

IUPAC Technical Report

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Standard electrode potentials involving radicals in aqueous solution: inorganic radicals (IUPAC Technical Report)

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Abstract: Recommendations are made for standard potentials involving select inorganic radicals in aqueous solution at 25 °C. These recommendations are based on a critical and thorough literature review and also by performing derivations from various literature reports. The recommended data are summarized in tables of standard potentials, Gibbs energies of formation, radical pK_a 's, and hemicolligation equilibrium constants. In all cases, current best estimates of the uncertainties are provided. An extensive set of Data Sheets is appended that provide original literature references, summarize the experimental results, and describe the decisions and procedures leading to each of the recommendations.

Keywords: aqueous solutions; chemical equilibrium; chemical thermodynamics; inorganic chemistry; IUPAC Physical and Biophysical Chemistry Division; oxidation; radicals; standard electrode potentials.

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1 Introduction

Radicals, both organic and inorganic, tend to be highly reactive. Nevertheless, they are widely encountered as intermediates in chemical reactions; their individual reactivities are central among the factors that determine the rates and products of the overall reactions in which they are involved. For reactions where the radicals are present in the aqueous phase, electrode potentials involving the radicals are among the most powerful indicators of reactivity. Electrode potentials involving radicals are often more directly related to reactivity than are electrode potentials of non-radicals, because the former more often correlate to specific steps in the reaction mechanisms.

The determination of radical electrode potentials has greatly expanded in the last three decades, largely through the application of pulse radiolysis and flash photolysis. These techniques are well suited to the generation of transient radicals and the measurement of their reaction equilibria. It is largely through the manipulation of the radical equilibrium constants that the current bounty of radical electrode potentials has been obtained.

In 1989, two comprehensive reviews on radical standard potentials appeared. Wardman's review emphasized organic radicals [1], while Stanbury's review considered inorganic radicals exclusively [2]. Both of these reviews are now rather dated. Another valuable compendium is Steenken's 1985 list of electron transfer equilibria involving radicals [3]. A related review emphasizing H-atom bond dissociation "free" (Gibbs) energies has also appeared [4]. The relevant primary literature has expanded greatly and numerous major corrections have been made. With the benefit of these prior reviews, we are now in an improved position to appreciate the interconnected complexity of the various measurements. The work of the current IUPAC Task Group differs from the two prior reviews in that it doesn't attempt to make recommendations on all known radical electrode potentials, but rather focuses on a subset that has been judged to be of greater importance. It also makes a greater effort to apply the principles of error propagation in assessing the various potentials. This document presents the results of the IUPAC Task Group as they relate to inorganic radicals. Of necessity, some careful consideration of organic radicals is also included, because in some cases the inorganic radical potentials are derived from measurements of equilibrium constants for reactions with organic radicals. Some of the standard potentials discussed here were presented at the "Medicinal Redox Inorganic Chemistry" conference held at the University of Erlangen-Nürnberg in 2013 [5].

2 Definitions and conventions

We limit the scope to those species, radical or otherwise, having sufficient lifetime to be vibrationally equilibrated with the solvent; this restriction allows the full forces of classical thermodynamics to be employed.

We consider radicals to be species, either neutral or ionic, that bear an unpaired electron, and we exclude transition-metal complexes as a matter of convenience.

Use of the radical “dot” in chemical formulas to indicate radical species is redundant when the exact elemental composition and electronic charge of the species is specified, as is usually the case with the species in the current review. On the other hand, its use can be helpful for those who are not intimately familiar with the chemistry involved. In the present document, an effort has been made to use the dots consistently in the summary Tables, but in the supporting data sheets its use is less consistent. Both practices are in agreement with the current guidelines for inorganic nomenclature [6, 7].

By the term “standard electrode potential”, E° , we refer to half reactions of the following type:



where n is an integer, often 1, either Ox or Red can be a radical, and E° is taken relative to the normal hydrogen electrode (NHE). On occasion we use here the shorthand expression “standard potential” to refer to standard electrode potentials. By convention, these reactions are always written as reductions – the associated potentials were previously known as “standard reduction potentials” – and they can be more complex than the simple example given above. Standard electrode potentials, rigorously speaking, refer to electrode potentials specified under conditions where all species are at unit activity. The standard state for such activities in the present review is usually the ideal 1 M aqueous solution. Species in solution that can also exist as gases, such as O_2 , can be referred to the 1 M aqueous standard state or to the 100 kPa (1 bar, ~1 atm) pressure standard state, and in such cases we have taken care to designate the state explicitly. For water the standard state is the pure solvent (at unit activity, not 55.5 M). Standard electrode potentials are related to equilibrium constants (K_{eq}) through the relationship

$$E^\circ = -(RT/nF)\ln K_{\text{eq}} \quad (2)$$

where $K_{\text{eq}} = \prod a_{\text{prod}}^x / \prod a_{\text{react}}^y$, i.e. the product of the equilibrium activities of the products (a_{prod}) divided by the product of the equilibrium activities of the reactants (a_{react}), all raised to the power of their appropriate stoichiometric coefficients x and y . In practice, when one is dealing with radicals, it is usually easier to determine equilibrium constants than it is to measure equilibrium electrode potentials directly.

