

# REDUCTION POTENTIALS INVOLVING INORGANIC FREE RADICALS IN AQUEOUS SOLUTION

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- I. Introduction
- II. The Hydrated Electron
- III. Hydrogen
- IV. Oxygen
- V. The Halogens
  - A. Fluorine
  - B. Chlorine
  - C. Bromine
  - D. Iodine
  - E. Astatine
- VI. The Heavier Chalcogens
  - A. Sulfur
  - B. Selenium
  - C. Tellurium
  - D. Polonium
- VII. Group V
  - A. Nitrogen
  - B. Phosphorus
  - C. Arsenic
  - D. Antimony
  - E. Bismuth
- VIII. Group IV
  - A. Carbon
  - B. Silicon
  - C. Germanium
  - D. Tin
  - E. Lead
- IX. Group III
  - A. Boron
  - B. Aluminum
  - C. Gallium
  - D. Indium
  - E. Thallium

- X. Group II
  - A. Zinc, Cadmium, and Mercury
  - B. The Alkali Earths
- XI. The Alkali Metals
- XII. The Rare Gases
- XIII. Appendix
  - References
  - Note Added in Proof

## 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  $\Delta_f G^\circ$  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 ex-

pressed 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,  $\Delta G_f^0$ ; 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  $E(ctts) = 1.35E(X^-/X\cdot) + 3.55$ , 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

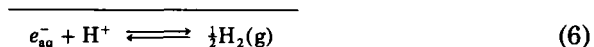
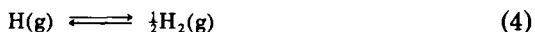
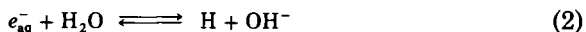
than 1.35. It must be assumed that the equation is derived empirically from the data for the halides, for which it is a good approximation. The factor of 1.35 thus represents the complex contributions of reorganizational energies as they occur for the halides. With the revised potentials for the halides presented in this review (excluding  $F^-$ ) the equation is still a very good fit:  $E(ctts) = 1.49E(X^-/X\cdot) + 3.45$ . 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:



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



The equilibrium constant for reaction (2),  $3.9 \times 10^{-5} M$ , 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  $\Delta G^0$  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  $\Delta_r G^0 = 277$  kJ/mol for the hydrated electron.

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



which was reported by Anbar and Neta (16). Their equilibrium constant,  $2.5 \times 10^{-4}$ , leads to  $\Delta_r G^0$  for  $e_{\text{aq}}^-$  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  $e_{\text{aq}}^-$  that leads to the electron dimer,  $(e_{\text{aq}}^-)_2$ , have been disputed, but there is still evidence that  $e_{\text{aq}}^-$  forms some other precursor to  $\text{H}_2$  (313). The proposal for  $(e_{\text{aq}}^-)_2$  has recently been revived (85).

### III. Hydrogen

The potential associated with the  $\text{H}^+/\text{H}$  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  $\text{H}_2$  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  $\Delta_r G^0 = 223$  kJ/mol for the hydrogen atom.

The hydride ion,  $\text{H}^-$ , has been proposed in the base-catalyzed exchange between  $\text{D}_2$  and  $\text{H}_2\text{O}$ , in the base-catalyzed conversion of *para*- $\text{H}_2$  (86, 153, 329), and in certain radiation chemistry systems (88). The

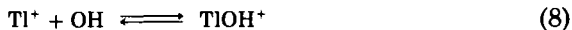
evidence from base catalysis is uncontested, but, as noted in Czapski's review (88), the evidence from radiation chemistry is not compelling. Presumably such a species, if formed, would be difficult to detect because it would be instantly protonated. The free energy of formation of  $H^-$  can be estimated 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

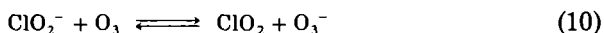
Like that of the hydrated electron and the hydrogen atom, the potential of the hydroxyl radical has long been the subject of estimates based on thermochemical cycles involving the free energy of hydration of  $OH$ ; the results of these calculations appear, for example, in *Standard Potentials* (pp. 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



and



The sum of these equilibria relates the potential of the  $\text{OH}/\text{OH}^-$  couple to that of the  $\text{Tl}^{2+}/\text{Tl}^+$  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



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  $\text{ClO}_2/\text{ClO}_2^-$  couple this led to 1.01 V as the potential of the  $\text{O}_3/\text{O}_3^-$  couple. Equilibrium constants for the reactions



and



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 constants, 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  $\text{OH}/\text{OH}^-$  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  $\text{H}_2\text{O}$ ; thus the derived potential of 2.72 V for the  $(\text{H}^+, \text{OH})/\text{H}_2\text{O}$  couple is of interest.

The  $\text{p}K_a$  of OH is well established as  $11.9 \pm 0.2$  (103, 120). This result was obtained in a study of the pH dependence of the reaction of OH with

$\text{Fe}(\text{CN})_6^{4-}$  (247). Confirmation of this result was found in the reaction of OH with  $\text{CO}_3^{2-}$ , which gave  $\text{p}K_a = 11.8 \pm 0.2$  (326), and in the reaction of OH with  $\text{SCN}^-$ , which gave  $\text{p}K_a = 11.9 \pm 0.15$  (2). This  $\text{p}K_a$ , in combination with the above value for  $\Delta_r G^0$  for OH, leads to  $\Delta_r G^0 = 94 \text{ kJ/mol}$  for  $\text{O}^-$  and  $E^0 = 1.77 \text{ V}$  for the  $\text{O}^-/\text{OH}^-$  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  $\text{H}_2\text{O}$  to form  $\text{H}_2\text{O}_2$ . 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  $\Delta_r G^0$  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  $\text{O}(^3P)_{\text{aq}}$ . Henglein (160), using an old value of  $\Delta_r G^0 = 103 \text{ kJ/mol}$  for  $\text{O}^-$  and an estimated hydration free energy of 10 kJ/mol for O, calculated  $E^0 = 1.4 \text{ V}$  for the  $\text{O}/\text{O}^-$  couple; with  $\Delta_r G^0 = 94 \text{ kJ/mol}$  for  $\text{O}^-$  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  $\text{O}(^3P)_{\text{aq}}$ , 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  $\text{BrO}_3^-$ , by abstracting an oxygen atom (184).

Potentials can now be calculated for the one-electron reductions of  $\text{H}_2\text{O}_2$  to  $\text{OH} + \text{OH}^-$  and of  $\text{HO}_2^-$  to  $\text{O}^- + \text{OH}^-$ ; these are  $-0.03$  and  $-0.04 \text{ V}$ , 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  $\text{O}_3/\text{O}_3^-$  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  $\Delta_r G^0 = 77 \text{ kJ/mol}$  for  $\text{O}_3^-$ ; these results are probably fairly accurate because they confirm the potential of the  $\text{OH}/\text{OH}^-$  couple. There is considerable uncertainty expressed in Czapski's review concerning the  $\text{p}K_a$  of  $\text{HO}_3$  (88); on the basis of chemical analogy he estimated a  $\text{p}K_a$  of  $-2$ . In a recent investigation it was asserted that  $\text{HO}_3$  has a  $\text{p}K_a$  of 6.15, although it splits into OH and oxygen before it has time to dissociate into  $\text{O}_3^-$  (60). Subsequently the  $\text{p}K_a$  was corrected to  $8.2 \pm 0.1$  (61). It is prudent to await confirmation of these results.



Superoxide ( $\text{O}_2^-$ ) and the peroxy radical ( $\text{HO}_2$ ) have been intensively studied, and a good account of their thermochemistry is presented in *Standard Potentials* (pp. 60–63). They are related by the  $\text{p}K_a$  of  $\text{HO}_2$ , which is  $4.8 \pm 0.1$  (51). The reduction potential of the  $\text{O}_2/\text{O}_2^-$  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  $\text{O}_2$  pressure. When expressed relative to the 1 M standard state of  $\text{O}_2$ , the potential is  $-0.16$  V. Standard NBS data permit calculation of  $\Delta_r G^\circ = 4.4$  kJ/mol and 31.8 kJ/mol for  $\text{HO}_2$  and  $\text{O}_2^-$ , respectively. Some related potentials include 0.12 V for  $(\text{H}^+, \text{O}_2)/\text{HO}_2$ , 1.44 V for  $(\text{H}^+, \text{HO}_2)/\text{H}_2\text{O}_2$ , and 0.75 V for  $\text{HO}_2/\text{HO}_2^-$ .

The notion that  $\text{H}_2\text{O}^+$  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  $\text{H}_2\text{O}_2^+$ ...than for the opposite assumption..." The other item is a citation of the acid-catalyzed dismutation of  $\text{HO}_2$  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  $0.9 \times 10^6$  to  $1.1 \times 10^6$   $\text{M}^{-1} \text{sec}^{-1}$  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  $\Delta_r G^\circ = 95$  kJ/mol for  $^1\Delta_g\text{O}_2$  in the gas phase. The assumption of a free energy of hydration the same as that for  $^3\text{O}_2$  leads to  $\Delta_r G^\circ = 112$  kJ/mol for aqueous  $^1\Delta_g\text{O}_2$ , and thus  $E^\circ$  is 0.83 V for the  $^1\text{O}_2/\text{O}_2^-$  couple. Thus the observed quantitative yield of  $^1\text{O}_2$  in the oxidation of  $\text{O}_2^-$  by  $[\text{Ru}(\text{bpy})_3]^{3+}$  is thermodynamically acceptable (217).

Czapski, in his review (88), discusses the chemistry of  $\text{H}_2\text{O}_3$  and  $\text{H}_2\text{O}_4$ . There does not appear to be any evidence in support of the latter species in aqueous solution.  $\text{H}_2\text{O}_3$ , on the other hand, is fairly well characterized. Although its free energy is unknown, its reported  $\text{p}K_a$  is 9.5. Nangia and Benson have estimated  $\Delta_r H^\circ = -15.7$  for this species in the gas phase (224).

The dioxygenyl cation,  $\text{O}_2^+$ , exists in various media, but it has not been reported in aqueous solution. The gas-phase species is assigned  $\Delta_r G^\circ = 1164.315$  kJ/mol in the JANAF tables. As a very rough approximation it may be assumed that  $\text{O}_2^+$  has the same free energy of

hydration as  $\text{Na}^+$ , which leads to  $\Delta_f G^\circ = 330 \text{ kJ/mol}$  for  $\text{O}_2^+$ , and  $E^\circ = 3.2 \text{ V}$  for the  $\text{O}_2^+/\text{O}_2$  couple.

## V. The Halogens

### A. FLUORINE

Taube and Bray noted in 1940 that the standard potential for the  $\text{F(g)}/\text{F}^-$  couple is  $4.04 \text{ V}$  (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  $E^\circ$  of  $3.6 \text{ V}$  for the  $\text{F}/\text{F}^-$  couple and a corresponding  $\Delta_f G^\circ$  of  $68 \text{ kJ/mol}$  for  $\text{F}$ . The chemistry of  $\text{F}_2$  and  $\text{HOF}$  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  $\text{F}_2^-$  in aqueous solution, although the species has been detected in irradiated crystals. In the reversible reaction of  $\text{H}$  with  $\text{F}^-$  to give  $e_{\text{aq}}^-$  and  $\text{HF}$ , it has been argued that  $\text{HF}^-$  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  $\text{Cl}/\text{Cl}^-$  couple. The first of these was by Taube and Bray (310), in which it was estimated that the potential of the  $(\text{H}^+, \text{OH})/\text{H}_2\text{O}$  couple exceeded that of the  $\text{Cl}/\text{Cl}^-$  couple by  $0.12 \text{ V}$ . 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  $\text{Cl}/\text{Cl}^-$  COUPLE

| $E^\circ$ (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 $^3\text{DQ}$     |
| 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):



These equilibrium constants have been determined only once (173), but they are estimated to lead to an uncertainty in  $E^0$  of  $\pm 0.03$  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.



The equilibrium constant ( $1.9 \times 10^5 M^{-1}$ ) 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  $Cl^-$  ( $k = 8 \times 10^9 M^{-1} \text{ sec}^{-1}$ ) that is close to the value reported by Jayson, Parsons and Swallow ( $2.8 \times 10^{10} M^{-1} \text{ sec}^{-1}$ ) (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.

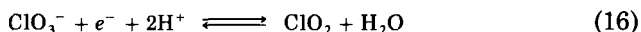
ClO has been reported as an intermediate in various photolytic and radiolytic systems (72, 73, 184, 186). No thermochemical data are available on this aqueous species, but the NBS tables give a value of  $\Delta_f G^\circ = 98.11$  kJ/mol for the gas-phase species, which is probably good within  $\pm 2$  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  $\Delta_f G^\circ = 108$  kJ/mol is obtained for aqueous ClO. By use of the NBS value of  $\Delta_f G^\circ = -36.8$  kJ/mol for  $ClO^-$  it is found that ClO is a good oxidant, with  $E^\circ = 1.50$  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  $E^\circ = 0.934 \pm 0.002$  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)  $\Delta_f G^\circ = 122 \pm 6$  kJ/mol for gaseous  $ClO_2$ . Considerably greater uncertainty is expressed in Darwent's tables, where a value of  $243 \pm 13$  kJ/mol is listed for the O-ClO bond dissociation energy at 0 K (91). More recently an upper limit of  $231 \pm 8$  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  $\Delta_f G^\circ$  of  $119 \pm 3$  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

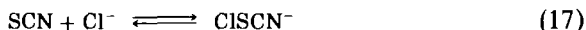
for  $\Delta_f G^0$  of aqueous  $\text{ClO}_2$  as determined from the gas-phase result and the solubility. A value of 29 kJ/mol is derived for  $\Delta_f G^0$  of  $\text{ClO}_2^-$  from this result and the reduction potential of  $\text{ClO}_2$  cited above.

There is no reported evidence of formation of  $\text{ClO}_2^+$  by oxidation of  $\text{ClO}_2$  or of formation of  $\text{ClO}_3^{2-}$  by reduction of  $\text{ClO}_3^-$ . Interconversion of  $\text{ClO}_2$  and  $\text{ClO}_3^-$  thus is contingent upon attachment of an oxygen atom. The above result for  $\text{ClO}_2$  and the NBS data for  $\text{ClO}_3^-$  lead to 1.14 V for the potential of the half-cell



Chlorine trioxide has been reported in many electron spin resonance (ESR) studies of irradiated crystals of  $\text{NaClO}_3$  and  $\text{Ba}(\text{ClO}_4)_2$ . 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  $S^0 = 253 \text{ J/K/mol}$  (that of  $\text{NO}_3$ ) and a hydration free energy of  $-10 \text{ kJ/mol}$  leads to  $\Delta_f G^0 = 194 \text{ kJ/mol}$  for aqueous  $\text{ClO}_3$  and  $E^0 = 2.1 \text{ V}$  for the  $\text{ClO}_3/\text{ClO}_3^-$  couple. The reported failure of OH to oxidize  $\text{ClO}_3^-$  may be taken in support of this calculated potential (72).

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



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

### C. BROMINE

Potentials reported for the  $\text{Br}/\text{Br}^-$  couple are collected in Table II. As with the  $\text{I}/\text{I}^-$  system there have been several estimates of the  $\text{Br}/\text{Br}^-$  potential by use of thermochemical cycles that involve the heat of formation of  $\text{Br(g)}$  (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  $\text{Mn}^{2+}$  by  $\text{Br}_2^-$  enabled them to calculate  $E^0$  for the  $\text{Br}_2^-/2 \text{ Br}^-$  couple (197); the reduction potential for the  $\text{Br}/\text{Br}^-$  couple can thus be obtained by using

TABLE II  
REPORTED REDUCTION POTENTIALS FOR THE  $\text{Br}/\text{Br}^-$  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 <sup>a</sup> | 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    |

<sup>a</sup> Calculated from Henglein's result for the  $\text{Br}_2^-/(2\text{Br}^-)$  couple with the assumption that  $K_{\text{eq}} = 1.1 \times 10^5 \text{ M}^{-1}$  for association of  $\text{Br}^-$  with  $\text{Br}$ .

the formation constant for the reaction

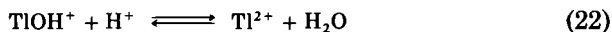


With this formation constant selected as  $1.1 \times 10^5 \text{ M}^{-1}$  (see below), we obtain  $E^0 = 1.92 \text{ V}$ , which is within the range of the thermochemical estimates. Martins (206) obtained his result by combining our accepted  $E^0$  for the  $\text{I}/\text{I}^-$  couple with equilibrium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



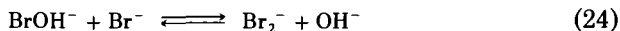
the latter relying on a previously reported equilibrium constant for reaction (18).

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



They combined these values with the known  $E^0$  for the  $\text{Ti}^{2+}/\text{Ti}^+$  couple

and reported equilibrium constants for reaction (18) and the following reactions:



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  $\Delta_r G^0 = 81 \text{ kJ/mol}$  for Br.

