.01
N_3/N_3^-	1.33	$TlCl_2/TlCl_2^-$	1.79
$(H^+, NF_2)/HNF_2$	0.91	Zn^{2+}/Zn^+	-1.6
$ON(SO_3)_2^{2-}/ON(SO_3)_2^{3-}$	-0.350	Zn^+/Zn	-1.0
$(H^+, PO_3^{2-})/HPO_3^{2-}$	1.61	Cd^{2+}/Cd^+	-1.4
HPO_3^-/HPO_3^{2-}	1.26	Cd^+/Cd	-0.3
$H_2PO_4/H_2PO_4^-$	2.4	Hg^{2+}/Hg^+	0.00
PO_5^{2-}/PO_5^{3-}	1.9	$(Hg^{2+}, Hg^+)/Hg_2^{2+}$	1.83
$H_2AsO_3/H_2AsO_3^-$	< 1.31	$Hg_2^{2+}/(Hg, Hg^+)$	-0.50
$(H^+, CO)/HCO$	-1.54	Hg^+/Hg	1.33
CO_2/CO_2^-	-1.8	$HgOH^+/HgOH$	-0.09
HCO_2/HCO_2^-	1.36	$XeF_2/(XeF, F^-)$	0.9
CO_3^-/CO_3^{2-}	1.5	$XeF/(Xe, F^-)$	3.37
CO_3/CO_3^-	2.3	$(H^+, XeO_3)/HXeO_3$	> 0.67
$CF_4/(CF_3, F^-)$	-1.45		

[a] All potentials relative to NHE, with $[H^+] = 1\ M$, and the standard state for all species being the 1 *M* solution.

TABLE A-II

PROVISIONAL GIBBS FREE ENERGIES OF FORMATION IN AQUEOUS SOLUTION

Radical	$\Delta_f G^0$ (kJ/mol)	Radical	$\Delta_f G^0$ (kJ/mol)
e^-_{aq}	277	NH_2	192
H	223	NO	102
H_2^+	543	NO_2	63
O	251	NO_3^{2-}	> -70
OH	26	NO_3	131
O^-	94	$N_2H_4^+$	129
O_3^-	77	N_2H_3	170
HO_2	4.4	N_3	477
O_2^-	31.8	N_6^-	828
O_2^+	330	NF_2	68
F	68	PO_3^{2-}	−655
Cl	101	HPO_3^-	−688
Cl_2^-	−61	HCO	28
$ClOH^-$	−104	CO_2^-	−208
ClO	108	HCO_2	−216
ClO_2	119	CO_3^-	−383
ClO_3	194	HCO_3	−426
$ClSCN^-$	114	CN	422
Br	81	OCN	159
Br_2^-	−52	SCN	250
$HOBr^-$	−96	$(SCN)_2^-$	313
OBr	96	$SCNOH^-$	84
BrO_2	144	$SCNS_2O_3^{2-}$	−315
$BrSCN^-$	126	In	222
I	77	Tl	161
I_2^-	−3	Tl_2	248
IOH^-	−93	Tl_2^+	109
IO	138	Tl^{2+}	186
HIO_3^-	< -190	$TlOH^+$	−24.6
IO_3^{2-}	< -126	$Tl(OH)_2$	−218
$ISCN^-$	151	$TlCl^+$	27
HS	116	$TlCl_2$	−123
SO_2^-	−275	$TlCl_3^-$	−260
SO_3^-	−426	Pb^+	72
SO_4^-	−510	Zn^+	7
HSO_5	−500	Cd^+	58
$S_2O_3^-$	−392	Hg^+	165
$S_4O_6^{3-}$	−931	HgOH	−43
SF_5	−822	XeF	46
FSO_3	−465	$HXeO_3$	< 450
HSe	104	$HOOXeO_2$	< 550
$H_2Se_2^-$	124	$H_3XeO_6^{2-}$	180
$HSeO_4^-$	−358	$HXeO_5^{2-}$	420
SeO_3^-	−202	$HOOXe(OH)_2O_3^{2-}$	280
NH_3^+	179		

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NOTE ADDED IN PROOF

Despite the thermochemical accessibility of $^1O_2$ in the reaction of O_2^- with $[Ru(bpy)_3]^{3+}$, it has been argued recently that $^1O_2$ is not a major product (*337*). Closer reading of Ref. *324* reveals that this paper raises considerable doubts about our present understanding of Cl_2^-. The authors of Ref. *324* have also reinvestigated the chemistry of Br_2^-, and here too, they find major discrepancies with prior work (*338*). The chemistry of $S_2O_8^{2-}$ has been reviewed, with extended discussion of the mechanism of hydrolysis (*339*). Our selection of data for the HNO_2/NO_2^- system has been confirmed (*340*). Two comprehensive compilations of rate constants have appeared; one summarizes the reactions of e_{aq}^-, OH, and H (*341*), while the other treats reactions of inorganic free radicals (*342*).

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