It is often necessary to report formal potentials, E°' , rather than standard potentials, because of a lack of reliable means to estimate the activity coefficients (γ). This is typically the case when the reaction involves ionic species and the measurement is performed at high ionic strength. Formal potentials are defined in the IUPAC Green Book, as in eq. 3 [8]:

$$E_{\text{eq}} = E^\circ' - (RT/nF) \sum \nu_i \ln(c_i/c^\circ) \quad (3)$$

Here, c_i represents the concentration of species i , c° is a normalizing standard concentration (usually 1 M), and ν_i is that species' stoichiometric coefficient. This definition is analogous to the Nernst equation except that it is expressed in terms of concentrations, and it allows for various species concepts. For example, in the case of S(IV) the species might be SO_3^{2-} , HSO_3^- , SO_2 , or the sum of all. This definition also allows for E°' values to be defined at specific nonstandard pH values. To avoid ambiguity in the species definitions, in the present work we generally write out the relevant half-cell reaction, and for reactions involving the proton we normally refer to pH 0. Formal potentials for the species' under consideration here can often be related to standard potentials through the activity coefficients:

$$E^\circ = E^\circ' + RT/nF \ln(\prod \gamma_{\text{prod}}^x / \prod \gamma_{\text{react}}^y) \quad (4)$$

Likewise, it is often useful or necessary to report formal equilibrium quotients (K_f) rather than equilibrium constants. These are related through the expression

$$K_{\text{eq}} = K_f (\prod \gamma_{\text{prod}}^x / \prod \gamma_{\text{react}}^y) \quad (5)$$

Even further removed from the thermodynamic ideal are “midpoint” potentials, E_m . These are E_{eq} values obtained when the oxidized and reduced species are at equal concentration. They are typically reported when

the reaction is likely to be pH dependent and data are available at only a specific pH (often pH 7, E_7). Note that midpoint potentials will be strongly concentration dependent when the stoichiometric coefficients, ν_i , are not equal. In principle, midpoint potentials can be derived from standard potentials, but the derivation requires knowledge of the pK_a values involved. For a detailed discussion of these points the reader is referred to the introductory material in Wardman's review on the potentials of radicals [1]. Related to midpoint potentials are apparent potentials, E_{ap}° . Apparent potentials are defined at a specific pH, like midpoint potentials, but the activities of the oxidized and reduced species in the Nernst equation do not take the state of protonation into account. Thus, apparent potentials do not necessarily imply any knowledge of the pK_a 's involved.

3 Methods for determination of standard potentials

A wide variety of methods have been employed to determine standard potentials involving inorganic radicals, as has been reviewed elsewhere [9]. A brief summary is given here.

a) Electrochemical Methods.

- a, i) Potentiostatic methods have been used only in a few special cases, such as in the chemistry of ClO_2^\cdot . The reason for this limitation is that inorganic radicals are usually highly reactive, so it is impossible to establish conditions where the concentrations are stable on the time frame of the measurements.
- a, ii) Cyclic voltammetry (CV) shortens the time frame of the electrochemical methods, and it has been used successfully in a few cases. However, the lifetimes of most inorganic radicals are too brief even for CV.
- a, iii) Pulse radiolysis provides an entry into very short time frames, and attempts have been made to apply electrochemical measurements to species generated by pulse radiolysis. Unfortunately, these efforts have not as yet provided reliable measurements or estimates of standard potentials involving inorganic radicals.
- a, iv) An intriguing technique is to generate photoelectrons in solution by laser irradiation of an electrode and then to use the electrode to probe the electrochemistry of the radicals generated from the photoelectrons. The method, however, remains to be developed as a reliable source of thermodynamic data.

b) Equilibrium Constant Measurements. The vast majority of standard electrode potentials summarized in this review have been obtained by Hess' law methods where an equilibrium constant is measured somehow and combined with other thermochemical data to derive the reported potential. These derivations frequently make use of published values of $\Delta_f G^\circ$, and this review normally makes the assumption that the values published in the NBS tables [10] are of reference quality. The various types of radical equilibrium constants used in these derivations are described below.

- b, i) **Solubilities.** The solubilities of ClO_2^\cdot and NO^\cdot have been measured unambiguously because solutions of these radicals are stable. These solubility measurements then afford a method to determine the solution-phase standard potentials from the known gas-phase energetics of these species. The solubility of NO_2^\cdot has also been measured, but in this case the method is complex and relies on an understanding of the kinetics of dissolution and of disproportionation of $\text{NO}_2^\cdot(aq)$.
- b, ii) **Homolysis Equilibria.** Homolysis at sigma bonds generally yields radicals, and determination of these equilibrium constants can lead rather directly to electrode potentials. In the case of $\text{S}_2\text{O}_4^{2-}$ it has been possible to measure the homolysis equilibrium constant by direct ESR detection of the $\text{SO}_2^{\cdot-}$ radicals. Homolysis equilibrium constants have been measured for unstable species such as N_2O_4 by use of transient methods such as flash photolysis and pulse radiolysis to establish the equilibria. A third method is to derive the equilibrium constant from the ratio of the forward and reverse rate constants ($K_{eq} = k_f/k_r$); an example of this method is provided by $\text{S}_2\text{O}_8^{2-}$, where k_f is determined from the kinetics of its oxidation of various substrates and k_r is obtained from transient measurements on the recombination of $\text{SO}_4^{\cdot-}$.

- b, iii) Electron-Transfer Equilibria.** Equilibrium constants for electron-transfer reactions are probably the most widely used data for deriving standard potentials involving radicals. A typical example is the reaction of O_3 with ClO_2^- :



In this case the equilibrium constant was determined from the ratio of k_f and k_r , and it was used to determine the standard one-electron electrode potential of O_3 relative the well-established reference potential of ClO_2^{\cdot} . Equilibrium constants have also been measured for a substantial number of electron transfer reactions where neither of the component half reactions can be considered as having a reliable reference potential; nevertheless, such reactions are valuable in determining standard potentials, although the thermochemical derivations are necessarily more lengthy.