While the consistency between the reported "experimental"  $E^0$  values for the Br/Br<sup>-</sup> couple is encouraging, it should be noted that all values rely upon the reported equilibrium constant for reaction (18). As noted in Fournier de Violet's review (127), the magnitude of this formation constant is contentious, with reported results ranging from  $3.3 \times 10^3$  to  $2.2 \times 10^5 \text{ M}^{-1}$ . The most recent value is  $1.1 \times 10^5 \text{ M}^{-1}$ , 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



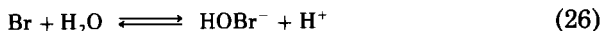
the equilibrium constant is 9.6 (186). It appears that they obtained this value by measuring the rate of reaction of Br atoms with OH<sup>-</sup> and combining this value with the published rate constant for dissociation of BrOH<sup>-</sup> to Br + OH<sup>-</sup> and the equilibrium constant for dissociation to Br<sup>-</sup> + OH. By using the recently reported  $E^0$  for OH (= 1.90 V; see above) we obtain  $E^0 = 1.96 \text{ V}$  for the Br/Br<sup>-</sup> 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  $\Delta_r G^0 = -52 \text{ kJ/mol}$  for Br<sub>2</sub><sup>-</sup>,  $E^0 = 1.62 \text{ V}$  for the Br<sub>2</sub><sup>-</sup>/2Br<sup>-</sup> couple, and  $E^0 = 0.58 \text{ V}$  for the Br<sub>2</sub>/Br<sub>2</sub><sup>-</sup> couple.

It is of some interest to note that Taube in 1948 determined a value of 1.7 V for the Br<sub>2</sub><sup>-</sup>/2Br<sup>-</sup> couple by a careful analysis of the catalysis by Mn<sup>2+</sup> of the reaction of Br<sub>2</sub> with oxalic acid (308). He also derived a value of  $10^4 \text{ M}^{-1}$  for the equilibrium constant of reaction (18). In his analysis Taube used a potential of 1.6 V for the Mn<sup>3+</sup>/Mn<sup>2+</sup> couple. A value of 1.5 V for the Mn<sup>3+</sup>/Mn<sup>2+</sup> couple is presently recommended in *Standard Potentials*; if Taube's data are corrected to this new Mn<sup>3+</sup>/Mn<sup>2+</sup> potential, a potential of 1.6 V is derived for the Br<sub>2</sub><sup>-</sup>/2Br<sup>-</sup> 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.

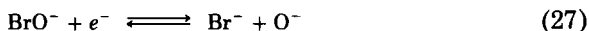
$\text{IBr}^-$  has been observed in inorganic glasses (319), but it has yet to be detected in aqueous solution. Catalysis by  $\text{Br}^-$  of the oxidation of  $\text{I}^-$  by  $[\text{Fe}(\text{phen})_3]^{3+}$  has been attributed to stabilization of nascent  $\text{I}$  by  $\text{Br}^-$  (171),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

As required by the above equilibria, hydrolysis of  $\text{Br}$  occurs in alkaline media according to



with an equilibrium constant of  $3.1 \times 10^{-11} M$  (186). This establishes  $\Delta_r G^0 = -96 \text{ kJ/mol}$ , and with NBS data for  $\text{HOBr}$ ,  $E^0 = 0.14 \text{ V}$  for the  $\text{HOBr}/\text{HOBr}^-$  couple. Rapid reduction of  $\text{HOBr}$  by  $\text{O}_2^-$  has been reported (305), and it is consistent with the favorable driving force.

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



which has a calculated potential of  $-0.24 \text{ V}$ . Thus the observed reduction is thermodynamically viable.

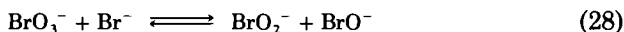
In the NBS tables is reported a value for  $\Delta_r G^0$  of  $108.22 \text{ kJ/mol}$  for  $\text{BrO}$  in the gas phase, and according to Huber and Herzberg this is probably good within  $\pm 1 \text{ kJ/mol}$  (168a). As a rough estimate, the hydration free energy of  $\text{BrO}$  may be taken as that of  $\text{ICl}$ ,  $-12 \text{ kJ/mol}$ , which leads to  $\Delta_r G_{\text{aq}}^0 = 96 \text{ kJ/mol}$ . The reduction potential of the  $\text{OBr}/\text{OBr}^-$  couple is calculated as  $1.34 \text{ V}$  with NBS data for  $\text{OBr}^-$ . This potential is consistent with the rapid reduction of  $\text{OBr}$  by  $\text{O}_3^-$  (184) and the rapid oxidation of  $\text{OBr}^-$  by  $\text{Br}$  and  $\text{OH}$  (186) and  $\text{Br}_2^-$  (67).

There do not appear to be any reports of oxidation of  $\text{BrO}$ . One-electron reduction of  $\text{BrO}_2^-$  has been reported in the diffusion-controlled reaction with  $e_{\text{aq}}^-$ , and the products are claimed to be  $\text{BrO}$  and  $2\text{OH}^-$  (67); presumably  $\text{BrO}_2^{2-}$  is an intermediate.  $\text{HBrO}_2$  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  $\text{BrO}_2^-$ , oxidizing  $\text{BrO}_2^-$  to  $\text{BrO}_2$  is a relatively common process. NBS data for  $\text{BrO}_2$ ,  $\text{BrO}_2^-$ , and  $\text{HBrO}_2$  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  $27.2 \text{ kJ/mol}$  for  $\Delta_r G^0$  of  $\text{BrO}_2^-$  (198), which was obtained from direct measurement of the equilibrium constant of the



reaction



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

The reaction



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 ( $2 \times 10^7 M^{-1} \text{sec}^{-1}$ ) was measured directly by Buxton and Dainton (67). The forward rate constant ( $1.0 \times 10^4 M^{-2} \text{sec}^{-1}$ ) was obtained by making the risky assumption that it was twice the rate constant for isotope exchange in  $\text{BrO}_3^-/\text{Br}_2/\text{HClO}_4$  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  $\text{HBrO}_2$  and that the  $\text{p}K_a$  of  $\text{HBrO}_2$  is 2. The value for the  $\text{p}K_a$  was simply a guess, based on Pauling's empirical rules. From the equilibrium constant and the  $\text{p}K_a$  they obtained a value of  $\Delta_r G^0 = 144 \text{ kJ/mol}$  for  $\text{BrO}_2$  and an  $E^0 = 1.33 \text{ V}$  for the  $\text{BrO}_2/\text{HBrO}_2$  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  $\text{Br}_2\text{O}_4$  to  $2\text{BrO}_2$  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  $K_{\text{eq}}$  for reaction (29). More recently Tyson (322) has shown that the FKN value of  $\Delta_r G^0$  for  $\text{BrO}_2$  is actually independent of the  $\text{p}K_a$  of  $\text{HBrO}_2$ . Thus we calculate  $E^0 = 1.21 \text{ V}$  for the  $\text{BrO}_2/\text{BrO}_2^-$  couple. Most recently Field and Forsterling obtained  $K_{\text{eq}} = 0.9 \times 10^{-6} M^{-1}$  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  $\text{BrO}_2$  to obtain a new  $\text{p}K_a$  ( $= 4.9$ ) and  $\Delta_r G^0 = -0.4 \text{ kJ/mol}$  for  $\text{HBrO}_2$ . This now establishes  $E^0 = 1.50 \text{ V}$  for the  $\text{BrO}_2/\text{HBrO}_2$  couple, which is substantially different from the original FKN result. The discrepancy between the calculated  $\text{p}K_a$  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  $\text{HBrO}_2$  is less acidic than  $\text{HClO}_2$ .

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  $\text{BrO}_2/\text{BrO}_2^-$  couple or of the  $pK_a$  of  $\text{HBrO}_2$  would be quite welcome. In a study of the pH dependence of the decomposition of  $\text{Br(III)}$  in weakly acidic media Massagli *et al.* inferred that  $\text{HBrO}_2$  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  $\text{BrO}_2$  and  $\text{Br}_2\text{O}_4$  are protonated in acidic media (259).

Examples of the one-electron reduction of  $\text{BrO}_3^-$  to  $\text{BrO}_2$  are discussed in Thomspson's review (315). The potential for the couple, obtained by using our  $\Delta_f G^0$  for  $\text{BrO}_2$ , is 1.16 V.

It is claimed that  $\text{BrO}_3$  is generated in the relatively slow oxidation of  $\text{BrO}_3^-$  by OH (11), but no thermochemical data are available for this radical. Reduction of  $\text{BrO}_4^-$  by the hydrated electron yields  $\text{BrO}_3^-$  and  $\text{O}^-$  (237). A potential of 0.06 V can be calculated for the  $\text{BrO}_4^-/(\text{BrO}_3^-, \text{O}^-)$  couple.

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



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

#### D. IODINE

In Table III are listed the various reported values for the  $\text{I}/\text{I}^-$  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<sup>-</sup> COUPLE

| $E^0$ (V) | Year | Reference | Author                 | Technique                      |
|-----------|------|-----------|------------------------|--------------------------------|
| 1.33      | 1986 | 277       | Schwarz and Bielski    | Pulse radiolysis equilibrium   |
| 1.36      | 1982 | 233       | Nord <i>et al.</i>     | Kinetics and pulse radiolysis  |
| <1.2      | 1981 | 256       | Raycheba and Margerum  | Redox kinetics                 |
| 1.33      | 1980 | 294       | Stanbury <i>et al.</i> | Redox kinetics                 |
| 1.38      | 1978 | 232       | Nord <i>et al.</i>     | 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         | <?>                            |

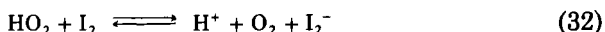
chemical cycle that uses proton affinities, electron affinities, and an estimate of the  $pK_a$  of HI (240); that his result is somewhat discordant is to be expected considering the cumulative errors of the method. The outcome of these estimates is that the potential should certainly be in the range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

The first reliable experimental measurement of  $E^0$  for I/I<sup>-</sup> 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<sup>-</sup> by [Os(bpy)<sub>3</sub>]<sup>3+</sup> (232). In 1980 Stanbury *et al.* published the results of a kinetic study of the oxidation of I<sup>-</sup> 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 ( $1.2 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ , which is probably good within factor of 2) led to an assignment of the reduction potential for the I/I<sup>-</sup> 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<sup>-</sup> by some Cu(III) peptide complexes (256); they arrived at an upper limit of 1.2 V for the I/I<sup>-</sup> 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  $1 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ . 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  $\text{I}_2^-$  with  $[\text{Os}(\text{bpy})_3]^{2+}$  (233); on combining this rate constant with the third-order rate constant for oxidation of  $\text{I}^-$  by  $[\text{Os}(\text{bpy})_3]^{3+}$  they calculated  $E^0$  for the  $\text{I}_2^-/2\text{I}^-$  couple. This  $E^0$ , when combined with the equilibrium constant for the reaction



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  $E^0 = 1.33 \text{ V}$  for the  $\text{I}/\text{I}^-$  couple (277). They arrived at their result in a pulse radiolysis study by measuring the equilibrium constant for the reaction



and combining it with known values for the equilibrium constant of reaction (31) and the  $\text{O}_2/\text{HO}_2$  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  $\text{I}_{\text{aq}}^-$ .

Polyhalide radical anions have recently been reviewed;  $\text{I}_4^-$  and  $\text{I}_6^-$  have been observed in *tert*-butanol solution, but they are unknown in aqueous solution (127). The equilibrium constant for formation of  $\text{I}_2^-$  [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  $\text{I}_2^-$  are listed in Table IV (32, 36, 128, 129, 149, 314, 318). As noted in Fournier 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. Fournier de Violet suggested that the pulse radiolysis results might be in error because of unrecognized adduct formation

TABLE IV

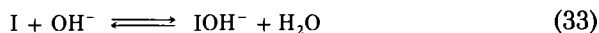
REPORTED FORMATION CONSTANTS FOR  $I_2^-$ 

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



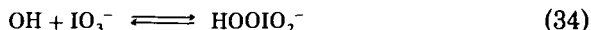
with a  $pK_a$  for the iodine atom of  $11.7 \pm 1.0$ , which leads to  $\Delta_f G^0 = -93 \pm 6$  kJ/mol for  $IOH^-$ . This value, when combined with NBS data, leads to an  $E^0$  of  $0.03 \pm 0.06$  V for the  $HIO/HIO^-$  redox couple; however, we are not aware of any studies that have implicated 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  $\pm 20$  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  $\Delta_f G_{\text{aq}}^0 = 138 \pm 20$  kJ/mol. With NBS data for  $\text{IO}^-$  this result gives  $E^0 = 1.8 \pm 0.2$  V for the  $\text{IO}/\text{IO}^-$  couple and  $E^0 = 2.5$  V for the  $(\text{H}^+, \text{IO})/\text{HIO}$  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  $\text{IO}^-$  by  $\text{I}_2^-$  and  $\text{O}^-$ . 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  $\text{I}_2^-$  is highly endothermic. Buxton and Sellers also report the oxidation of HIO by  $\text{I}_2^-$ , but this reaction must also be highly endothermic.

$\text{IO}_2$  has been observed in irradiated crystals by ESR (75), but as discussed below recent studies indicate that I(IV) in aqueous solution exists as  $\text{HIO}_3^-$  and  $\text{IO}_3^{2-}$ . There is a report of the reaction of  $\text{IO}_2^-$  with  $\text{IO}^-$  and  $\text{I}_2\text{OH}^-$  and of the Raman spectrum of  $\text{IO}_2^-$  in aqueous solutions of decomposing  $\text{IO}^-$  (334). Presumably one-electron oxidation of  $\text{IO}_2^-$  could lead to  $\text{IO}_2$  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  $\text{HIO}_2$  (234). By analogy with the chemistry of other halogens,  $E^0 = 1.0$  V for the  $\text{IO}_2/\text{HIO}_2$  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  $\text{HIO}_3^-$  and  $\Delta_f G^0 < -120$  kJ/mol for  $\text{IO}_3^{2-}$  (185). Central to their argument is the assumption that OH reacts with  $\text{IO}_3^-$  according to



with  $\Delta G^0 < 0$ . The indicated free energy was obtained by the relationship  $\Delta_f G^0(\text{HOOIO}_2^-) - \Delta_f G^0(\text{HIO}_3^-) = \Delta_f G^0(\text{H}_2\text{O}_2) - \Delta_f G^0(\text{H}_2\text{O})$ . In a previous study these workers reported that the above reaction yields  $\text{IO}_3$  (183), but this was revised because it was considered that formation of  $\text{IO}_3$  would be too endothermic. The value for  $\text{IO}_3^{2-}$  was obtained from that for  $\text{HIO}_3^-$  by using Pauling's rule for estimation of acidity constants ( $\text{p}K_a = 12.3$ ). Buxton and Sellers (70) subsequently measured the  $\text{p}K_a$  of  $\text{HIO}_3^-$  as 13.3, which corrects the upper limit of  $\Delta_f G^0$  for  $\text{IO}_3^{2-}$  to  $-126$  kJ/mol. These results suggest  $E^0 > -0.02$  and  $> 0.60$  V for the  $\text{IO}_3^-/\text{IO}_3^{2-}$  and  $\text{HIO}_3/\text{HIO}_3^-$  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  $\text{IO}_3^-$

produces a peroxy 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  $\Delta_f G^0 = -57 \text{ kJ/mol}$  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



was found to have an equilibrium constant of  $4.8 \times 10^{-4} M$  (272). This establishes  $\Delta_f G^0$  for  $ISCN^-$  as  $151 \text{ kJ/mol}$ , 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 ( $\approx 8 \text{ hr}$ ) 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  $1.08 \text{ V}$  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<sub>3</sub>SH, 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<sub>2</sub>S 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<sup>-</sup> potential as 1.4 V (162); unfortunately, this result was based erroneously on the bond enthalpy of H<sub>2</sub>S 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



was reported to have a formation constant of  $2.5 \times 10^4 \text{ M}^{-1}$  at pH 7, but this is only a conditional value because the  $pK_a$  values of both HS and H<sub>2</sub>S<sub>2</sub><sup>-</sup> are uncertain. It is claimed that in acid solution H<sub>2</sub>SSH<sub>2</sub><sup>+</sup> is formed by protonation of H<sub>2</sub>S<sub>2</sub><sup>-</sup>, and that the intermediate state of protonation, H<sub>2</sub>SSH, is unstable (81). Thus the  $E^0$  value calculated by Surdhar and Armstrong for H<sub>2</sub>S<sub>2</sub><sup>-</sup>/2HS<sup>-</sup> (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<sub>8</sub> (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<sub>2</sub>O<sub>2</sub><sup>-</sup> by photolysis of S<sub>2</sub>O<sub>3</sub><sup>2-</sup> (101), but the results have been shown to be, at least in part, spurious (40).