- b, iv) Acid/Base Equilibria.** Proton-transfer reactions can be crucial in understanding the reactivity of radicals, as is exemplified by superoxide. HO_2^{\cdot} has a pK_a of 4.8. It is thermodynamically unstable with respect to disproportionation. Disproportionation via the reaction of HO_2^{\cdot} with itself or $O_2^{\cdot -}$ is very fast. However, direct disproportionation via reaction of $O_2^{\cdot -}$ with itself is undetectably slow, so alkaline solutions of $O_2^{\cdot -}$ are remarkably persistent. Determinations of pK_a 's have been performed for a significant number of radicals, and they have been performed by a large suite of techniques. These pK_a 's have been used in a large number of derivations of radical standard potentials, and, because of their intrinsic importance, they are summarized below in Table 3.

- b, v) Hemicolligation Equilibria.** Reactions in which radicals bind to non-radical species are defined as hemicolligations. They can occur between a radical and its reduced form that produce a symmetrical radical adduct or between a radical and some other non-radical to form a non-symmetrical adduct. Two prominent such reactions are



and



Reactions of this type can have a profound effect on the net reactivity of the radicals, and they are often unavoidable in reactive systems. Equilibrium constants have been measured for a good number of hemicolligation reactions, have been used extensively in deriving radical standard potentials, and are summarized in Table 4.

- b, vi) Nucleophilic Displacement Equilibria.** In these reactions a nucleophile displaces another nucleophile from a radical. A typical example is



Although these reactions can be considered as equivalent to the sum of two hemicolligations, their equilibrium constants often can be more easily measured than those of the component hemicolligations. These displacement equilibria are important in the present review primarily for their use in deriving standard potentials through thermochemical cycles.

- c) Methods Involving Estimates.** For certain important radicals there is no complete experimental thermochemical cycle available, and portions of the cycle must be obtained by making reasonable estimates. An important example is the hydrogen atom: although equilibrium constants have been measured for reactions that convert the aqueous hydrogen atom into other species (notably the hydrated electron), none of these reactions connects to a suitable reference redox couple. The best current solution to the problem is to make an estimate of the solvation energy of the hydrogen atom and then combine this estimate with other reliable data to derive the H^+/H^{\cdot} electrode potential. There is good reason to believe that the uncertainties introduced in this example are relatively small. In general the current report relies on such thermochemical estimates only when direct experimental data are unavailable.

- d) **Quantum Calculations.** It is becoming increasingly common to use quantum calculations to obtain radical electrode potentials. The methods typically entail a relatively accurate calculation of the energetics of the gas-phase radical and another calculation of the radical solvation energy. It has recently been shown that these computational methods can fail disastrously [11], so the present review makes little use of them.

4 Criteria for selection of recommended data

The recommended values in the Tables of this report are based on results published in the peer-reviewed scientific literature. The Task Group has reviewed these primary publications to confirm their plausibility, scientific soundness, and adherence to established chemical principles. When there are multiple independent reports on the same results, the individual reports have been compared to determine the degree of agreement among them, and to identify outliers and assess whether there is just cause for rejecting them. Individual reports may be rejected because the experimental method or conditions are insufficiently documented and the method has been shown to be unreliable. Non-rectifiable errors have been identified in the data handling, or the results are not internally consistent. In cases where there are multiple acceptable reports of a given result, the reviewers have assigned a subjective weighting to each report based on an assessment of the care taken in the experiments and the typical accuracy of the method. These filtered results are then averaged, optimized, and their uncertainties assigned as described below.

5 Uncertainties

In the present review, all recommended data [E° values (Table 1), pK_a 's (Table 3), $\Delta_f G^\circ$ values (Table 2), hemi-colligation equilibrium constants (Table 4)] are presented with associated uncertainties in two significant digits, up to 19. These uncertainties are given as $\pm 1\sigma$, and they are intended to indicate the best estimate of the overall uncertainty as arising from all contributions. Typically the least of these contributions are the statistical fluctuations in the direct measurements of a given quantity. Much more important are systematic errors, many of which are difficult to anticipate. Many of the recommended data are derived by combining various thermochemical quantities, and hence propagation of error must be taken into account. The level of uncertainty in the NBS $\Delta_f G^\circ$ values is frequently underappreciated in the broader chemical community. For some results there are multiple independent reports for the same quantity, for example as with the pK_a of HO^\bullet ; in such situations each individual report is examined for plausibility and technical excellence, outliers are rejected, then remaining reports are averaged, and a subjective assessment of the uncertainty is assigned. The specific rationale for these assignments is provided in the detailed data sheets appended. In the language of metrology, these uncertainty estimates are of Type A (from statistical treatment of repeated measurements) and Type B (estimates from experience), and ISO standards mandate that both types of uncertainties are equally valid and can be freely combined; these concepts are briefly reviewed elsewhere [12].

6 Use of thermochemical networks

As is discussed above, a large number of radical equilibrium constants of various types have been measured and combined with the standard potentials of reference couples to derive standard potentials of radicals through Hess' law-type calculations. Some of these equilibria share common radical species and hence lead to thermochemical networks. These networks can be very useful for determining radical standard potentials. When the networks are linear or branched it is a simple process to combine adjacent equilibrium constants with appropriate reference potentials to derive potentials of interest; in such calculations appropriate

attention must be paid to the cumulative effects of error propagation. Occasionally there are loops in the networks, which form closed thermochemical cycles. These closed thermochemical cycles afford excellent tests of the data, because the associated Gibbs energy changes must sum to zero. Failure to meet this criterion within reasonable uncertainty limits is a signal that at least some of the data are seriously flawed. When this criterion is met, suitable adjustments of the individual equilibrium constants (within their uncertainties) can be made to achieve exact closure. Assessment and use of these thermochemical networks can be performed manually, although consistent results are difficult to achieve when the networks are large. Larger networks can be solved in an automated and consistent way through use of appropriate computerized approaches such as ATcT, Active Thermochemical Tables [13]. In the present review, some of the recommended data are the result of manual assessment while others have been generated by use of ATcT. In its standard format, the ATcT software is optimized for evaluation of gas-phase enthalpies; for the present purposes the ATcT software has been adapted to work with Gibbs energies in solution. The method thus consists of defining the reaction network, converting relevant reference potentials and equilibrium constants to $\Delta_r G^\circ$ values and associated uncertainties, and localizing the thermochemical network by incorporating auxiliary values of $\Delta_r G^\circ$ (usually from the NBS tables) as network termini; the ATcT output then consists of a set of optimized $\Delta_r G^\circ$ values and uncertainties for the radicals of interest, and these are then combined with reference values of $\Delta_r G^\circ$ to derive the E° values. This method has been applied to a subset of the data presented here, as described in Data Sheet 7.

7 Important reference couples

There are a few redox couples that have attained particular significance, either because of their centrality as reference couples for determining other standard potentials or because of their general importance in inorganic radical chemistry. Aspects of these redox couples are highlighted here.

The $\text{ClO}_2^\cdot / \text{ClO}_2^-$ couple ($\text{ClO}_2^\cdot + e^- \rightleftharpoons \text{ClO}_2^-$) is of great importance in this review because it has been used extensively in establishing equilibria with other radicals and because its standard potential is known with unusually high accuracy. These characteristics are largely a consequence of the remarkable stability of both ClO_2^\cdot and ClO_2^- in aqueous solution and the facile inter-conversions between them. As a result, it is not difficult to obtain reversible electrochemistry with this couple, perform classical equilibrium potentiostatic measurements, and extrapolate them to conditions of thermochemical ideality. The outcome is a reliable and genuinely *standard* value for E° .

The hydroxyl radical is of general importance because it is one of the three radicals intrinsic to water (HO^\cdot , H^\cdot , and e_{aq}^-), it is the only one of the three to have its electrode potential determined without extra-thermodynamic assumptions or approximations, and occupies a central position in the largest of the thermochemical networks in this review. Its potential has been determined by two independent routes. The first of these has its origins in thallium chemistry and rests specifically on the redox potentials of the unstable species Tl^{2+} , which are determined relative to the well-established $\text{Fe}^{3+}/\text{Fe}^{2+}$ reference potential. The second route depends on the pK_a of HO^\cdot , the hemicolligation of $\text{O}^{\cdot-}$ with O_2 , the electron-transfer equilibrium of $\text{O}_3^{\cdot-}$ with ClO_2^\cdot , and the use of the $\text{ClO}_2^\cdot / \text{ClO}_2^-$ redox couple as a reliable reference. The excellent agreement between these two routes provides strong support for the recommended potential of this important species.

$\text{Br}_2^{\cdot-}$ is widely used as an oxidant, and equilibrium constants have been measured for at least 12 of its reactions. Its electrode potential is considered well established because of the good agreement between several independent derivations. Notable among these are a derivation based on the equilibrium constants for 1) its reaction with OH^- to form $\text{BrOH}^{\cdot-}$ and bromide and 2) the dissociation of $\text{BrOH}^{\cdot-}$ to form Br^- and HO^\cdot .

The trinitrogen(·) radical, N_3^\cdot , is important generally because it is often used as a mild nonspecific oxidant. It holds special importance in this review because of its frequent use in establishing redox equilibria that can be used to establish electrode potentials that involve radicals. The standard electrode potential of the $\text{N}_3^\cdot / \text{N}_3^-$ redox couple has been determined in several ways with good agreement. It has been measured electrochemically (under irreversible conditions), and it has been derived from equilibria with four other

reference redox couples ($[\text{IrCl}_6]^{2-}/[\text{IrCl}_6]^{3-}$, $[\text{Ru}(\text{bpy})_3]^{3+}/[\text{Ru}(\text{bpy})_3]^{2+}$, $\text{ClO}_2^{\cdot}/\text{ClO}_2^-$, and $\text{Br}_2^{\cdot-}/2\text{Br}^-$). Note that use of $\text{N}_3^{\cdot}/\text{N}_3^-$ as a reference potential at very high azide concentrations requires consideration of the association between N_3^{\cdot} and N_3^- (Data Sheet 86).

There are also some organic radicals that are important in providing reference potentials for the inorganic radicals recommended here. These include species such as the phenoxyl radical, TEMPO, the tryptophan radical cation, and the promethazine (phenothiazine) radical. Evaluations of their electrode potentials are provided in the supplementary data sheets.

8 Tables

Table 1: Inorganic standard electrode potentials.