S(III) is found as dithionite, S<sub>2</sub>O<sub>4</sub><sup>2-</sup>, which is in homolytic equilibrium with SO<sub>2</sub><sup>-</sup> in aqueous solution as in reaction (37).

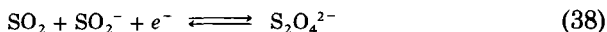


The equilibrium constant for this reaction  $[(0.6-1.4) \times 10^{-9} \text{ M}]$  was



determined from ESR measurements in three laboratories with good agreement (194). This establishes  $E^0 = -0.26$  V for the  $\text{SO}_2/\text{SO}_2^-$  couple (293), and  $\Delta_r G^0 = -275$  kJ/mol for  $\text{SO}_2^-$ . The conditional potential of the  $\text{SO}_2^-/\text{S(IV)}$  system is pH dependent because of formation of  $\text{HSO}_3^-$ , and this has been treated by Mayhew (212). Recently the  $\text{SO}_2/\text{SO}_2^-$  system was investigated by direct cyclic voltammetry studies of acidic  $\text{SO}_2$  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  $\text{SO}_2^-$ . The potential so obtained ( $-0.288$  V) differs significantly from that presented above; the origin of this discrepancy is unclear because the  $\text{SO}_2^-$  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  $1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  (111, 112, 158). Furthermore, these authors observed a pH dependence in the cyclic voltammetry which was taken as evidence that  $\text{SO}_2^-$  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.  $\text{S}_2\text{O}_4^-$  has not been reported in aqueous solution, but its existence in nonaqueous media is well established (137). Thus oxidation of  $\text{S}_2\text{O}_4^{2-}$  presumably leads to  $\text{S}_2\text{O}_4^-$  in aqueous media. Because of the lack of data regarding  $\text{S}_2\text{O}_4^-$  we will simply write



for which the calculated potential is 0.255 V.

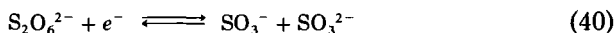
The chemistry of  $\text{SO}_3^-$  has recently been reviewed by Neta and Huie (226). This radical decays with second-order kinetics that appear to be pH dependent, as are the relative yields of  $\text{SO}_4^{2-}$  and  $\text{S}_2\text{O}_6^{2-}$  (111). These results seem to suggest that  $\text{SO}_3^-$  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  $\text{SO}_3^-$  in strongly acidic media no dependence of the spectrum was found over the range pH 11.3 to 61.2%  $\text{HClO}_4$  (93). The first estimate of the potential of the  $\text{SO}_3^-/\text{SO}_3^{2-}$  couple was made by Anast and Margerum on the basis of the kinetics of oxidation of  $\text{SO}_3^{2-}$  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  $\text{SO}_3^-$  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  $\text{SO}_3^-/\text{SO}_3^{2-}$  couple, i.e., substantially greater than Huie and Neta's value. This recent result is based on an apparent electron transfer equilibrium between  $\text{SO}_3^-$  and  $\text{ClO}_2^-$  to form  $\text{SO}_3^{2-}$  and  $\text{ClO}_2$ . We question the validity of this method because the reaction of  $\text{ClO}_2$  with  $\text{SO}_3^{2-}$  seems to involve atom transfer (305a).

From Huie and Neta's potential of the  $\text{SO}_3^-/\text{SO}_3^{2-}$  couple other results can be derived. Thus  $\Delta_f G^0 = -426$  kJ/mol for  $\text{SO}_3^-$ . From Guthrie's estimate of  $\Delta_f G^0 = -402$  kJ/mol for aqueous  $\text{SO}_3$  (150) we obtain  $E^0 = 0.25$  V for the  $\text{SO}_3/\text{SO}_3^-$  couple. Direct measurement of the  $\text{SO}_3^{2-}/\text{S}_2\text{O}_6^{2-}$  half-cell potential (0.07 V) by use of a Au(I)-catalyzed electrode (95) establishes  $\Delta_f G^0 = -960$  kJ/mol for  $\text{S}_2\text{O}_6^{2-}$ . Thus the reaction



has an equilibrium constant of  $1 \times 10^{-19}$  M, and one-electron reduction of dithionite as in



has  $E^0 = -0.49$  V. These two values form the quantitative basis for the general observation that dithionite is quite inert. The substantially weaker bonding in dithionite may be due to the fact that the unpaired electron in  $\text{SO}_3^-$  resides in a  $\sigma$  orbital whereas in  $\text{SO}_2^-$  it is in a  $\pi$  orbital.

$\text{SO}_4^-$  is a well-established species that is an enormously powerful oxidant. Thus it can even oxidize  $\text{Cl}^-$ . There is some evidence that it can be protonated in acidic media (100), but the  $\text{p}K_a$  does not appear to be established. In a study of the decomposition of  $\text{S}_2\text{O}_8^{2-}$  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. Ebersson has estimated the potential for the  $\text{SO}_4^-/\text{SO}_4^{2-}$  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  $\text{HSO}_4^-$ , 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 Ebersson's estimates. The agreement may be fortuitous because there is little basis for expecting Shizuka's equation to apply to divalent anions.

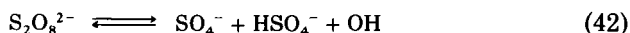
A firmer estimate can be obtained from the persulfate decomposition

data of Kolthoff and Miller (187), which can be extrapolated to yield a homolysis rate constant of  $1.1 \times 10^{-8} \text{ sec}^{-1}$  at  $25^\circ\text{C}$ . The recombination rate constant for  $\text{SO}_4^-$  is  $2k = 1.0 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$  (157). The ratio of these two rate constants yields a value for the homolysis equilibrium constant: i.e.,  $K_{\text{eq}} = 2.3 \times 10^{-17} \text{ M}$  for reaction (41).



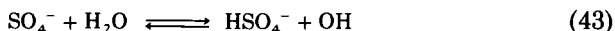
The tabulated  $\Delta_f G^\circ$  for  $\text{S}_2\text{O}_8^{2-}$  has changed substantially with the various editions of the NBS tables, but the newest value,  $-1114.9 \text{ kJ/mol}$ , leads to  $\Delta_f G^\circ = -510 \text{ kJ/mol}$  for  $\text{SO}_4^-$  and  $E^\circ = 2.43 \text{ V}$  for the  $\text{SO}_4^-/\text{SO}_4^{2-}$  couple. An additional result is the potential for direct one-electron reduction of persulfate:  $E^\circ = 1.45 \text{ V}$  for the  $\text{S}_2\text{O}_8^{2-}/(\text{SO}_4^-, \text{SO}_4^{2-})$  couple.

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



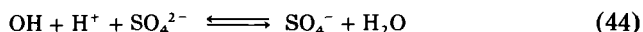
which continues to be defended by Fronaeus (131). The relative merits of the various proposals have been discussed in detail by Wilmarth and Haim (330). If Fronaeus' mechanism is correct then the potential derived above for the  $\text{SO}_4^-/\text{SO}_4^{2-}$  couple is still useful as a lower limit.

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



A forward rate constant of  $3 \times 10^3 \text{ sec}^{-1}$  has been reported for this reaction, although the authors caution that it may only be an upper limit (158). The reverse rate constant,  $1.6 \times 10^6 \text{ M}^{-1} \text{ sec}^{-1}$ , is relatively well established (121). An equilibrium constant of  $K_{\text{eq}} < 2 \times 10^{-3} \text{ M}$  is obtained from the ratio of these rate constants, and from NBS data and  $\Delta_f G^\circ$  for OH we derive  $\Delta_f G^\circ < -517 \text{ kJ/mol}$  for  $\text{SO}_4^-$  and  $E^\circ < 2.36 \text{ V}$  for the  $\text{SO}_4^-/\text{SO}_4^{2-}$  couple. The mild disagreement between these results and those obtained from homolysis of persulfate is not understood, but the fact that  $\text{Cl}^-$  is rapidly oxidized by  $\text{SO}_4^-$  although its  $E^\circ$  is  $2.41 \text{ V}$  favors the homolysis results.

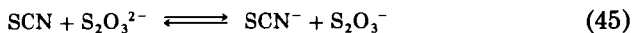
In yet another treatment Furholz and Haim obtain a value of  $2.6 \text{ V}$  for the  $\text{SO}_4^-/\text{SO}_4^{2-}$  couple (135). This result was obtained by using a value of  $10^3 \text{ M}^{-2}$  for the equilibrium



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  $\text{SO}_5^-$ , which is formed in the reaction of  $\text{SO}_3^-$  with  $\text{O}_2$ , as well as in the oxidation of  $\text{HSO}_5^-$  by OH (208). The state of protonation and related  $\text{p}K_a$  of "HSO<sub>5</sub>" is unknown, although Huie and Neta propose  $\text{p}K_a < 2$  (170). The fact that the radical is formed in the reaction with  $\text{O}_2$  with  $k = 1.5 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$  (170) suggests that the  $\Delta_r G^0$  for  $\text{SO}_5^-$  is less than that for  $\text{SO}_3^-$ , i.e., less than  $-426 \text{ kJ/mol}$ . Recent studies of the chemistry of  $\text{HSO}_5^-$  have established  $E^0 = 1.842 \pm 0.010 \text{ V}$  for the  $\text{HSO}_5^-/\text{HSO}_4^-$  couple (246), which gives  $\Delta_r G^0 = -638 \text{ kJ/mol}$  for  $\text{HSO}_5^-$ . Combination of this result with the above limit for  $\text{SO}_5^-$  (or  $\text{HSO}_5$ ) sets an absolute upper limit of 2.2 V for the  $\text{HSO}_5/\text{HSO}_5^-$  couple. In view of Ebersson's success in estimating the  $\text{SO}_4^-$  potential by using an estimated O-H homolysis energy (106), the same approach may be applied to  $\text{SO}_5^-$ . According to Benson, the peroxidic O-H bond enthalpy is  $377 \text{ kJ/mol}$  (44), while Steele and Appelman report  $\Delta_r H^0 = -798 \text{ kJ/mol}$  for aqueous  $\text{HSO}_5^-$  (296). These values lead to  $\Delta_r H^0 = -639 \text{ kJ/mol}$  for aqueous  $\text{SO}_5^-$ , or  $\Delta_r H^0 = -661 \text{ kJ/mol}$  for  $\text{HSO}_5$  (the assumption being made that  $\text{SO}_5^-$  and  $\text{SO}_4^{2-}$  have the same enthalpy of protonation). With the further crude assumption that  $S^0 = 188 \text{ J/K/mol}$  for  $\text{HSO}_5$  (the same as acetic acid), we obtain  $E^0 = 1.70 \text{ V}$  for the  $\text{HSO}_5/\text{HSO}_5^-$  couple. On the basis of studies of the reactions of  $\text{SO}_5^-$  with  $\text{I}_2^-$ , 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  $1.4 \pm 0.3 \text{ V}$  for the  $\text{HSO}_5/\text{HSO}_5^-$  couple and  $\Delta_r G^0 = -500 \pm 30 \text{ kJ/mol}$  for  $\text{HSO}_5$ .

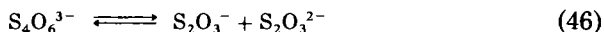
Thiosulfate ( $\text{S}_2\text{O}_3^{2-}$ ) can be oxidized to its radical,  $\text{S}_2\text{O}_3^-$ . In a study of the oxidations by coordination complexes, Wilmarth and co-workers assigned a potential of 1.35 V to the  $\text{S}_2\text{O}_3^-/\text{S}_2\text{O}_3^{2-}$  couple (331). Their assignment was derived by combining Schoneshofer's equilibrium constant ( $K_{\text{eq}} = 2.7 \times 10^4$ ) (269) for the reaction



with the potential previously derived for the  $\text{SCN}/\text{SCN}^-$  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,  $E^0 = 1.35 \text{ V}$  for the  $\text{S}_2\text{O}_3^-/\text{S}_2\text{O}_3^{2-}$  couple and  $\Delta_r G^0 = -392 \text{ kJ/mol}$  for  $\text{S}_2\text{O}_3^-$  are tentatively accepted.

In Schoneshofer's study of the  $\text{SCN}^-/\text{S}_2\text{O}_3^-$  system the radicals were

generated by oxidation of  $\text{SCN}^-$  with OH (269). In another of his studies the reaction of OH with  $\text{S}_2\text{O}_3^{2-}$  was employed (270). This study yielded a  $pK_a$  of 6.2 for  $\text{HS}_4\text{O}_6^{2-}$  and a value of  $K_{eq}$  less than  $10^{-6}$   $M$  for the reaction

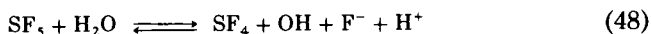


In a subsequent study Mehnert and co-workers reinvestigated this system and found that  $\text{S}_2\text{O}_3\text{OH}^{2-}$  is an intermediate in the reaction and that  $\text{S}_2\text{O}_3^-$  is generated only by decomposition of  $\text{S}_4\text{O}_6^{3-}$  as in reaction 46 with  $k = 2.5 \times 10^6 \text{ sec}^{-1}$  (213). If we assume a diffusion-controlled rate constant of  $2 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$  for the reverse process, then a value of  $1.3 \times 10^{-3} \text{ M}$  is obtained for the equilibrium constant, in contrast with Schoneshofer's result. This value of  $1.3 \times 10^{-3} \text{ M}$ , with use of the above value for  $\Delta_f G^0$  of  $\text{S}_2\text{O}_3^-$ , leads to  $\Delta_f G^0 = -931 \text{ V}$  for  $\text{S}_4\text{O}_6^{3-}$  and  $E^0 = 1.18 \text{ V}$  for the  $\text{S}_4\text{O}_6^{3-}/2\text{S}_2\text{O}_3^{2-}$  couple. By using NBS data for  $\text{S}_4\text{O}_6^{2-}$  a potential of  $-1.13 \text{ V}$  can be derived for the  $\text{S}_4\text{O}_6^{2-}/\text{S}_4\text{O}_6^{3-}$  redox couple.

Sulfur hexafluoride is reported to be reduced to the pentafluoride by the hydrated electron and that  $\text{SF}_5$  has a significant lifetime (29). A potential for the reaction



can be calculated by using the gas-phase thermochemical data for  $\text{SF}_5$  tabulated by Herron (164) and the assumption of equal hydration free energies for  $\text{SF}_6$  and  $\text{SF}_5$ . The result of these calculations is  $E^0 = 0.05 \text{ V}$  and  $\Delta_f G^0 = -822 \text{ kJ/mol}$  for aqueous  $\text{SF}_5$ . It has been proposed (19) that  $\text{SF}_5$  hydrolyzes as in



In a subsequent study (29) it was found that  $\text{SF}_5$  could account for the oxidizing properties and that there was no need to postulate reaction (48). With Herron's thermochemical data for  $\text{SF}_5$  and  $\text{SF}_4$  and the assumption of a hydration free energy of  $\text{SF}_4$  the same as that of  $\text{SF}_6$ , we calculate  $\Delta G^0 = 105 \text{ kJ/mol}$  for reaction (48), and thus conclude that this process will not occur. The oxidizing power of  $\text{SF}_5$  can be represented in reaction (49)



for which  $E^0 = 1.64 \text{ V}$  can be derived, which is consistent with the observation that  $\text{SF}_5$  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.

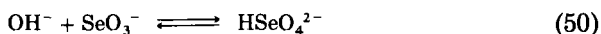
Radicals derived from  $SCN^-$  and  $CS_2$  are discussed in the section on carbon (Section VIII,A), except for the species  $XSCN^-$ , which are discussed in the relevant halogen sections.

## B. SELENIUM

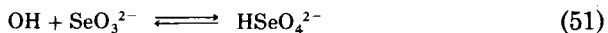
A direct investigation of the radicals derived from  $HSe^-$  was conducted in a pulse radiolysis study by Schoneshofer and co-workers (273). Among other things, they were able to determine  $pK_a$  values for  $H_2Se_2$  and  $HSe_2^-$  (1.7 and 9.3), the spectra of  $HSe$  and  $Se^-$ , and the dissociation 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



with  $K_{\text{eq}} = 0.78 M^{-1}$ . 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



by measuring the rates of the forward and reverse rates ( $K_{\text{eq}} = 4.8 \times 10^3 M^{-1}$ ) (181). With use of their previously determined value for  $\Delta_f G^0$  of OH they derived the following results:  $\Delta_f G^0 = -358 \text{ kJ/mol}$  for  $\text{HSeO}_4^{2-}$ , and  $\Delta_f G^0 = -202 \text{ kJ/mol}$  for  $\text{SeO}_3^{2-}$ . 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:  $E^0 = 1.68 \text{ V}$  for the  $\text{SeO}_3^-/\text{SeO}_3^{2-}$  couple. From the above results we calculate  $E^0 = -0.97 \text{ V}$  for the  $\text{HSeO}_4^-/\text{HSeO}_4^{2-}$  couple. It is notable that Se(V), unlike S(V), does not form an adduct with  $\text{O}_2$ .