Half-reaction	Electrode potential/V	Data Sheet #
Table 1.1: Electron, Hydrogen and Oxygen		
$\text{e}^- \rightleftharpoons \text{e}^{\cdot-}(\text{aq})$	-2.88 ± 0.02	1.1
$\text{H}^+ + \text{e}^- \rightleftharpoons \text{H}^{\cdot}(\text{aq})$	-2.31 ± 0.03	1.3
$\text{O}(\text{?P}) + \text{e}^- \rightleftharpoons \text{O}^{\cdot-}$	$+1.6 \pm 0.1$	2
$\text{O}(\text{?P}) + \text{H}^+ + \text{e}^- \rightleftharpoons \text{HO}^{\cdot}$	$+2.3 \pm 0.1$	2
$\text{O}_2(\text{g}) + \text{e}^- \rightleftharpoons \text{O}_2^{\cdot-}$	-0.35 ± 0.02	3
$\text{O}_2(\text{aq}) + \text{e}^- \rightleftharpoons \text{O}_2^{\cdot-}$	-0.18 ± 0.02	3
${}^1\Delta_8 \text{O}_2(\text{g}) + \text{e}^- \rightleftharpoons \text{O}_2^{\cdot-}$	$+0.64 \pm 0.01$	4
${}^1\Delta_8 \text{O}_2(\text{aq}) + \text{e}^- \rightleftharpoons \text{O}_2^{\cdot-}$	$+0.81 \pm 0.01$	4
$\text{O}_2(\text{g}) + \text{e}^- + \text{H}^+ \rightleftharpoons \text{HO}_2^{\cdot}$	-0.07 ± 0.02	3
$\text{O}_2(\text{aq}) + \text{H}^+ + \text{e}^- \rightleftharpoons \text{HO}_2^{\cdot}$	$+0.10 \pm 0.02$	3
$\text{HO}_2^{\cdot} + \text{e}^- + \text{H}^+ \rightleftharpoons \text{H}_2\text{O}_2$	$+1.46 \pm 0.01$	5
$\text{H}_2\text{O}_2 + \text{e}^- + \text{H}^+ \rightleftharpoons \text{HO}^{\cdot} + \text{H}_2\text{O}$	$+0.80 \pm 0.01$	6
$\text{HO}^{\cdot} + \text{e}^- + \text{H}^+ \rightleftharpoons \text{H}_2\text{O}$	$+2.730 \pm 0.017$	7
$\text{OH}^{\cdot} + \text{e}^- \rightleftharpoons \text{OH}^-$	$+1.902 \pm 0.017$	7
$\text{O}_3(\text{g}) + \text{e}^- \rightleftharpoons \text{O}_3^{\cdot-}$	$+0.91 \pm 0.02$	23
$\text{O}_3(\text{aq}) + \text{e}^- \rightleftharpoons \text{O}_3^{\cdot-}$	$+1.03 \pm 0.02$	23
Table 1.2: Halogens		
Table 1.2a: Chlorine		
$\text{Cl}^{\cdot}(\text{aq}) + \text{e}^- \rightleftharpoons \text{Cl}^-(\text{aq})$	$+2.432 \pm 0.018$	7
$\text{Cl}_2^{\cdot-}(\text{aq}) + \text{e}^- \rightleftharpoons 2\text{Cl}^-(\text{aq})$	$+2.126 \pm 0.017$	7
$\text{Cl}_2(\text{aq}) + \text{e}^- \rightleftharpoons \text{Cl}_2^{\cdot-}(\text{aq})$	$+0.666 \pm 0.017$	7
$\text{ClOH}^{\cdot}(\text{aq}) + \text{e}^- \rightleftharpoons \text{Cl}^- + \text{OH}^-(\text{aq})$	$+1.912 \pm 0.018$	7
$\text{ClOH}^{\cdot}(\text{aq}) + \text{e}^- + \text{H}^+(\text{aq}) \rightleftharpoons \text{Cl}^-(\text{aq}) + \text{H}_2\text{O}(\text{l})$	$+2.740 \pm 0.018$	7
$\text{HOCl}(\text{aq}) + \text{e}^- \rightleftharpoons \text{ClOH}^{\cdot}(\text{aq})$	$+0.25 \pm 0.08$	7
$\text{ClO}_2^{\cdot}(\text{aq}) + \text{e}^- \rightleftharpoons \text{ClO}_2^-$	$+0.935 \pm 0.003$	24
$\text{ClO}_3^{\cdot}(\text{aq}) + \text{e}^- \rightleftharpoons \text{ClO}_3^-(\text{aq})$	$+2.38 \pm 0.03$	7
$\text{ClO}^{\cdot}(\text{aq}) + \text{e}^- \rightleftharpoons \text{ClO}^-(\text{aq})$	$+1.39 \pm 0.03$	25
Table 1.2b: Bromine		
$\text{Br}_2^{\cdot-}(\text{aq}) + \text{e}^- \rightleftharpoons 2\text{Br}^-(\text{aq})$	$+1.63 \pm 0.02$	26
$\text{Br}_2(\text{aq}) + \text{e}^- \rightleftharpoons \text{Br}_2^{\cdot-}(\text{aq})$	$+0.55 \pm 0.02$	26
$\text{Br}^{\cdot}(\text{aq}) + \text{e}^- \rightleftharpoons \text{Br}^-(\text{aq})$	$+1.96 \pm 0.02$	26
$\text{BrO}_2^{\cdot}(\text{aq}) + \text{e}^- \rightleftharpoons \text{BrO}_2^-(\text{aq})$	$+1.290 \pm 0.005$	40
Table 1.2c: Iodine		
$\text{I}_2^{\cdot-} + \text{e}^- \rightleftharpoons 2\text{I}^-$	$+1.05 \pm 0.02$	45
$\text{I}^{\cdot} + \text{e}^- \rightleftharpoons \text{I}^-$	$+1.35 \pm 0.02$	45
$\text{I}_2(\text{aq}) + \text{e}^- \rightleftharpoons \text{I}_2^{\cdot-}$	$+0.19 \pm 0.02$	45

Table 1 (continued)

Half-reaction	Electrode potential/V	Data Sheet #
Table 1.3: Chalcogens		
$\text{SO}_4^{\cdot-}(\text{aq}) + \text{e}^- \rightleftharpoons \text{SO}_4^{2-}(\text{aq})$	$+2.437 \pm 0.019$	7
$\text{S}_2\text{O}_8^{2-}(\text{aq}) + \text{e}^- \rightleftharpoons \text{SO}_4^{\cdot-}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$	$+1.44 \pm 0.08$	7
$\text{SO}_3^{\cdot-}(\text{aq}) + \text{e}^- \rightleftharpoons \text{SO}_3^{2-}(\text{aq})$	$+0.73 \pm 0.02$	59
$\text{SO}_5^{\cdot-}(\text{aq}) + \text{e}^- \rightleftharpoons \text{SO}_5^{2-}$	$+0.81 \pm 0.01$	66
$\text{S}_2\text{O}_3^{\cdot-}(\text{aq}) + \text{e}^- \rightleftharpoons \text{S}_2\text{O}_3^{2-}$	$+1.35 \pm 0.03$	71
$\text{S}_4\text{O}_6^{\cdot 3-}(\text{aq}) + \text{e}^- \rightleftharpoons 2\text{S}_2\text{O}_3^{2-}$	$+1.10 \pm 0.01$	71
$\text{HS}^{\cdot}(\text{aq}) + \text{H}^+ + \text{e}^- \rightleftharpoons \text{H}_2\text{S}(\text{aq})$	$+1.54 \pm 0.03$	77
$\text{S}^{\cdot-} + \text{e}^- + \text{H}^+ \rightleftharpoons \text{HS}^-$	$+1.33 \pm 0.03$	77
$\text{S}^{\cdot-} + \text{e}^- + 2\text{H}^+ \rightleftharpoons \text{H}_2\text{S}(\text{aq})$	$+1.74 \pm 0.03$	77
$\text{HS}^{\cdot}(\text{aq}) + \text{e}^- \rightleftharpoons \text{HS}^-$	$+1.13 \pm 0.03$	77
$\text{HS}_2^{\cdot-} + \text{e}^- \rightleftharpoons \text{HS}_2^{\cdot 2-}$	-1.13 ± 0.05	77
$\text{SeO}_3^{\cdot-} + \text{e}^- \rightleftharpoons \text{SeO}_3^{2-}$	$+1.68 \pm 0.03$	78
$\text{SeO}_3^{\cdot-} + \text{H}^+ + \text{e}^- \rightleftharpoons \text{HSeO}_3^-$	$+2.18 \pm 0.03$	78
$\text{TeO}_3^{\cdot-} + \text{e}^- \rightleftharpoons \text{TeO}_3^{2-}$	$+1.74 \pm 0.03$	79
$\text{TeO}_3^{\cdot-} + \text{H}^+ + \text{e}^- \rightleftharpoons \text{HTeO}_3^-$	$+2.31 \pm 0.03$	79
Table 1.4: Group 5		
$\text{NO}_3^{\cdot}(\text{aq}) + \text{e}^- \rightleftharpoons \text{NO}_3^-(\text{aq})$	$+2.466 \pm 0.019$	7
$\text{N}_3^{\cdot}(\text{aq}) + \text{e}^- \rightleftharpoons \text{N}_3^-(\text{aq})$	$+1.33 \pm 0.01$	80
$\text{NO}^{\cdot}(\text{aq}) + \text{H}^+ + \text{e}^- \rightleftharpoons \text{HNO}(\text{aq})$	-0.15 ± 0.02	22
$\text{HNO}(\text{aq}) + \text{H}^+ + \text{e}^- \rightleftharpoons \text{H}_2\text{NO}^+(\text{aq})$	$+0.52 \pm 0.04$	87
$\text{H}_2\text{NO}^{\cdot} + 2\text{H}^+ + \text{e}^- \rightleftharpoons \text{NH}_3\text{OH}^+$	$+1.253 \pm 0.010$	87
$\text{H}_2\text{NO}^{\cdot} + \text{H}^+ + \text{e}^- \rightleftharpoons \text{NH}_2\text{OH}$	$+0.900 \pm 0.010$	87
$\text{NO}_2^{\cdot}(\text{aq}) + \text{e}^- \rightleftharpoons \text{NO}_2^-$	$+1.04 \pm 0.02$	88
$\text{PO}_3^{\cdot 2-} + \text{H}^+ + \text{e}^- \rightleftharpoons \text{HPO}_3^{2-}$	$+1.54 \pm 0.04$	96
$\text{H}_2\text{PO}_4^{\cdot} + \text{e}^- \rightleftharpoons \text{H}_2\text{PO}_4^-$	$+2.75 \pm 0.01$	97
Table 1.5: Group 4		
$\text{CO}_2(\text{aq}) + \text{e}^- \rightleftharpoons \text{CO}_2^{\cdot-}$	-1.90 ± 0.02	98
$\text{CO}_3^{\cdot-}(\text{aq}) + \text{e}^- \rightleftharpoons \text{CO}_3^{2-}$	$+1.57 \pm 0.03$	99
$\text{CO}_2^{\cdot-} + \text{H}^+ + \text{e}^- \rightleftharpoons \text{HCO}_2^-$	$+1.52 \pm 0.03$	100
$\text{SCN}^{\cdot} + \text{e}^- \rightleftharpoons \text{SCN}^-$	$+1.61 \pm 0.02$	101
$(\text{SCN})_2^{\cdot-} + \text{e}^- \rightleftharpoons 2\text{SCN}^-$	$+1.30 \pm 0.02$	101
Table 1.6: Group 3		
$\text{Tl}^{2+} + \text{e}^- \rightleftharpoons \text{Tl}^+$	$+2.225 \pm 0.007$	21
$\text{Tl}^{3+}(\text{aq}) + \text{e}^- \rightleftharpoons \text{Tl}^{2+}(\text{aq})$	$+0.34 \pm 0.08$	7
$\text{TlOH}^+(\text{aq}) + \text{e}^- + \text{H}^+(\text{aq}) \rightleftharpoons \text{Tl}^+(\text{aq}) + \text{H}_2\text{O}(\text{l})$	$+2.507 \pm 0.013$	7
$\text{TlOH}^{2+}(\text{aq}) + \text{e}^- \rightleftharpoons \text{TlOH}^+(\text{aq})$	$+0.12 \pm 0.08$	7
$\text{TlOH}^{2+}(\text{aq}) + \text{e}^- + \text{H}^+(\text{aq}) \rightleftharpoons \text{Tl}^{2+}(\text{aq}) + \text{H}_2\text{O}(\text{l})$	$+0.40 \pm 0.08$	7
Table 1.7: Zn, Cd, Hg		
$\text{HgCl}_2(\text{aq}) + \text{e}^- \rightleftharpoons \text{HgCl}(\text{aq}) + \text{Cl}^-$	-0.55 ± 0.02	102