$\text{SeO}_4^-$  has been reported in the reactions of OH and  $\text{CO}_3^{2-}$  with  $\text{SeO}_4^{2-}$  (298). Because  $\text{CO}_3^{2-}$  is not an especially strong oxidant ( $E^0 = 1.5 \text{ V}$ ), it may be assumed that  $\text{SeO}_4^-$  is also not an especially strong oxidant. A potential in the range of 1.4 V for the  $\text{SeO}_4^-/\text{SeO}_4^{2-}$  couple would not be unreasonable. The second-order decay of  $\text{SeO}_4^-$  is of some interest in that the preparation of  $\text{Se}_2\text{O}_8^{2-}$  has not been reported. A problematic issue is that  $\text{SeO}_4^-$  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  $\text{CO}_3^{2-}$  could oxidize  $\text{SeO}_4^{2-}$ .

Species analogous to those found in sulfur chemistry, such as  $\text{SeO}_2(\text{O}_2)^{2-}$ ,  $\text{SO}_3\text{Se}^{2-}$ ,  $\text{SeO}_3\text{S}^{2-}$ , and  $\text{Se}_x\text{S}_y\text{O}_6^{2-}$ , 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  $(\text{CdSe})_n/(\text{CdSe})_n^-$  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  $\text{TeO}_3^-$  and the rate constant for generation of this species by reaction of OH with  $\text{TeO}_3^{2-}$  have been reported (3, 4). Some information about Te(III) and Te(V) may also be

gleaned from two  $\gamma$ -radiolysis studies (90, 152). Leipoldt and co-workers report that in the absence of Os(VIII) catalysis,  $\text{TeO}_3^{2-}$  is not oxidized by  $\text{Mo(CN)}_8^{3-}$  (200), which implies that  $\text{TeO}_3^-$  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  $\text{PoH}$  (245) and some electrochemical evidence of  $\text{Po(III)}$  as an intermediate in the oxidation of  $\text{Po(II)}$  to  $\text{Po(IV)}$  in aqueous hydrochloric acid (24).

### VII. Group V

#### A. NITROGEN

The chemistry of atomic nitrogen,  $\text{N}(^4\text{S})$ , in aqueous solution has been investigated by bubbling a stream of active nitrogen into water (83). It was found that  $\text{N}(^4\text{S})$  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  $\text{N}(^4\text{S})$ .

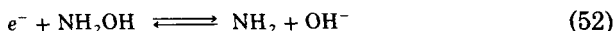
$\text{NH}_3^+$  is often generated by reduction of  $\text{NH}_2\text{OH}$  with  $\text{Ti(III)}$  (140), and it can be deprotonated to form  $\text{NH}_2$ . The associated  $\text{p}K_a$  has been reported variously as 3.65,  $6.7 \pm 0.2$ , and 2.3. The value of 6.7 has been widely cited (290), but it appears that the value of 2.3 is more likely correct (165). Endicott estimated a potential of 2.7 V for the  $\text{NH}_3^+/\text{NH}_3$  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  $\text{p}K_a$  of  $\text{NH}_3^+$ , for which the incorrect value of 6.7 was used. Another estimate of  $E^0 = 1.9$  V was also based on  $\text{p}K_a = 6.7$  (230). An estimate of  $E^0$  may be derived by using the value of  $\Delta_f G^0 = 199.8$  kJ/mol for  $\text{NH}_2$  in the gas phase, as listed in the JANAF tables. The assumption of a hydration free energy of  $-8$  kJ/mol for  $\text{NH}_2$  (a subjectively weighted average of  $\Delta_{\text{hyd}} G^0$  for  $\text{H}_2\text{S}$ ,  $\text{NH}_3$ , and half of  $\text{N}_2\text{H}_4$ ) leads to  $\Delta_f G^0 = 192$  kJ/mol for aqueous  $\text{NH}_2$  and, making use of  $\text{p}K_a = 2.3$  for  $\text{NH}_3^+$ , to  $\Delta_f G^0 = 179$  kJ/mol for aqueous  $\text{NH}_3^+$  and  $E^0 = 2.13$  V for the  $\text{NH}_3^+/\text{NH}_3$  couple.

It has been argued that  $\text{NH}_2$  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  $\text{NH}_2$  radical. The identity of the associated reaction was not specified (10), but it may reasonably be assumed to be  $\text{NH}_2/\text{NH}_2^-$ . An estimate of the  $E^0 = 0.25$  V for this couple may be obtained from the above  $\Delta_r G^0$  for  $\text{NH}_2$  and  $\Delta_r G^0 = 168$  kJ/mol for  $\text{NH}_2^-$  [derived from Pearson's estimate (240) of  $\text{p}K_a = 34$  for  $\text{NH}_3$ ]. From a similar calculation Pearson obtained  $E^0 = 0.22$  V (240). These latter estimates appear too low in view of the reactivity of  $\text{NH}_2$  relative to other free radicals. The disagreement may be due, perhaps, to the estimated  $\text{p}K_a$  of  $\text{NH}_3$ .

As noted above, reduction of hydroxylamine leads to formation of  $\text{NH}_2$ . No evidence has been presented in support of  $\text{NH}_2\text{OH}^-$  as an intermediate. The appropriate standard potential thus refers to the half-cell



No value of  $\Delta_r G^0$  for  $\text{NH}_2\text{OH}$  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  $\text{NH}_2\text{OH}/(\text{NH}_2, \text{OH}^-)$  couple. In the case of  $\text{NH}_3\text{OH}^+$  it is reported that reaction with the hydrated electron yields OH and  $\text{NH}_3$ . By use of thermochemical data from *Standard Potentials*,  $E^0$  for the  $\text{NH}_3\text{OH}^+ / (\text{NH}_3, \text{OH})$  couple is calculated as  $-0.58$  V.

Nitrene,  $\text{NH}$ , 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  $\text{NH}_2\text{OH}$ .

Oxidation of hydroxylamine by OH leads to  $\text{NHOH}$  (or its tautomer  $\text{NH}_2\text{O}$ ), which can be protonated; the  $\text{p}K_a$  of  $\text{NH}_2\text{OH}^+$  is reported as  $4.2 \pm 0.1$  (290). On the basis of its UV spectrum Simic and Hayon argued that  $\text{NHOH}$  was the predominant tautomer. There do not seem to be any estimates of  $E^0$  for the  $\text{NH}_2\text{OH}^+/\text{NH}_2\text{OH}$  couple in the literature. There is a report (283) of the oxidation of hydroxylamine by  $\text{IrCl}_6^{2-}$  in acidic solution for which the rate law is

$$-d[\text{IrCl}_6^{2-}]/dt = k[\text{IrCl}_6^{2-}][\text{NH}_3\text{OH}^+]/[\text{H}^+] \quad (53)$$

If it is assumed that this reflects a mechanism in which  $\text{NH}_2\text{OH}$  is oxidized, then the rate constant for electron transfer is  $7.3 \times 10^3 \text{ M}^{-1} \text{ sec}^{-1}$ . An upper limit of  $1 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$  for the reverse reaction establishes  $E^0 \leq 1.26$  V for the  $\text{NH}_2\text{OH}^+/\text{NH}_2\text{OH}$  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  $\text{Fe}(\text{CN})_6^{3-}$  (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  $196.8 \pm 0.1$  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  $\text{NO}^-$  has a triplet ground state, and the singlet state is  $6050\text{ cm}^{-1}$  (72 kJ/mol) higher in energy (168). It is argued that both singlet and triplet states of HNO (NOH) and of  $\text{NO}^-$  can be generated in aqueous solution (102). A  $\text{p}K_a$  of 4.7 was reported for "HNO" in a pulse radiolysis study in which  $\text{NO}^-$  was generated by reaction of  $e_{\text{aq}}^-$  with NO and "HNO" was generated by reaction of H with NO (147). It is unclear what electronic states are involved in this  $\text{p}K_a$  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  $\text{NO}^-$ . If equal hydration energies for  $^1\text{NO}^-$  and  $^3\text{NO}^-$  are assumed and entropy effects are neglected,  $\Delta_f G^0$  for aqueous  $^3\text{NO}^-$  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  $1.9 \times 10^{-3}$  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  $\text{NO}^-$  it is now possible to calculate  $E^0 = -0.35$  V for the  $\text{NO}/^1\text{NO}^-$  couple and  $E^0 = 0.39$  V for the  $\text{NO}/^3\text{NO}^-$  couple. This latter result is consistent with the suggestion that  $[\text{Ru}(\text{NH}_3)_6]^{2+}$  is capable of reducing NO to  $\text{NO}^-$  (5).

Equilibrium constants have been reported for the association of NO with  $\text{NO}^-$  and the association of the resulting  $\text{N}_2\text{O}_2^-$  with  $\text{H}^+$  (281). In principle it would be possible to calculate redox potentials involving  $\text{N}_2\text{O}_2^-$  and  $\text{HN}_2\text{O}_2$ , but because of the current uncertainty in the electronic state of  $\text{NO}^-$  in these reactions such a calculation is reserved for the future.

A hydrolyzed form of NO,  $\text{H}_2\text{NO}_2$ , has been detected in the reaction of  $e_{\text{aq}}^-$  with  $\text{NO}_2^-$ , and  $\text{p}K_a$  values have been determined for both deprotonation steps (144).  $\text{HNO}_2^-$  is also implicated in certain chemical reductions of  $\text{HNO}_2$  (251). All of these species appear to be unstable with respect to NO, but values  $\Delta_f G^0$  for them are not available.

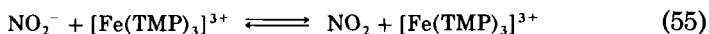
In strongly acidic media nitrous acid is in equilibrium with  $\text{NO}^+$ , and one pathway for reduction of nitrous acid is reduction of  $\text{NO}^+$  to  $\text{NO}$ . Likewise,  $\text{NO}$  is oxidized via  $\text{NO}^+$  in certain cases (252). The calculated potential of the  $\text{NO}^+/\text{NO}$  couple is dependent on  $\Delta_f G^\circ$  of  $\text{HNO}_2$  and the equilibrium constant for production of  $\text{NO}^+$ ; both of these parameters are somewhat uncertain. An early value of 1.45 V was reported in an electrochemical study of the  $\text{NO}/\text{HNO}_2$  equilibrium (266); an assumed value for the formation constant of  $\text{NO}^+$  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 ( $\Delta H^\circ = -44 \pm 2 \text{ kJ/mol}$ ) for hydrolysis of  $\text{NO}^+$  as given by the reaction



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  $\text{NO}^+$ . A value for  $\Delta_f H^\circ$  of 78 kJ/mol for aqueous  $\text{NO}$  can be derived from  $\Delta_f H^\circ$  of gaseous  $\text{NO}$  and its heat of hydration (328). These data lead to a value of  $-99 \text{ kJ/mol}$  for the standard enthalpy change of the  $\text{NO}^+/\text{NO}$  half-cell.

Direct oxidation of  $\text{NO}_2^-$  can yield  $\text{NO}_2$ , and  $\text{NO}_2$  derived from various sources is often reduced to  $\text{NO}_2^-$ . Rapid bimolecular disproportionation of  $\text{NO}_2$  in solution vitiates a simple electrochemical measurement of the potential for the  $\text{NO}_2/\text{NO}_2^-$  couple, but estimates have been reported on numerous occasions. Endicott (110) cited a value of 1.13 V for the  $(\text{H}^+, \text{NO}_2)/\text{HNO}_2$  couple, apparently taken from the data in Latimer (195). Berdnikov and Bazhin estimated a value of  $1.0 \pm 0.1 \text{ V}$  for the  $\text{NO}_2/\text{NO}_2^-$  couple by use of an estimated hydration energy of  $\text{NO}_2$  (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  $1.03 \pm 0.04 \text{ V}$ , which was based on an estimate of the solubility of  $\text{NO}_2$  (331). A value of 0.993 V estimated by Ram and Stanbury (251) was based on a measurement of the solubility of  $\text{NO}_2$ . This value was revised to 1.045 V by using revised data for  $\text{NO}_2^-$  (252). Finally, an experimental value of 1.04 V was obtained by measuring the forward and reverse rates of the reaction



and using the known potential of the  $\text{Fe}(\text{III})/\text{Fe}(\text{II})$  couple (252). These results bear out the conclusions in Schwartz and White's exhaustive

review of the solubility of  $\text{NO}_2$  (275), and they lead to  $\Delta_f G^\circ = 63 \text{ kJ/mol}$  for aqueous  $\text{NO}_2$ .

Bontempelli *et al.* studied the  $\text{NO}_2^+/\text{NO}_2$  couple in acetonitrile (54). A potential of 1.51 V can be derived for this couple in aqueous solution from the equilibrium fraction of  $\text{NO}_2^+$  present in dilute solutions of nitric acid in 68.3% sulfuric acid, the acidity function of that solvent, and the  $\text{p}K_a$  of aqueous  $\text{HNO}_3$ . The reactivity of this couple has been discussed by Eberson and Radner (108).

As with  $\text{NO}$ , Gratzel *et al.* have reported hydrolyzed forms of  $\text{NO}_2$ , i.e.,  $\text{H}_2\text{NO}_3$ ,  $\text{HNO}_3^-$ , and  $\text{NO}_3^{2-}$ , and the  $\text{p}K_a$  values that interrelate them: 4.8 and 7.5 (145). Because  $\text{H}_2\text{NO}_3$  and the others are unstable with respect to  $\text{NO}_2$ , we calculate  $\Delta_f G^\circ > -104 \text{ kJ/mol}$  for  $\text{NO}_3^{2-}$ . Thus  $\text{NO}_3^{2-}$  is a reducing agent, with  $E^\circ < -0.05 \text{ V}$  for the  $\text{NO}_3^-/\text{NO}_3^{2-}$  couple. Consistent with this estimate is the report that  $\text{NO}_3^{2-}$  rapidly reduces  $\text{O}_2$ , benzoquinone, and methyl viologen (126). Because methyl viologen has an  $E^\circ = -0.44 \text{ V}$  and the rate of electron transfer is  $3.3 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ , a potential less than  $-0.4 \text{ V}$  may be inferred for the  $\text{NO}_3^-/\text{NO}_3^{2-}$  couple on the basis that the reverse reaction can hardly be much faster. Thus  $\Delta_f G^\circ > -70 \text{ kJ/mol}$  for  $\text{NO}_3^{2-}$ .

$\text{NO}_3$  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  $E^\circ$  for the  $\text{NO}_3/\text{NO}_3^-$  couple as  $2.3 \pm 0.1 \text{ V}$  (45). This was obtained from gas-phase data and estimated hydration energies. A recent direct measurement of the equilibrium constant for the  $\text{NO}_2 + \text{NO}_3 \rightleftharpoons \text{N}_2\text{O}_3$  reaction in the gas phase (321) allows us to calculate a value of  $\Delta_f G^\circ = 123 \text{ kJ/mol}$  for  $\text{NO}_3$  in the gas phase. By using the same estimate of the hydration free energy as was used by Berdnikov and Bazhin (45), we obtain  $\Delta_f G^\circ = 131 \text{ kJ/mol}$  for aqueous  $\text{NO}_3$  and  $E^\circ = 2.49 \text{ V}$  for the  $\text{NO}_3/\text{NO}_3^-$  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  $\text{NO}_3$ , Neta and Huie estimated the potential to lie in the range 2.3–2.6 V (227). In summary,  $E^\circ$  for the  $\text{NO}_3/\text{NO}_3^-$  couple is not well established. A tentative value of 2.5 V is recommended along with the corresponding  $\Delta_f G^\circ = 131 \text{ kJ/mol}$  for  $\text{NO}_3$ .

Both  $\text{N}_2\text{O}_3$  and  $\text{N}_2\text{O}_3^{2-}$  are well-established species in aqueous solution (146). Akhtar *et al.* (5) have found that  $\text{N}_2\text{O}_3^{2-}$  is rapidly oxidized by  $[\text{Ru}(\text{NH}_3)_6]^{3+}$ , which suggests that  $\text{N}_2\text{O}_3^-$  may be a significant intermediate. Further studies on this possibility would be of interest.

The cation radical of hydrazine,  $\text{N}_2\text{H}_4^+$ , can be generated chemically

and pulse radiolytically. An upper limit of 0.94 V was calculated by Stanbury on the assumption that  $\text{Fe}(\text{CN})_6^{3-}$  oxidized  $\text{N}_2\text{H}_4$  via  $\text{N}_2\text{H}_4^+$  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  $3 \times 10^6 \text{ M}^{-1} \text{ sec}^{-1}$  was deduced, and this set an upper limit 0.73 V for the  $\text{N}_2\text{H}_4^+/\text{N}_2\text{H}_4$  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  $8.1 \pm 0.15 \text{ eV}$  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  $\Delta_r G^\circ = 129 \text{ kJ/mol}$  for  $\text{N}_2\text{H}_4^+$ . Hayon and Simic reported that  $\text{N}_2\text{H}_4^+$  has a  $\text{p}K_a$  of  $7.1 \pm 0.1$  (157a); accordingly  $\Delta_r G^\circ = 170 \text{ kJ/mol}$  for  $\text{N}_2\text{H}_3$ .