Table 2: Gibbs energies of formation, $\Delta_f G^\circ$.

Radical	$\Delta_f G^\circ/\text{kJ mol}^{-1}$	Data Sheet #
e_{aq}^-	+278 ± 2	1.1
$\text{O}^{\bullet-}$	+93.1 ± 1.7	2
OH^\bullet	+26.3 ± 1.6	7
$\text{O}_2^{\bullet-}$	+33.8 ± 1.9	3
$\text{HO}_2^\bullet(\text{aq})$	+7 ± 2	3
$\text{O}_3^{\bullet-}$	+75 ± 2	23
$\text{H}^\bullet(\text{aq})$	+223 ± 2	1.1
$\text{Cl}^\bullet(\text{aq})$	+103.4 ± 1.7	7
$\text{Cl}_2^{\bullet-}(\text{aq})$	-57.3 ± 1.6	7
$\text{ClOH}^\bullet(\text{aq})$	-104.0 ± 1.7	7
$\text{ClO}^\bullet(\text{aq})$	+97 ± 3	25
$\text{ClO}_2^\bullet(\text{aq})$	+110 ± 10	24
$\text{ClO}_3^\bullet(\text{aq})$	+221.6 ± 3	7
$\text{Br}_2^{\bullet-}$	-51 ± 2	26
Br^\bullet	+85 ± 2	26
$\text{BrO}_2^\bullet(\text{aq})$	+152 ± 4	40
BrOH^\bullet	-93 ± 2	26
BrSCN^\bullet	+129 ± 3	26
$\text{I}_2^{\bullet-}$	-2.1 ± 1.9	45
I^\bullet	+78.8 ± 2	45
IOH^\bullet	-82.7 ± 2	45
$\text{S}^{\bullet-}$	+140 ± 3	77
HS^\bullet	+121 ± 3	77
$\text{HSS}^{\bullet 2-}$	+129 ± 4	77
$\text{SO}_3^{\bullet-}$	-416 ± 2	59
$\text{SO}_4^{\bullet-}(\text{aq})$	-509.4 ± 1.8	7
$\text{SO}_5^{\bullet-}(\text{aq})$	-506 ± 3	66
$\text{S}_2\text{O}_3^{\bullet-}$	-392 ± 8	71
$\text{S}_4\text{O}_6^{\bullet 3-}$	-939 ± 8	71
$\text{SeO}_3^{\bullet-}$	-202 ± 3	78
$\text{HSeO}_4^{\bullet 2-}$	-358 ± 3	78
$\text{TeO}_3^{\bullet-}$	-214 ± 3	79
$\text{HTeO}_4^{\bullet 2-}$	-394 ± 3	79
$\text{TeO}_4^{\bullet 3-}$	-319 ± 3	79
$\text{N}_3^\bullet(\text{aq})$	+476 ± 8	80
$\text{NO}^\bullet(\text{aq})$	+102.0 ± 0.2	90
$\text{H}_2\text{NO}^\bullet(\text{aq})$	+66 ± 3	87
$\text{NO}_2^\bullet(\text{aq})$	+62.3 ± 0.5	88
$\text{NO}_3^\bullet(\text{aq})$	+126.7 ± 1.8	7
$\text{CO}_2^{\bullet-}$	-205 ± 2	98
$\text{CO}_3^{\bullet-}$	-373 ± 3	99
SCN^\bullet	+248 ± 2	101
$(\text{SCN})_2^{\bullet-}$	+310 ± 2	101
ISCN^\bullet	+152 ± 2	45
Tl^{2+}	+182.3 ± 1.2	7
TlOH^+	-27.6 ± 1.3	7

Table 3: Inorganic radical pK_a s and related hydrolysis.