The major route to the azidyl radical,  $\text{N}_3$ , is through oxidation of azide. The potential of the  $\text{N}_3/\text{N}_3^-$  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  $[\text{Co}(\text{NH}_3)_5\text{N}_3]^{2+}$ . An estimate of 1.87 V was derived from the ctt's spectrum of  $\text{N}_3$ , but this was shown subsequently to be based on an erroneous assignment of the UV spectrum. An estimate of  $1.37 \pm 0.22 \text{ V}$  was obtained from the gas-phase proton affinity of  $\text{N}_3^-$ ; a recent redetermination of the electron affinity of  $\text{N}_3$  supports the value of  $\Delta_r H^\circ$  used in this calculation (172). In yet another estimate, based on the relative reactivity of  $\text{N}_3$  and other radicals, an  $E^\circ$  of 2.0 V was reported (189a). In the recent experimental studies cited above reliable results were obtained, with Ram and Stanbury finding  $E^\circ = 1.33 \pm 0.02 \text{ V}$  by measuring the forward and reverse rates for the oxidation of  $\text{N}_3^-$  by  $\text{IrCl}_6^{2-}$  (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  $\text{N}_3$  and  $\text{Br}^-$ , while the second was obtained electrochemically, with the assumption that the electrochemically produced  $\text{N}_3$  decayed by a second-order homogeneous process. Further confirmation of these results is reported in a mechanistic study of the reaction of  $\text{Br}_2 + \text{N}_3^-$ , in which the potential was assigned an upper limit of 1.365 V (6). Thus recommended values are  $E^\circ = 1.33 \text{ V}$  for the  $\text{N}_3/\text{N}_3^-$  couple and  $\Delta_r G^\circ = 477 \text{ kJ/mol}$  for aqueous  $\text{N}_3$ .

Unlike the halogens,  $\text{N}_3$  forms an adduct with its parent anion only weakly. The formation constant of  $\text{N}_6^-$  is reported as  $0.33 \text{ M}^{-1}$  (65), which leads to  $\Delta_r G^\circ = 828 \text{ kJ/mol}$ . It is conceivable that  $\text{N}_6^-$  could be oxidized to  $\text{N}_6$ , but it is not yet certain whether  $\text{N}_6$  is a bound state in aqueous solution (261). There is evidence that  $\text{HN}_3^-$  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



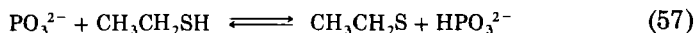
has a potential of 0.91 V. Thus  $NF_2$  is predicted to be a good oxidant but not strong enough to decompose water.

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  $Fe(CN)_6^{3-}$  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).

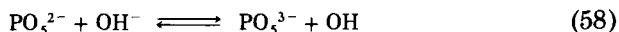
$\text{HPO}_3^-$  and  $\text{PO}_3^{2-}$  are relatively well understood. The  $pK_a$  of  $\text{HPO}_3^-$  was determined by Behar and Fessenden (41), and its value was refined to 5.75 by Schafer and Asmus (262). By working in strongly acidic media Davis *et al.* used ESR measurements to assign  $pK_a$  values of  $-1.7$  and  $0.0$  to  $\text{H}_3\text{PO}_3^+$  and  $\text{H}_2\text{PO}_3$ , respectively (93). Schafer and Asmus (263) obtained a value of 800 for the equilibrium constant of the reaction



From theoretical considerations and gas-phase data, Surdhar and Armstrong have obtained  $E^0 = 1.44$  V for the  $\text{CH}_3\text{CH}_2\text{S}/\text{CH}_3\text{CH}_2\text{SH}$  couple (304). Thus Schafer and Asmus' result is important in that it allows us to calculate the potential of the  $\text{PO}_3^{2-}/\text{HPO}_3^{2-}$  couple as 1.61 V. A value for  $\Delta_f G^0$  of  $-810$  kJ/mol for  $\text{HPO}_3^{2-}$  is cited in *Standard Potentials* (apparently Latimer's estimate), which leads to a value of  $\Delta_f G^0 = -655$  kJ/mol for  $\text{PO}_3^{2-}$ . From the  $pK_a$  of  $\text{HPO}_3^-$  we calculate  $\Delta_f G^0 = -688$  kJ/mol for  $\text{HPO}_3^-$  and  $E^0 = 1.26$  V for the  $\text{HPO}_3^-/\text{HPO}_3^{2-}$  couple.  $\text{HPO}_3^{2-}$  is protonated on P, but according to Gilbert *et al.*  $\text{HPO}_3^-$  is protonated on O (139), so the potential of 1.26 V does not correspond to a simple electron transfer.

The phosphate radical,  $\text{PO}_4^{2-}$ , which can be generated by photolysis or reduction of  $\text{P}_2\text{O}_8^{4-}$ , has been shown to engage in acid/base equilibria: thus  $pK_a = 5.7$  for  $\text{H}_2\text{PO}_4$  and  $pK_a = 8.9$  for  $\text{HPO}_4^-$  (209). No estimate seems to have been reported for the  $E^0$  of these radicals, but in view of the similar reactivity of  $\text{H}_2\text{PO}_4$  and  $\text{SO}_4^-$ ,  $\text{H}_2\text{PO}_4$  clearly is a strongly oxidizing species, with a potential near  $2.4 \pm 0.2$  V.

$\text{PO}_5^{2-}$  can be generated by reaction of  $\text{PO}_3^{2-}$  with  $\text{O}_2$  (262) or by oxidation of  $\text{HPO}_5^{2-}$  with  $\text{OH}$  (208). Schafer and Asmus determined a  $pK_a$  of 3.4 for  $\text{HPO}_5^-$  (262). Maruthamuthu and Neta reported that  $\text{PO}_5^{2-}$  oxidized  $\text{OH}^-$  with a rate constant of  $6.2 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$  (208). This observation is of interest in that it suggests that the reaction



is reversible. If so, then the potential of the  $\text{PO}_5^{2-}/\text{PO}_5^{3-}$  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  $\text{H}_2\text{AsO}_3^-$  rather than  $\text{AsO}_2^-$  (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  $\text{Mo(CN)}_8^{3-}$  proceeds near pH 9 with rate  $= k[\text{Mo(CN)}_8^{3-}][\text{As(OH)}_3][\text{OH}^-]$  with  $k = 1.5 \times 10^5 \text{ M}^{-2} \text{ sec}^{-1}$ ; the reaction was also found to be catalyzed by alkali metal ions (199). If it is assumed that the reaction occurs via  $\text{H}_2\text{AsO}_3^-$  ( $\text{p}K_a$  for  $\text{As(OH)}_3 = 9.2$ ), then the second-order rate constant for this species is  $3 \text{ M}^{-1} \text{ sec}^{-1}$ . If it is further assumed that the reaction generates  $\text{H}_2\text{AsO}_3$  and that the reverse reaction cannot exceed diffusion control, then  $E^0 < 1.31 \text{ V}$  for the  $\text{H}_2\text{AsO}_3/\text{H}_2\text{AsO}_3^-$  couple. Unfortunately, nothing is known of the  $\text{p}K_a$  values for As(IV).

As(VI) tentatively has been reported in a spin-trapping study of the reaction of  $\text{SO}_4^-$  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  $\text{Cl}^-$ -catalyzed paths (219), that the oxidation by  $\text{Fe(CN)}_6^{3-}$  is second order in  $[\text{Sb(III)}]$  (176), and that reduction of  $\text{SbCl}_6^-$  by  $\text{Fe}^{2+}$  and  $\text{Fe(CN)}_6^{4-}$  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  $\text{IrCl}_6^{3-}$ , 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

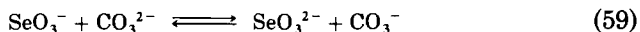
The selection of molecules and of depth of coverage appropriate in a discussion of the "inorganic" chemistry of carbon is a debatable issue. The present review takes the middle ground, with C—H and C—C bonds usually being inadmissible.



Reduction of CO by the hydrated electron might be expected to yield  $\text{CO}^-$  or HCO. However, by the use of pulse radiolysis Raef and Swallow demonstrated that the first detectable species is  $\text{HC(OH)}_2$  (250). Presumably  $\text{CO}^-$  undergoes very rapid hydrolysis. It is difficult to estimate accurately the energetics of the  $\text{CO}/\text{CO}^-$  couple, but the  $\text{CO}/\text{HCO}$  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  $\text{CO}/\text{HCO}$  couple. The chemistry of  $\text{HC(OH)}_2$  is beyond the scope of this review.

The reduction potential of the  $\text{CO}_2/\text{CO}_2^-$  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  $\text{CO}_2^-$ . Since  $\text{HCO}_2$  has a  $\text{p}K_a$  of 1.4 it is found that  $\Delta_f G^0$  for  $\text{HCO}_2$  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  $\text{HCO}_2/\text{HCO}_2^-$  couple is calculated as 1.36 V, but the mechanistic significance of this result is unclear because the site of protonation in  $\text{HCO}_2$  is not known.

The carbonate radical is generated by the reaction of OH or  $\text{SO}_4^-$  with  $\text{CO}_3^{2-}$ . In an early study Chen *et al.* generated the radical by flash photolysis of  $[\text{Co}(\text{NH}_3)_4\text{CO}_3]^+$  (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  $\text{p}K_a$  of  $9.6 \pm 0.3$  for  $\text{HCO}_3$  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  $\text{p}K_a$ , concluding that it lies between 7.0 and 8.2 (114). An early estimate of  $E^0 = 1.85$  V for the  $\text{CO}_3^-/\text{CO}_3^{2-}$  couple was presented without a clear basis (265). Henglein estimated the potential of the  $\text{CO}_3^-/\text{CO}_3^{2-}$  couple as 1.5 V on the basis that  $\text{Br}_2^-$  does not completely oxidize  $\text{CO}_3^{2-}$  while  $\text{CO}_3^-$  does oxidize  $\text{I}^-$  (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 Ebersson calculated  $E^0 = 2.14$  V on thermochemical grounds by estimating the bond energy of the O—H bond in  $\text{HCO}_3^-$  (106). With a potential this high,  $\text{Br}_2^-$  certainly would not oxidize  $\text{CO}_3^{2-}$  very quickly. A recent study showed that the reaction



proceeds with a rate constant of  $6.2 \times 10^6 \text{ M}^{-1} \text{ sec}^{-1}$  (181). If it is assumed that the reaction as written may be uphill and that it is driven

by other reactions of  $\text{CO}_3^-$ , then an upper limit to the reverse rate constant of  $10^{10} \text{ M}^{-1} \text{ sec}^{-1}$  is imposed by diffusion control. With the known  $E^0$  for the  $\text{SeO}_3^-/\text{SeO}_3^{2-}$  couple these calculations establish an upper limit of 1.87 V for the  $\text{CO}_3^-/\text{CO}_3^{2-}$  couple. Most likely the reverse rate constant is substantially less than  $10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ , 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  $\text{CO}_3^-/\text{CO}_3^{2-}$  couple is tentatively recommended, as is a  $\text{p}K_a$  of 7.6 for  $\text{HCO}_3^-$ . These results lead to  $\Delta_f G^0 = -383 \text{ kJ/mol}$  for  $\text{CO}_3^-$  and  $-426 \text{ kJ/mol}$  for  $\text{HCO}_3^-$ .

There is an intriguing report that  $\text{CO}_3^-$  can be oxidized to  $\text{CO}_3$  by triplet-state duroquinone in micellar solutions (264). From Benson's data we calculate  $\Delta_f G^0 = -171 \pm 16 \text{ kJ/mol}$  for  $\text{CO}_3$  in the gas phase (43). By applying a correction of 10 kJ/mol for hydration of  $\text{CO}_3$  we obtain  $E^0 = 2.3 \pm 0.2 \text{ V}$  for the  $\text{CO}_3/\text{CO}_3^-$  couple, which shows that  $\text{CO}_3$  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.  $\text{CF}_4$  appears to be unreactive, even with  $e_{\text{aq}}^-$ , but  $\text{CF}_3\text{Cl}$ ,  $\text{CF}_3\text{Br}$ , and  $\text{CF}_3\text{I}$  are reduced to  $\text{CF}_3$  (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  $\text{CF}_3$ . These calculations lead to  $E^0 = -1.45$ ,  $-0.67$ ,  $-0.58$ , and  $-0.65 \text{ V}$  for the  $\text{CF}_4/(\text{CF}_3, \text{F}^-)$ ,  $\text{CF}_3\text{Cl}/(\text{CF}_3, \text{Cl}^-)$ ,  $\text{CF}_3\text{Br}/(\text{CF}_3, \text{Br}^-)$ , and  $\text{CF}_3\text{I}/(\text{CF}_3, \text{I}^-)$  couples, respectively. The calculated potential for  $\text{CF}_4$  indicates that  $e_{\text{aq}}^-$  should be capable of reducing  $\text{CF}_4$ . 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  $\text{SF}_6$  by  $e_{\text{aq}}^-$  is clearly attributable to the enormous driving force for the reaction.

$\text{CCl}_3$  is generated by reduction of  $\text{CCl}_4$  (191, 202). The NBS tables do not supply a value of  $\Delta_f G^0$  for  $\text{CCl}_3$ , but the JANAF tables cite  $92 \pm 8 \text{ kJ/mol}$  for this species. With the same approximations as above for the  $\text{CF}_3$  systems, we calculate  $E^0 = -0.23 \text{ V}$  for the  $\text{CCl}_4/(\text{CCl}_3, \text{Cl}^-)$  couple. Despite the apparent ease of reduction of  $\text{CCl}_4$ , Koster and Asmus reported that it was not reduced by  $\text{CO}_2^-$  (191).

The chemistry of  $\text{CBr}_3$  has not been explored as extensively as that of its lighter congeners, but it is claimed to be formed in the reaction of  $e_{\text{aq}}^-$  with  $\text{CBr}_4$  (169). There has been substantial disagreement regarding  $\Delta_f H^0$  for  $\text{CBr}_4$  in the gas phase; the most recent value is  $83.9 \pm$

3.4 kJ/mol (50). A value of  $56.2 \pm 1.8$  kcal/mol has been reported for the  $\text{CBr}_3\text{--Br}$  bond dissociation enthalpy (179). By using the NBS value of 358 J/K/mol for the entropy of  $\text{CBr}_4$ , estimating an entropy of 324 J/K/mol for  $\text{CBr}_3$  by analogy with  $\text{BBr}_3$ , and assuming equal hydration free energies for  $\text{CBr}_4$  and  $\text{CBr}_3$ , we derive a value of  $E^0 = -0.07$  V for the  $\text{CBr}_4/(\text{CBr}_3, \text{Br}^-)$  couple.

The mixed halomethyl radicals  $\text{CF}_2\text{Cl}$  and  $\text{CFCl}_2$  were reported to be generated in the reductions of  $\text{CF}_2\text{Cl}_2$  and  $\text{CFCl}_3$  (27). The  $\Delta_f G^0$  values for  $\text{CF}_2\text{Cl}_2$  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  $\Delta_f H^0 = -665$  kcal/mol for  $\text{CF}_2\text{Cl}$  has been estimated (192). By estimating the entropy of  $\text{CF}_2\text{Cl}$  as 272 J/K/mol in analogy with  $\text{BF}_2\text{Cl}$ , and assuming equal hydration free energies for  $\text{CF}_2\text{Cl}_2$  and  $\text{CF}_2\text{Cl}$ , we find  $E^0 = -0.59$  V for the  $\text{CF}_2\text{Cl}_2/(\text{CF}_2\text{Cl}, \text{Cl}^-)$  couple. A similar calculation makes use of  $\Delta_f H^0 = -21.3$  kcal/mol for  $\text{CFCl}_2$  (320),  $S^0 = 272$  J/K/mol (by analogy with  $\text{BFCl}_2$ ), and  $\Delta_f G^0 = -249$  kJ/mol for  $\text{CFCl}_3$  (from the JANAF tables). The result is  $E^0 = -0.44$  V for the  $\text{CFCl}_3/(\text{CFCl}_2, \text{Cl}^-)$  couple.

A series of peroxy radicals can be generated by reaction of  $\text{O}_2$  with various trihalomethyl radicals (169). The most widely known of these is  $\text{CCl}_3\text{O}_2$ , but  $\text{CF}_3\text{O}_2$  and  $\text{CBr}_3\text{O}_2$  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  $\text{CS}_2$  Roebke and co-workers identified several derivative species (258).  $\text{SC(OH)S}$ , its conjugate base, and the  $\text{p}K_a$  (4.4) that relates them were determined from the reaction of  $\text{CS}_2$  with OH.  $\text{SCSH}$  and its  $\text{p}K_a$  (1.6) were determined by the reactions of  $e_{\text{aq}}^-$  and H with  $\text{CS}_2$ . 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  $\text{CN}^-$  by OH yields an adduct (39), and photolysis of  $\text{Mo(CN)}_8^{3-}$ , 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  $\text{SO}_4^-$  with  $\text{CN}^-$ , was detected as a spin adduct of  $\text{CH}_2=\text{NO}_2^-$  (82).

An estimate of  $E^0 = 1.9 \pm 0.3$  V for the  $\text{CN/CN}^-$  couple was obtained by Berdnikov and Bazhin by using a thermochemical cycle (45). Endicott obtained a value of  $\approx 2.8$  V for the  $\text{CN/HCN}$  couple, presumably by a similar method (110). When this is corrected by the  $\text{p}K_a$  of HCN a value of 2.26 V for the  $\text{CN/CN}^-$  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<sup>-</sup> 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  $435 \pm 10$  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<sup>-</sup> 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)<sub>2</sub><sup>-</sup> was reported in study of the reaction of  $e_{aq}^-$  with (CN)<sub>2</sub> (105). Its reactivity is essentially unknown. Various species have been suggested in the reaction of OH with CN<sup>-</sup> and HCN and of O<sup>-</sup> with CN<sup>-</sup>, 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<sup>-</sup>, Martins and Kemp estimated  $E^0 = 2.15$  V for the OCN/OCN<sup>-</sup> couple (207). Although this method gave an unreasonably high value for the SO<sub>3</sub><sup>-</sup>/SO<sub>3</sub><sup>2-</sup> couple, the high potential reported for the OCN/OCN<sup>-</sup> couple is consistent with the very high energy of the cts absorption of OCN<sup>-</sup>. 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<sub>2</sub>). 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<sup>-</sup> couple. As discussed in a recent paper by Alfassi *et al.* the hydroxyl radical adds to OCN<sup>-</sup>, 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<sub>2</sub>)<sub>3</sub><sup>-</sup> and NO<sub>2</sub> (248). An estimate of  $E^0$  for this couple can be made by using published values of  $\Delta_f H^0$  for C(NO<sub>2</sub>)<sub>4</sub> and HC(NO<sub>2</sub>)<sub>3</sub> 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<sub>2</sub>, entropies from the NBS tables, and  $pK_a = 0.06$  for HC(NO<sub>2</sub>)<sub>3</sub> (284). It is assumed that HC(NO<sub>2</sub>)<sub>3</sub> and C(NO<sub>2</sub>)<sub>4</sub> have identical heats of hydration and identical partial molar entropies. The outcome is  $E^0 = 0.93$  V for the C(NO<sub>2</sub>)<sub>4</sub>/(C(NO<sub>2</sub>)<sub>3</sub><sup>-</sup>, NO<sub>2</sub>) 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:



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 <i>et al.</i>  | Calculated from ctts <sup>a</sup> energy |
| 1.62      | 1978 | 232       | Nord <i>et al.</i>     | Kinetics, $SCN^- + [Fe(bpy)_3]^{3+}$     |
| 1.68      | 1978 | 232       | Nord <i>et al.</i>     | Kinetics, $SCN^- + [Fe(bpy)_3]^{3+}$     |
| 1.66      | 1980 | 294       | Stanbury <i>et al.</i> | Kinetics, relative to I                  |
| 1.60      | 1982 | 206       | Martins                | Kinetics, relative to I                  |
| 1.62      | 1986 | 277       | Schwarz and Bielski    | Relative to I                            |

<sup>a</sup> ctts, Charge-transfer-to-solvent band.

Association of SCN with  $\text{SCN}^-$  to form  $(\text{SCN})_2^-$  yields a species having a S-S bond (327). Baxendale *et al.* (36) first reported a value for the association constant of  $2 \times 10^5 \text{ M}^{-1}$ . This result was confirmed by Behar and co-workers (39a). In a recent study Elliot and Sopchyshyn obtained a value of  $1.1 \times 10^5 \text{ M}^{-1}$ , 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  $K_{\text{eq}} = 1.6 \times 10^5 \text{ M}^{-1}$  is adopted in this review, which establishes  $\Delta_f G^0 = 313 \text{ kJ/mol}$  for  $(\text{SCN})_2^-$ .

The above free energy for  $(\text{SCN})_2^-$  leads to  $E^0 = 1.32 \text{ V}$  for the  $(\text{SCN})_2^-/2\text{SCN}^-$  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  $\text{SCN}^-$  by  $[\text{Os}(\text{bpy})_3]^{3+}$ . An anomalous value of 1.25 V was calculated by Butler *et al.* on the basis of an old potential for  $\text{I}/\text{I}^-$  (64).

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

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

Another species,  $\text{SCNS}_2\text{O}_3^{2-}$ , was detected by Schoneshofer (269), and the equilibrium constant for its dissociation to SCN and  $\text{S}_2\text{O}_3^{2-}$  was measured as  $3.1 \times 10^{-8} \text{ M}$ . By use of our selected  $\Delta_f G^0$  for SCN a value of  $-315 \text{ kJ/mol}$  is calculated for  $\Delta_f G^0$  of  $\text{SCNS}_2\text{O}_3^{2-}$ . Furthermore,  $E^0 = 1.19 \text{ V}$  is calculated for the  $\text{SCNS}_2\text{O}_3^{2-}/(\text{SCN}^-, \text{S}_2\text{O}_3^{2-})$  couple.

Selenocyanate has been investigated by pulse radiolysis (21). These studies showed that OH reacts with  $\text{SeCN}^-$  to yield a transient which was identified as  $(\text{SeCN})_2^-$ . A potential of 0.9–1.0 V was estimated for the  $(\text{SeCN})_2^-/(2\text{SeCN}^-)$  couple by use of an empirical relationship between the one-electron and two-electron reduction potentials for  $\text{I}^-$ ,  $\text{Br}^-$ ,  $\text{Cl}^-$ , and  $\text{SCN}^-$ ; in applying the method, 0.42 V was adopted for the  $(\text{SeCN})_2^-/(2\text{SeCN}^-)$ , 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  $(\text{SeCN})_2^-/(2\text{SeCN}^-)$  couple is not well supported. An estimate of the potential of the  $\text{SeCN}/\text{SeCN}^-$  couple of 1.27 V was reported by Abdullah and Kemp (1). This result was based on Shizuka's equation that relates ctt energies and  $E^0$  values, and in view of the inaccurate result this method yields

for  $\text{SCN}^-$ , the present result for  $\text{SeCN}^-$  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  $\text{IrCl}_6^{2-}$  occurs with a second-order dependence on [thiourea], a complex pH dependence, and hints of copper catalysis (244). Oxidation by  $\text{Cu}(\text{me}_2\text{-phen})^{2+}$  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

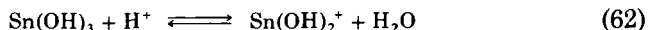
The free-radical chemistry of silicon is extremely limited. The only report appears to be a study of  $\text{SiO}_3^-$  generated by a reaction of  $\text{SO}_4^-$  (193). It was proposed that the species acted as an oxidant toward various organic species by undergoing H-atom transfer rather than electron transfer.

## C. GERMANIUM

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

## D. TIN

The existence of  $\text{Sn}(\text{I})$  may be inferred from reports of the reactions of H and  $e_{\text{aq}}^-$  with  $\text{SnO}_2^{2-}$ ,  $\text{SnF}_3^-$ , and certain complexes of  $\text{Sn}(\text{II})$  (14a, 14b). However, rather little is known of these species. The chemistry of  $\text{Sn}(\text{III})$  is better documented. As summarized by Cannon, this oxidation state is frequently found for intermediates in reactions of  $\text{Sn}(\text{II})$  with one-electron oxidants (77). Asmus *et al.* generated  $\text{Sn}(\text{III})$  in a pulse radiolysis study by reaction of OH with  $\text{Sn}(\text{II})$  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



with  $\text{p}K \approx 2.9 \pm 0.3$ . Shinohara *et al.* recently reported that UV photolysis of  $\text{Sn}(\text{IV})$  in chloride media generated  $\text{Sn}(\text{III})$  by elimination of Cl, and under similar conditions  $\text{Sn}(\text{II})$  photoreduced  $\text{H}^+$  to generate  $\text{Sn}(\text{III})$  (287). They found that the  $\text{Sn}(\text{III})$  so generated reduced  $\text{O}_2$  to

$\text{HO}_2$ , which indicates the substantial reducing power of  $\text{Sn(III)}$ . In an early report a value of 0.7 V was cited for the  $\text{Sn(III)/Sn(II)}$  couple, but no reference of basis for the value was provided (46).

### E. LEAD

Baxendale and Dixon estimated  $E^0 = -(1.1-1.5)$  V for the  $\text{Pb}^{2+}/\text{Pb}^+$  couple by estimating the hydration free energy of  $\text{Pb}^+$  (37). Breitenkamp *et al.* estimate  $E^0 = -1.0$  V on the basis that reduction of  $\text{Pb}^{2+}$  by  $\text{CH}_2\text{OH}$  is fairly slow (57). From this they deduced a potential of  $\approx -0.9$  V for reduction of  $\text{Pb}^+$  to atomic Pb. These latter potentials imply that the disproportionation of  $\text{Pb}^+$  is not strongly driven. Nevertheless, Breitenkamp *et al.* reported a rate constant of  $1.7 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$  for the second-order decay of  $\text{Pb}^+$ . The potential of  $-1.0$  V for the  $\text{Pb}^{2+}/\text{Pb}^+$  couple leads to  $\Delta_f G^0 = 72 \text{ kJ/mol}$  for  $\text{Pb}^+$ .

In alkaline media  $\text{Pb(II)}$  is reduced to a hydrolyzed  $\text{Pb(I)}$  species, and in nonalkaline media at high  $\text{Pb}^{2+}$  concentrations,  $\text{Pb}^+$  reacts to form  $\text{Pb}_2^{3+}$  (300). By investigating the pulse radiolysis of  $\text{Pb(II)}$  in concentrated chloride solutions Sukhov and Ershov were able to identify  $\text{PbCl}$  and to set an upper limit to the association constant of  $0.5 \text{ M}^{-1}$  (302).

Lead (III) has been generated by oxidation of  $\text{Pb(II)}$  with  $\text{OH}$  (300). On the basis that  $\text{Pb}^{2+}$  is oxidized by  $\text{OH}$  but not by  $\text{HO}_2$  it was suggested that the  $\text{Pb}^{3+}/\text{Pb}^{2+}$  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  $\text{Pb}^{4+}/\text{Pb}^{3+}$  couple, and from the known  $\text{Pb}^{4+}/\text{Pb}^{2+}$  potential he derived  $E^0 = 1.6 \pm 0.3$  V for the  $\text{Pb}^{3+}/\text{Pb}^{2+}$  couple (115). Sukhov and Ershov (302) cite their prior paper (300) as the source of the value for  $\text{p}K_a \approx 4$  for  $\text{Pb}^{3+}$ ; however, the cited paper does not report the  $\text{p}K_a$ .

From experiments in chloride-containing media Sukhov and Ershov (302) found evidence for  $\text{PbCl}^{2+}$ , which is formed with an association constant of  $4 \times 10^2 \text{ M}^{-1}$ . Gogolev and co-workers also investigated  $\text{Pb(III)}$  in hydrochloric acid solutions (141, 143). They found evidence for at least two chloro complexes, and noted that the  $\text{Pb(IV)/Pb(III)}$  couple is strong enough to oxidize  $\text{Cl}_2^-$ ; i.e.,  $E^0 > 0.7$  V.

## IX. Group III

### A. BORON

Borohydride is rapidly oxidized by  $\text{N}_3$ ,  $\text{Br}_2^-$ , and  $(\text{SCN})_2^-$  (166). A UV/visible spectrum of the intermediate was obtained and attributed to  $\text{BH}_4$ . It is not obvious to this writer that the species observed could



not be  $\text{BH}_3^-$ . The weaker oxidant,  $\text{Fe}(\text{CN})_6^{3-}$ , does not oxidize  $\text{BH}_4^-$ , but rather its hydrolysis product,  $\text{BH}_3\text{OH}^-$  (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  $\text{Al}^{2+}$ , 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  $\text{Ga}^{3+}/\text{Ga}^{2+}$  and  $\text{Ga}^{2+}/\text{Ga}$  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 " $\text{GaCl}_2$ " in aqueous solution. It is now known that the compound under investigation was  $\text{Ga}[\text{Ga}^{\text{III}}\text{Cl}_4]$ , 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  $e_{\text{aq}}^-$ , and that  $\text{Ga}^{2+}$  is hydrolyzed with  $\text{p}K_a > 3.3$ . They also identified  $\text{Ga}(\text{OH})_6^{4-}$  in alkaline media. On the basis of the reactivity of  $\text{Ga}^{2+}$  with organic radicals they suggested that Ga(II) is a reasonably good oxidant.

## D. INDIUM

$\text{In}^+$  is a species of limited stability, but, as discussed in *Standard Potentials*, there is a fairly reliable value of  $-0.126$  V for the  $\text{In}^+/\text{In}$  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  $\text{In}^+/\text{In}$  couple. To our knowledge homogeneous reduction of  $\text{In}^+$  has not yet been reported.

Latimer's discussion of  $\text{In}^{2+}$  (195), like that of  $\text{Ga}^{2+}$ , is unreliable because it was based on the incorrect belief that  $\text{InCl}_2$  is a compound of In(II). In their study of the chemistry of aqueous  $\text{In}^+$ , Taylor and Sykes found that  $\text{In}^+$  does not reduce  $\text{Cr}^{3+}$ , and thus they estimated  $E^0 > -0.41$  V for the  $\text{In}^{2+}/\text{In}^+$  couple (311). On the other hand, they found

that  $\text{In}^+$  reacts with  $\text{O}_2$  with a rate constant of  $1.7 \times 10^3 \text{ M}^{-1} \text{ sec}^{-1}$  and with  $\text{FeOH}^{2+}$  with  $k = 1.1 \times 10^3 \text{ M}^{-1} \text{ sec}^{-1}$  (312). These observations suggest that  $E^0$  is probably less than 0.4 V for the  $\text{In}^{2+}/\text{In}^+$  couple, and thus  $\Delta_f G^0$  for  $\text{In}^{2+}$  is bracketed between  $-50$  and  $+26 \text{ kJ/mol}$ . Likewise,  $E^0$  for the  $\text{In}^{3+}/\text{In}^{2+}$  couple must lie between  $-0.50$  and  $-1.30 \text{ V}$ . Sukhov and Ershov reported that  $\text{In}^{3+}$  reacted undetectably slowly with  $\text{CO}_2^-$  and  $\text{H}$  (301), which suggests that the potential of the  $\text{In}^{3+}/\text{In}^{2+}$  couple may be closer to the value of  $-1.30 \text{ V}$ . In the first of two pulse radiolysis studies of  $\text{In}^{3+}$  it was reported that  $\text{In}^{2+}$  has a  $\text{p}K_a > 5.0$  (301); in the second study it was reported that  $\text{p}K_a = 4.5 \pm 0.2$ , 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.

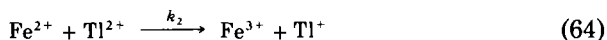
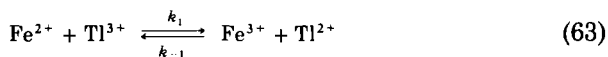
### E. THALLIUM

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

Cercek and co-workers reported that atomic thallium combines with  $\text{Tl}^+$  to form  $\text{Tl}_2^+$  with an association constant of  $2.3 \times 10^3 \text{ M}^{-1}$  (79). Schwarz and Dodson (279) recently cited unpublished data that suggest a value of  $160 \text{ M}^{-1}$ . By using the result of Cercek *et al.* we calculate  $\Delta_f G^0 = 109 \text{ kJ/mol}$  for  $\text{Tl}_2^+$ , and  $E^0 = -1.80 \text{ V}$  for the  $2\text{Tl}^+/\text{Tl}_2^+$  couple. Likewise, Butler and Henglein calculated  $E^0 = -1.7 \text{ V}$  (63). Froben *et al.* found that in the gas phase diatomic thallium is weakly bound with bond enthalpy of  $41 \text{ kJ/mol}$  at  $0 \text{ K}$  (130). These workers measured the Raman spectrum of  $\text{Tl}_2$  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  $\Delta_f G^0 = 251 \text{ kJ/mol}$  for  $\text{Tl}_2$  in the gas phase, and the assumption of a free energy of hydration of  $-3 \text{ kJ/mol}$  (that of  $\text{I}_2$ ) leads to  $\Delta_f G^0 = 248 \text{ kJ/mol}$  for aqueous  $\text{Tl}_2$ . Thus  $E^0 = -1.44 \text{ V}$  for the  $\text{Tl}_2^+/\text{Tl}_2$  couple. The value of  $E^0 = -1.5 \text{ V}$  reported by Butler and Henglein (63) rests upon an older value for the dissociation energy of  $\text{Tl}_2$ .

Experimental determinations of the redox potentials involving  $\text{Tl}^{2+}$  were reported in two concurrent independent publications in 1974. In one of them, by Falcinella *et al.*,  $\text{Tl}^{2+}$  was generated by flash photolysis

of Tl(III) (118). These workers measured the rate of reduction of  $\text{Tl}^{2+}$  by  $\text{Co}^{2+}$ . 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  $\text{Co}^{3+}$ , they obtained  $E^0 = 2.22 \pm 0.05$  V for the  $\text{Tl}^{2+}/\text{Tl}^+$  couple. They also measured the rate of oxidation of  $\text{Tl}^{2+}$  by  $\text{Fe}^{3+}$  and by similar argument derived  $E^0 = 0.33 \pm 0.05$  V for the  $\text{Tl}^{3+}/\text{Tl}^{2+}$  couple. From these two potentials they derived the potential of the  $\text{Tl}^{3+}/\text{Tl}^+$  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  $\text{Tl}^{2+}$  (278). They measured the rate of reduction of  $\text{Tl}^{2+}$  by  $\text{Fe}^{2+}$ . They also repeated prior studies of the oxidation of  $\text{Fe}^{2+}$  by  $\text{Tl}^{3+}$  under conditions appropriate to the pulse radiolysis work (1 M  $\text{HClO}_4$ ). This reaction has the mechanism



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  $\text{Tl}^{3+}/\text{Tl}^{2+}$  couple. Combination of this result with the standard potential for the  $\text{Tl}^{3+}/\text{Tl}^+$  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  $\text{Fe}^{2+}$ -induced exchange between  $\text{Tl}^{3+}$  and  $\text{Tl}^+$  (98). He measured  $k_2/(k_1 k_{\text{III}})$  and  $k_1/k_{\text{III}}$ , where  $k_{\text{III}}$  is the rate constant of electron exchange between  $\text{Tl}^{3+}$  and  $\text{Tl}^{2+}$ . He then used independently determined values of  $k_1$  and  $k_{\text{III}}$  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  $\text{Tl}^{3+}/\text{Tl}^{2+}$  couple, and with the  $\text{Tl}^{3+}/\text{Tl}^+$  potential he obtained  $E^0 = 2.20$  V for the  $\text{Tl}^{2+}/\text{Tl}^+$  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  $\text{Tl}^{2+}$ . In the first report a  $\text{p}K_a$  of  $4.6 \pm 0.2$  was determined for  $\text{Tl}^{2+}$  (238). In the second report the first was confirmed, with  $\text{p}K_a = 4.65$ ; in addition, the  $\text{p}K_a (= 7.7 \pm 0.2)$  of  $\text{TlOH}^+$  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  $\text{Tl}^{3+}/\text{Tl}^{2+}$  couple; i.e., not significantly different. Schwarz and Dodson (279) recently pointed out that  $\text{Tl}^{2+}$  is in

equilibrium with  $\text{OH} + \text{Tl}^+$ ; correcting for this effect leads to  $\text{p}K_a = 4.72$  for  $\text{Tl}^{2+}$ .

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

Association of  $\text{Tl}(\text{II})$  with chloride has been studied by Dodson and Schwarz (99). They determined stability constants of  $6.2 \times 10^4$ ,  $1.9 \times 10^3$ , and  $13 M^{-1}$  for  $\text{TlCl}^+$ ,  $\text{TlCl}_2$ , and  $\text{TlCl}_3^-$ , respectively. The corresponding free energies of formation are 27,  $-123$ , and  $-260$  kJ/mol. NBS data for the  $\text{Tl}(\text{III})$  chlorides permit calculation of  $E^0 = 0.14$  V for the  $\text{TlCl}_2^+/\text{TlCl}^+$  couple,  $E^0 = 0.00$  V for the  $\text{TlCl}_2^+/\text{TlCl}_2$  couple, and  $E^0 = -0.15$  V for the  $\text{TlCl}_3/\text{TlCl}_3^-$  couple. Finally, by using NBS data for the  $\text{Tl}(\text{I})$  chlorides we calculate  $E^0 = 2.01$  V for the  $\text{TlCl}^+/\text{TlCl}$  couple and  $E^0 = 1.79$  V for the  $\text{TlCl}_2/\text{TlCl}_2^-$  couple.

## X. Group II

### A. ZINC, CADMIUM, AND MERCURY

$\text{Zn}^+$  is a recognized species in aqueous solution (69). The only known method to generate it is by reduction of  $\text{Zn}^{2+}$  with  $e_{\text{aq}}^-$ . The first estimate of the  $\text{Zn}^{2+}/\text{Zn}^+$  potential was performed by Baxendale and Dixon (37) by use of thermochemical cycles. This involved an estimate of the hydration energy of  $\text{Zn}^+$ , 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  $\text{Zn}^+$  is the same as that of  $\text{Zn}^{2+}$ , 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  $\text{Cu}^+$ , 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  $e_{\text{aq}}^-$  with  $\text{Zn}^{2+}$  (14). In view of the

general failure of  $e_{\text{aq}}^-$  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  $\text{Zn}^+$  with  $[\text{Co}(\text{NH}_3)_6]^{3+}$  (225). In this calculation it was assumed that the self-exchange rate constant of the  $\text{Zn}^{2+}/\text{Zn}^+$  couple was somewhere between  $10^0$  and  $10^9 \text{ M}^{-1} \text{ sec}^{-1}$ , which accounts for the large uncertainty on  $E^0$ . Since the time of that publication the self-exchange rate constant of the  $[\text{Co}(\text{NH}_3)_6]^{3+/2+}$  has been revised from  $3 \times 10^{-12}$  to  $8 \times 10^{-6} \text{ M}^{-1} \text{ sec}^{-1}$  (40°C) (154), which would shift the potential to  $-1.6 \pm 0.4$  V. It is clear that the potential is not known with great certainty. Because  $e_{\text{aq}}^-$  does reduce  $\text{Zn}^+$ , the potential must be greater than  $-2.87$  V, and because  $\text{Zn}^+$  reduces  $[\text{Ru}(\text{bpy})_3]^{2+}$ ,  $E^0$  must be less than  $-1.3$  V (214). A provisional value of  $-1.6$  V is recommended for the  $\text{Zn}^{2+}/\text{Zn}^+$  couple, and, correspondingly,  $\Delta_r G^0 = 7 \text{ kJ/mol}$  for  $\text{Zn}^+$ . If it is assumed that the neutral zinc atom has a hydration free energy of  $10 \text{ kJ/mol}$ , then  $\Delta_r G^0$  is  $105 \text{ kJ/mol}$  for atomic zinc, and  $E^0$  for the  $\text{Zn}^+/\text{Zn}$  couple is  $-1.01$  V. Thus  $\text{Zn}^+$  is expected to disproportionate, as it does ( $k = 3.5 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$ ) (249).

In alkaline media it is reported that the reaction of  $e_{\text{aq}}^-$  with  $\text{Zn}(\text{II})$  is reversible and that the  $\text{Zn}(\text{I})$  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  $\text{p}K_{\text{a}} = 7-9$  for  $\text{Zn}^+$  (117).

$\text{Cd}^+$  is generally regarded as a weaker reducing agent than  $\text{Zn}^+$ . Baxendale and Dixon estimated the  $\text{Cd}^{2+}/\text{Cd}^+$  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  $e_{\text{aq}}^-$  (14), and Navon and Meyerstein obtained  $E^0 = -1.8 \pm 0.4$  V by applying Marcus theory to the reaction of  $\text{Cd}^+$  with  $[\text{Co}(\text{NH}_3)_6]^{3+}$  (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  $\text{Cd}^{2+}$  by  $\text{CO}_2^-$  (68) and the rapid reduction of  $[\text{Ru}(\text{bpy})_3]^{2+}$  by  $\text{Cd}^+$  (214). A tentatively recommended value of  $E^0$  is  $-1.4$  V for the  $\text{Cd}^{2+}/\text{Cd}^+$  couple, and thus  $\Delta_r G^0 = 58 \text{ kJ/mol}$  for  $\text{Cd}^+$ . The assumption of a hydration free energy of  $10 \text{ kJ}$  for the cadmium atom gives  $\Delta_r G^0 = 87 \text{ kJ/mol}$  for aqueous Cd and hence  $E^0 = -0.31$  V for the  $\text{Cd}^+/\text{Cd}$  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  $\text{Cd}^{2+}/\text{Cd}^+$  and it also had an arithmetic error.

Our recommended values place  $\text{Cd}^+$  as a weaker reducing agent than  $\text{Zn}^+$ , in accord with common sentiment. It is expected that both species should be quite reactive and that  $\text{Zn}^+$  should easily reduce  $\text{Cd}^+$ . 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  $\text{Zn}^+$  but like  $\text{Hg}^+$ ,  $\text{Cd}^+$  rapidly dimerizes to form  $\text{Cd}_2^{2+}$  (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.*,  $\text{Cd}^+$  and  $\text{Zn}^+$  react with  $\text{N}_2\text{O}$  to form  $\text{CdO}^+$  and  $\text{ZnO}^+$ , respectively (71). These species are reported to oxidize  $\text{Br}^-$  and  $\text{I}^-$  to  $\text{Br}_2^-$  and  $\text{I}_2^-$ , but  $\text{Cl}^-$  is unreactive. From this we may infer that these species are good oxidants with  $E^0 > 1.9$  V.

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

Unlike zinc(I) and cadmium(I), mercury(I) is stable and exists as  $\text{Hg}_2^{2+}$ . In a very early report, Cartledge calculated the dissociation constant to form  $\text{Hg}^+$  as  $10^{-31}$  M by estimating the hydration energy of  $\text{Hg}^+$  (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  $\text{Hg}_2^{2+}/\text{Hg}^+$  couple as 0.00 V. From his calculations we find  $\Delta_r G^0 = 165$  kJ/mol for  $\text{Hg}^+$ . Ershov, in his review (115), estimated  $E^0 = -1.4 \pm 0.3$  V for the  $\text{Hg}_2^{2+}/\text{Hg}^+$  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  $(\text{Hg}^+, \text{Hg}_2^{2+})/\text{Hg}_2^{2+}$  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  $\text{Hg}^+/\text{Hg}$  couple is 1.33 V, and it is  $-0.50$  V for the  $\text{Hg}_2^{2+}/(\text{Hg}, \text{Hg}^+)$  couple. Fujita *et al.* reported in a pulse radiolysis study of  $\text{HgO}$  that the  $pK_a$  of  $\text{Hg}^+$  is 5.1 (132). Thus  $\Delta_r G^0 = -43$  kJ/mol for  $\text{HgOH}$ , and  $E^0 = -0.09$  V for the  $\text{HgOH}^+/\text{HgOH}$  couple. It would be good to have experimental confirmation of these calculations. Qualitatively, the high potential of the  $(\text{Hg}_2^{2+}, \text{Hg}^+)/\text{Hg}_2^{2+}$  couple is consistent with the slow kinetics of oxidation of  $\text{Hg}_2^{2+}$  by  $[\text{Ru}(\text{bpy})_3]^{3+}$  and related complexes (156).

There is a disagreement regarding the mechanism of decay of  $\text{Hg}^+$ . Faraggi and Amozig claim that  $\text{Hg}^+$  undergoes a bimolecular recombination to give  $\text{Hg}_2^{2+}$  (119), while Fujita *et al.* claim that disproportionation occurs to give  $\text{Hg}$  and  $\text{Hg}_2^{2+}$ , which then combine to form  $\text{Hg}_2^{2+}$  (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  $\text{Hg(I)}$  is acidic, its decay should be pH dependent.

The species  $\text{HgCl}$ ,  $\text{HgBr}$ ,  $\text{HgI}$ ,  $\text{HgSCN}$ , and  $\text{HgCN}$  have been generated by reaction of  $e_{\text{aq}}^-$  with  $\text{HgX}_2$ . 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  $\text{C}(\text{NO}_2)_4$  and *p*-benzoquinone, which implies that they are good reducing agents, and they form adducts with  $\text{O}_2$  (175).

## B. THE ALKALI EARTHS

The alkali earths are somewhat problematic. As discussed in *Standard Potentials*, the experimental evidence in favor of  $\text{Be(I)}$  is substantial. There is some evidence that the species is  $\text{Be}_2^{2+}$ , 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  $\text{Mg}^+$ , and the existence of even this species appears dubious. Perrault cites three estimates of  $E^0$  for the  $\text{Mg}/\text{Mg}^+$  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  $\text{Mg}^+$  in *Standard Potentials*; this requires a potential of  $-2.054$  V for the  $\text{Mg}^{2+}/\text{Mg}^+$  couple. Such a potential might well be taken in support of the existence of  $\text{Mg}^+$ . We note, however that the cited  $\Delta_f H^0$  requires a hydration enthalpy of  $\text{Mg}^+$  some 150 kJ more exothermic than that of  $\text{Li}^+$ ! A more reasonable although rough estimate of  $E^0$  for the  $\text{Mg}^{2+}/\text{Mg}^+$  couple was obtained by Baxendale and Dixon by using NBS data for the enthalpy of  $\text{Mg}^+$  in the gas phase and assuming an entropy and a hydration enthalpy the same as that of  $\text{Na}^+$  (37). This leads to  $E^0 = -4.87$  V for the  $\text{Mg}^{2+}/\text{Mg}^+$  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

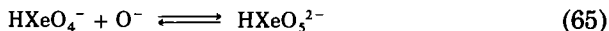
A casual look at *Standard Potentials* shows that the alkali metals are strong reducing agents. The weakest of these is Na with  $E^0 = -2.713$  V. The hydrated electron is a stronger reducing agent than this, which might suggest that it could reduce  $\text{Na}^+$ . However, the tabulated potentials 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  $\text{M}^+ - e_{\text{aq}}^-$  adducts has been reviewed by Buxton and Sellers (69).

## XII. The Rare Gases

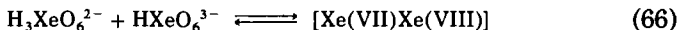
The thermochemistry of the rare gases and their compounds is discussed in *Standard Potentials*. The only aqueous free radical mentioned in that account is XeF, which is assigned a value of 46.0 kJ/mol for its standard free energy of formation. The associated redox couples are  $\text{XeF}_2/(\text{XeF}, \text{F}^-)$  and  $\text{XeF}/(\text{Xe}, \text{F}^-)$ , 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  $\text{Ti}^{3+}$  by  $\text{XeF}_2$  induces vinyl polymerization.

In an extensive study of the radiolysis and photolysis of  $\text{XeO}_3$ ,  $\text{HXeO}_4^-$ , and  $\text{HXeO}_6^{3-}$ , Klaning *et al.* identified a number of free radicals (185). Reaction of  $\text{XeO}_3$  with  $e_{\text{aq}}^-$  is claimed to give  $\text{HXeO}_3$ , although a rationale for this composition rather than  $\text{XeO}_3^-$  was not presented. It is suggested that OH adds to  $\text{XeO}_3$  to form  $\text{HOOXeO}_2$ , and that, because the reaction proceeds,  $\Delta_r G^0 < 550$  kJ/mol for  $\text{HOOXeO}_2$ . From the relationship  $\Delta_r G^0(\text{HOOXeO}_2) - \Delta_r G^0(\text{HXeO}_3) = \Delta_r G^0(\text{H}_2\text{O}_2) - \Delta_r G^0(\text{H}_2\text{O})$  they derive  $\Delta_r G^0 < 450$  kJ/mol for  $\text{HXeO}_3$ , and hence we find  $E^0 > 0.67$  V for the  $\text{XeO}_3/\text{HXeO}_3$  couple. On the other hand,  $\text{XeO}_3$  cannot be a very powerful one-electron oxidant in view of its slow oxidations of  $\text{Pu}^{3+}$  and  $\text{Mn}^{2+}$ .

Klaning *et al.* (185) suggest that there are two forms of Xe(VII). One,  $\text{HXeO}_5^{2-}$ , is formed by addition of OH and  $\text{O}^-$  to  $\text{HXeO}_4^-$  (the species formed from  $\text{XeO}_3$  in base); the other,  $\text{H}_3\text{XeO}_6^{2-}$ , arises from  $e_{\text{aq}}^-$  reacting with  $\text{HXeO}_6^{3-}$ . The two species seem to be chemically indistinguishable. They were able to determine forward and reverse rate constants for the reaction



from which they derive  $K_{\text{eq}} \approx 5 \times 10^4 \text{ M}^{-1}$  and hence  $\Delta_r G^0 = 420$  kJ/mol for  $\text{HXeO}_5^{2-}$ . 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  $\Delta_r G^0 = 180$  kJ/mol for  $\text{H}_3\text{XeO}_6^{2-}$ . The  $pK_a$  values for various degrees of protonation of the two Xe(VII) states were estimated by chemical analogy. Finally, for the reaction

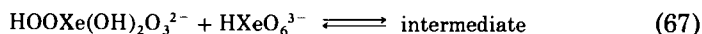


they determined  $K_{\text{eq}} = 1600 \text{ M}^{-1}$ . Because the state of hydration of the mixed-valence species is unknown, no free energy could be assigned.

Formal oxidation of  $\text{HXeO}_6^{3-}$  by OH was proposed to occur by



addition to form  $\text{HOOXe}(\text{OH})_2\text{O}_3^{2-}$ . By use of the relationship  $\Delta_f G^0[\text{HOOXe}(\text{OH})_2\text{O}_3^{2-}] - \Delta_f G^0(\text{HXeO}_5^{2-}) = \Delta_f G^0(\text{H}_2\text{O}_2) - \Delta_f G^0(\text{H}_2\text{O})$ , they derived  $\Delta_f G^0 = 280 \text{ kJ/mol}$  for  $\text{HOOXe}(\text{OH})_2\text{O}_3^{2-}$ . It was found that association occurred as in



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  $K_{\text{eq}} > 1 \times 10^3 \text{ M}^{-1}$  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  $\text{Xe}_2^+$ , which is isoelectronic with the well-known species  $\text{I}_2^+$ , has been generated in superacid media (297).

### XIII. Appendix

TABLE A-I

PROVISIONAL FREE-RADICAL REDUCTION POTENTIALS<sup>a</sup>

| Redox Couple                                     | $E^0$ (V) | Redox Couple   | $E^0$ (V) |
|--|-----------|--|-----------|
| $e_{\text{aq}}^-$                                | -2.87     | $\text{ClO}_2/\text{ClO}_2^-$                                      | 0.934     |
| $\text{H}/\text{H}^-$                            | 0.05      | $(2\text{H}^+, \text{ClO}_3^-)/(\text{ClO}_2, \text{H}_2\text{O})$ | 1.14      |
| $\text{H}^+/\text{H}$                            | -2.31     | $\text{ClO}_3/\text{ClO}_3^-$                                      | 2.1       |
| $\text{H}_2^+/\text{H}_2$                        | 5.45      | $\text{ClSCN}^-/(\text{Cl}^-, \text{SCN}^-)$                       | 1.58      |
| $\text{OH}/\text{OH}^-$                          | 1.90      | $\text{Br}/\text{Br}^-$  | 1.92      |
| $(\text{H}^+, \text{OH})/\text{H}_2\text{O}$     | 2.72      | $\text{Br}_2^-/2 \text{Br}^-$                                      | 1.62      |
| $(\text{H}^+, \text{O}^-)/\text{OH}^-$           | 1.77      | $\text{Br}_2/\text{Br}_2^-$  | 0.58      |
| $\text{O}/\text{O}^-$                            | 1.63      | $\text{HOBr}/\text{HOBr}^-$  | 0.14      |
| $\text{H}_2\text{O}_2/(\text{OH}, \text{OH}^-)$  | -0.03     | $\text{OBr}/\text{OBr}^-$  | 1.34      |
| $\text{HO}_2^-/(\text{OH}, \text{O}^-)$          | -0.04     | $\text{BrO}^-/(\text{Br}^-, \text{O}^-)$                           | -0.24     |
| $\text{O}_2/\text{O}_2^-$                        | -0.16     | $\text{BrO}_2/\text{BrO}_2^-$                                      | 1.21      |
| $(\text{H}^+, \text{O}_2)/\text{HO}_2$           | 0.12      | $(\text{H}^+, \text{BrO}_2)/\text{HBrO}_2$                         | 1.50      |
| $(\text{H}^+, \text{HO}_2)/\text{H}_2\text{O}_2$ | 1.44      | $(2\text{H}^+, \text{BrO}_3^-)/(\text{BrO}_2, \text{H}_2\text{O})$ | 1.16      |
| $\text{HO}_2/\text{HO}_2^-$                      | 0.75      | $\text{BrO}_4^-/(\text{BrO}_3^-, \text{O}^-)$                      | 0.06      |
| $^1\text{O}_2/\text{O}_2^-$                      | 0.83      | $\text{BrSCN}^-/(\text{Br}^-, \text{SCN}^-)$                       | 1.42      |
| $\text{O}_3/\text{O}_3^-$                        | 1.01      | $\text{I}/\text{I}^-$  | 1.33      |
| $\text{O}_2^+/\text{O}_2$                        | 3.2       | $\text{I}_2^-/2 \text{I}^-$  | 1.03      |
| $\text{F}/\text{F}^-$                            | 3.6       | $\text{I}_2/\text{I}_2^-$  | 0.21      |
| $\text{Cl}/\text{Cl}^-$                          | 2.41      | $\text{HIO}/\text{HIO}^-$  | 0.03      |
| $\text{Cl}_2^-/2 \text{Cl}^-$                    | 2.09      | $\text{IO}/\text{IO}^-$  | 1.8       |
| $\text{Cl}_2/\text{Cl}_2^-$                      | 0.70      | $\text{IO}_3^-/\text{IO}_3^{2-}$                                   | > -0.02   |
| $\text{HOCl}/\text{ClOH}^-$                      | 0.25      | $\text{HIO}_3/\text{HIO}_3^-$                                      | > 0.60    |
| $\text{ClO}/\text{ClO}^-$                        | 1.50      | $\text{ISCN}^-/(\text{I}^-, \text{SCN}^-)$                         | 1.14      |

(continued)

TABLE A-I (continued)

| Redox Couple   | $E^0$ (V) | Redox Couple  | $E^0$ (V) |
|--|-----------|---|-----------|
| HS/HS <sup>-</sup>   | 1.08      | CF <sub>3</sub> Cl/(CF <sub>3</sub> , Cl <sup>-</sup> )   | -0.67     |
| (S, H <sup>+</sup> )/HS  | 1.44      | CF <sub>3</sub> Br/(CF <sub>3</sub> , Br <sup>-</sup> )   | -0.58     |
| SO <sub>2</sub> /SO <sub>2</sub> <sup>-</sup>  | -0.26     | CF <sub>3</sub> I/(CF <sub>3</sub> , I <sup>-</sup> )   | -0.65     |
| (SO <sub>2</sub> , SO <sub>2</sub> <sup>-</sup> )/S <sub>2</sub> O <sub>4</sub> <sup>2-</sup>                | 0.255     | CCl <sub>4</sub> /(CCl <sub>3</sub> , Cl <sup>-</sup> )   | -0.23     |
| SO <sub>3</sub> <sup>-</sup> /SO <sub>3</sub> <sup>2-</sup>  | 0.63      | CBr <sub>4</sub> /(CBr <sub>3</sub> , Br <sup>-</sup> )   | -0.07     |
| SO <sub>3</sub> /SO <sub>3</sub> <sup>-</sup>  | 0.25      | CF <sub>2</sub> Cl <sub>2</sub> /(CF <sub>2</sub> Cl, Cl <sup>-</sup> )   | -0.59     |
| S <sub>2</sub> O <sub>6</sub> <sup>2-</sup> /(SO <sub>3</sub> <sup>-</sup> , SO <sub>3</sub> <sup>2-</sup> ) | -0.49     | CFCl <sub>3</sub> /(CFCl <sub>2</sub> , Cl <sup>-</sup> )   | -0.44     |
| SO <sub>4</sub> <sup>-</sup> /SO <sub>4</sub> <sup>2-</sup>  | 2.43      | CN/CN <sup>-</sup>  | 2.59      |
| S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> /(SO <sub>4</sub> <sup>2-</sup> , SO <sub>4</sub> <sup>-</sup> ) | 1.45      | OCN/OCN <sup>-</sup>  | 2.66      |
| HSO <sub>5</sub> /HSO <sub>5</sub> <sup>-</sup>  | 1.4       | C(NO <sub>2</sub> ) <sub>4</sub> /[C(NO <sub>2</sub> ) <sub>3</sub> <sup>-</sup> , NO <sub>2</sub> ]              | 0.93      |
| S <sub>2</sub> O <sub>3</sub> <sup>-</sup> /S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>                      | 1.35      | SCN/SCN <sup>-</sup>  | 1.63      |
| S <sub>4</sub> O <sub>6</sub> <sup>-</sup> /2 S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>                    | 1.18      | (SCN) <sub>2</sub> /2 SCN <sup>-</sup>  | 1.32      |
| S <sub>2</sub> O <sub>6</sub> <sup>2-</sup> /S <sub>4</sub> O <sub>6</sub> <sup>3-</sup>                     | -1.13     | (SCN) <sub>2</sub> /(SCN) <sub>2</sub> <sup>-</sup>   | 0.21      |
| SF <sub>6</sub> /(SF <sub>5</sub> , F <sup>-</sup> )   | 0.05      | SCNS <sub>2</sub> O <sub>3</sub> <sup>2-</sup> /(SCN <sup>-</sup> , S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> ) | 1.19      |
| SF <sub>5</sub> /(SF <sub>4</sub> , F <sup>-</sup> )   | 1.64      | SeCN/SeCN <sup>-</sup>  | 1.27      |
| FSO <sub>3</sub> /FSO <sub>3</sub> <sup>-</sup>  | 3.09      | (SeCN) <sub>2</sub> <sup>-</sup> /2 SeCN <sup>-</sup>   | 0.95      |
| HSe/HSe <sup>-</sup>   | 0.62      | Pb <sup>+</sup> /Pb   | -0.9      |
| (Se, H <sup>+</sup> )/HSe  | 1.02      | Pb <sup>2+</sup> /Pb <sup>+</sup>   | -1.0      |
| H <sub>2</sub> Se <sub>2</sub> <sup>-</sup> /2 HSe <sup>-</sup>  | 0.37      | Pb <sup>3+</sup> /Pb <sup>2+</sup>  | 1.6       |
| SeO <sub>3</sub> <sup>-</sup> /SeO <sub>3</sub> <sup>2-</sup>  | 1.68      | Pb <sup>4+</sup> /Pb <sup>3+</sup>  | 1.8       |
| HSeO <sub>4</sub> <sup>-</sup> /HSeO <sub>4</sub> <sup>2-</sup>  | -0.97     | In <sup>+</sup> /In   | -2.43     |
| NH <sub>3</sub> <sup>+</sup> /NH <sub>3</sub>  | 2.13      | Tl <sup>+</sup> /Tl   | -2.00     |
| NH <sub>2</sub> /NH <sub>2</sub> <sup>-</sup>  | 0.7       | 2 Tl <sup>+</sup> /Tl <sub>2</sub> <sup>+</sup>   | -1.80     |
| NH <sub>2</sub> OH/(NH <sub>2</sub> , OH <sup>-</sup> )  | -0.12     | Tl <sub>2</sub> <sup>+</sup> /Tl <sub>2</sub>   | -1.44     |
| NH <sub>3</sub> OH <sup>+</sup> /(NH <sub>3</sub> , OH)  | -0.58     | Tl <sup>2+</sup> /Tl <sup>+</sup>   | 2.22      |
| NH <sub>2</sub> OH <sup>+</sup> /NH <sub>2</sub> OH  | ≤ 1.26    | Tl <sup>3+</sup> /Tl <sup>2+</sup>  | 0.30      |
| NO/ <sup>1</sup> NO <sup>-</sup>   | -0.35     | TlOH <sup>2+</sup> /TlOH <sup>+</sup>   | 0.09      |
| NO/ <sup>3</sup> NO <sup>-</sup>   | 0.39      | Tl(OH) <sub>2</sub> <sup>+</sup> /Tl(OH) <sub>2</sub>   | -0.28     |
| NO <sup>+</sup> /NO  | 1.21      | TlOH <sup>+</sup> /TlOH   | 1.76      |
| NO <sub>2</sub> /NO <sub>2</sub> <sup>-</sup>  | 1.04      | Tl(OH) <sub>2</sub> /Tl(OH) <sub>2</sub> <sup>-</sup>   | 1.29      |
| NO <sub>2</sub> <sup>+</sup> /NO <sub>2</sub>  | 1.51      | TlCl <sup>2+</sup> /TlCl <sup>+</sup>   | 0.14      |
| NO <sub>3</sub> <sup>-</sup> /NO <sub>3</sub> <sup>2-</sup>  | < -0.40   | TlCl <sub>2</sub> <sup>+</sup> /TlCl <sub>2</sub>   | 0.00      |
| NO <sub>3</sub> /NO <sub>3</sub> <sup>-</sup>  | 2.5       | TlCl <sub>3</sub> /TlCl <sub>3</sub> <sup>-</sup>   | -0.15     |
| N <sub>2</sub> H <sub>4</sub> <sup>+</sup> /N <sub>2</sub> H <sub>4</sub>                                    | 0.01      | TlCl <sup>+</sup> /TlCl   | 2.01      |
| N <sub>3</sub> /N <sub>3</sub> <sup>-</sup>  | 1.33      | TlCl <sub>2</sub> /TlCl <sub>2</sub> <sup>-</sup>   | 1.79      |
| (H <sup>+</sup> , NF <sub>2</sub> )/HNF <sub>2</sub>   | 0.91      | Zn <sup>2+</sup> /Zn <sup>+</sup>   | -1.6      |
| ON(SO <sub>3</sub> ) <sub>2</sub> <sup>2-</sup> /ON(SO <sub>3</sub> ) <sub>2</sub> <sup>3-</sup>             | -0.350    | Zn <sup>+</sup> /Zn   | -1.0      |
| (H <sup>+</sup> , PO <sub>3</sub> <sup>2-</sup> )/HPO <sub>3</sub> <sup>2-</sup>                             | 1.61      | Cd <sup>2+</sup> /Cd <sup>+</sup>   | -1.4      |
| HPO <sub>3</sub> <sup>-</sup> /HPO <sub>3</sub> <sup>2-</sup>  | 1.26      | Cd <sup>+</sup> /Cd   | -0.3      |
| H <sub>2</sub> PO <sub>4</sub> /H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>                                  | 2.4       | Hg <sup>2+</sup> /Hg <sup>+</sup>   | 0.00      |
| PO <sub>5</sub> <sup>2-</sup> /PO <sub>5</sub> <sup>3-</sup>   | 1.9       | (Hg <sup>2+</sup> , Hg <sup>+</sup> )/Hg <sub>2</sub> <sup>2+</sup>   | 1.83      |
| H <sub>2</sub> AsO <sub>3</sub> /H <sub>2</sub> AsO <sub>3</sub> <sup>-</sup>                                | < 1.31    | Hg <sub>2</sub> <sup>2+</sup> /(Hg, Hg <sup>+</sup> )   | -0.50     |
| (H <sup>+</sup> , CO)/HCO  | -1.54     | Hg <sup>+</sup> /Hg   | 1.33      |
| CO <sub>2</sub> /CO <sub>2</sub> <sup>-</sup>  | -1.8      | HgOH <sup>+</sup> /HgOH   | -0.09     |
| HCO <sub>2</sub> /HCO <sub>2</sub> <sup>-</sup>  | 1.36      | XeF <sub>2</sub> /(XeF, F <sup>-</sup> )  | 0.9       |
| CO <sub>3</sub> <sup>-</sup> /CO <sub>3</sub> <sup>2-</sup>  | 1.5       | XeF/(Xe, F <sup>-</sup> )   | 3.37      |
| CO <sub>3</sub> /CO <sub>3</sub> <sup>-</sup>  | 2.3       | (H <sup>+</sup> , XeO <sub>3</sub> )/HXeO <sub>3</sub>  | > 0.67    |
| CF <sub>4</sub> /(CF <sub>3</sub> , F <sup>-</sup> )   | -1.45     |   |           |

<sup>a</sup> All potentials relative to NHE, with [H<sup>+</sup>] = 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                       |
| $HSO_3$       | -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                     | $HOXeO_2$            | < 550                   |
| $H_2Se_2^-$   | 124                     | $H_3XeO_6^{2-}$      | 180                     |
| $HSeO_4^-$    | -358                    | $HXeO_5^{2-}$        | 420                     |
| $SeO_3^-$     | -202                    | $HOXe(OH)_2O_3^{2-}$ | 280                     |
| $NH_3^+$      | 179                     |                      |                         |

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## NOTE ADDED IN PROOF

Despite the thermochemical accessibility of  $^1\text{O}_2$  in the reaction of  $\text{O}_2^-$  with  $[\text{Ru}(\text{bpy})_3]^{3+}$ , it has been argued recently that  $^1\text{O}_2$  is not a major product (337). Closer reading of Ref. 324 reveals that this paper raises considerable doubts about our present understanding of  $\text{Cl}_2^-$ . The authors of Ref. 324 have also reinvestigated the chemistry of  $\text{Br}_2^-$ , and here too, they find major discrepancies with prior work (338). The chemistry of  $\text{S}_2\text{O}_8^{2-}$  has been reviewed, with extended discussion of the mechanism of hydrolysis (339). Our selection of data for the  $\text{HNO}_2/\text{NO}_2^-$  system has been confirmed (340). Two comprehensive compilations of rate constants have appeared; one summarizes the reactions of  $e_{\text{aq}}^-$ ,  $\text{OH}$ , and  $\text{H}$  (341), while the other treats reactions of inorganic free radicals (342).

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