Reaction	K_a/M	pK_a	Data Sheet #
$H^*(aq) \rightleftharpoons e^-(aq) + H^+$	$(2.48 \pm 0.24) \times 10^{-10}$		1.2
$OH^*(aq) \rightleftharpoons O^{\cdot-} + H^+$		11.7 ± 0.1	116
$HO_2^*(aq) \rightleftharpoons O_2^{\cdot-} + H^+$		4.8 ± 0.1	3
$HO_3^*(aq) \rightleftharpoons O_3^{\cdot-} + H^+$	No recommendation		23
$Cl^*(aq) + H_2O(l) \rightleftharpoons ClOH^{\cdot-} + H^+$	5×10^{-6} , within a factor of 2		7
$Br^*(aq) + H_2O(l) \rightleftharpoons BrOH^{\cdot-} + H^+$		10.50 ± 0.07	26
$I^*(aq) + H_2O(l) \rightleftharpoons IOH^{\cdot-} + H^+$		13.3 ± 0.5	45
$HS^*(aq) \rightleftharpoons S^{\cdot-} + H^+$		3.4 ± 0.7	77
$HS_4O_6^{\cdot 2-} \rightleftharpoons S_4O_6^{\cdot 3-} + H^+$		6.2	71
$NH_2OH^{\cdot+} \rightleftharpoons NH_2O^{\cdot} + H^+$		<-5	105
$NH_2O^{\cdot} \rightleftharpoons NHO^{\cdot-} + H^+$		12.6 ± 0.3	105
$HPO_3^{\cdot-} \rightleftharpoons PO_3^{\cdot 2-} + H^+$		5.75 ± 0.05	106
$H_2PO_3^{\cdot} \rightleftharpoons HPO_3^{\cdot-} + H^+$	1.1		107
$H_3PO_3^{\cdot+} \rightleftharpoons H_2PO_3^{\cdot} + H^+$	54		107
$H_2PO_4^{\cdot} \rightleftharpoons HPO_4^{\cdot-} + H^+$		5.7 ± 0.4	108
$HPO_4^{\cdot-} \rightleftharpoons PO_4^{\cdot 2-} + H^+$		8.9 ± 0.2	108
$HPO_5^{\cdot-} \rightleftharpoons PO_5^{\cdot 2-} + H^+$		3.4 ± 0.2	109
$As(OH)_4^{\cdot} \rightleftharpoons As(OH)_3O^{\cdot-} + H^+$		7.38 ± 0.06	110
$As(OH)_4^{\cdot} \rightleftharpoons HAsO_3^{\cdot-} + H_2O + H^+$		3.85 ± 0.05	110
$HAsO_3^{\cdot-} \rightleftharpoons AsO_3^{\cdot 2-} + H^+$		7.81 ± 0.04	110
$HCO_2^{\cdot} \rightleftharpoons CO_2^{\cdot-} + H^+$		NR	100
$HCO_3^{\cdot} \rightleftharpoons CO_3^{\cdot-} + H^+$		< 0	99
$SCN^{\cdot} + H_2O \rightleftharpoons HOSCN^{\cdot-} + H^+$		12.5 ± 0.1	111
$Tl^{2+} + H_2O(l) \rightleftharpoons TlOH^{\cdot+} + H^+$	$(1.7 \pm 0.3) \times 10^{-5}$		7

Table 4: Hemicolligation equilibria.

Reaction	K/M^{-1}	Data Sheet #
$O_2(aq) + O^{\cdot-} \rightleftharpoons O_3^{\cdot-}$	$(1.4 \pm 0.1) \times 10^6$	23
$Cl^*(aq) + Cl^- \rightleftharpoons Cl_2^{\cdot-}$	$(1.4 \pm 0.2) \times 10^5$	10
$OH^*(aq) + Cl^- \rightleftharpoons ClOH^{\cdot-}$	0.70 ± 0.13	12
$Br^*(aq) + Br^- \rightleftharpoons Br_2^{\cdot-}$	$(3.9 \pm 1.2) \times 10^5$	33
$OH^*(aq) + Br^- \rightleftharpoons BrOH^{\cdot-}$	3.2×10^2 within factor of 2	34
$I^*(aq) + I^- \rightleftharpoons I_2^{\cdot-}$	1.35×10^5	52
$S^{\cdot-} + SH^- \rightleftharpoons HSS^{\cdot 2-}$	$(9 \pm 2) \times 10^3$	117
$S_2O_3^{\cdot-} + S_2O_3^{\cdot 2-} \rightleftharpoons S_4O_6^{\cdot 3-}$	$\log K = 4.1 \pm 0.5$	71
$N_3^*(aq) + N_3^- \rightleftharpoons N_6^{\cdot-}$	0.24 ± 0.08	85
$HAsO_3^{\cdot-} + H_2O \rightleftharpoons As(OH)_3O^{\cdot-}$	$pK = 3.53 \pm 0.11$	110
$SCN^*(aq) + SCN^- \rightleftharpoons (SCN)_2^{\cdot-}$	$(2.0 \pm 0.3) \times 10^5$	101
$S_2O_3^{\cdot-} + SCN^- \rightleftharpoons SCNS_2O_3^{\cdot 2-}$	1.2×10^3 within a factor of 2	75
$Tl(aq) + Tl^+ \rightleftharpoons Tl_2^{\cdot+}$	140 ± 7	112
$Tl^+ + OH^*(aq) \rightleftharpoons TlOH^{\cdot+}$	$(5.8 \pm 1.0) \times 10^3$	19
$Tl^{2+} + Cl^- \rightleftharpoons TlCl^{\cdot+}$	$(6.2 \pm 0.7) \times 10^4$	113
$TlCl^{\cdot+} + Cl^- \rightleftharpoons TlCl_2^{\cdot}$	$(1.9 \pm 0.4) \times 10^3$	114
$TlCl_2^{\cdot} + Cl^- \rightleftharpoons TlCl_3^{\cdot-}$	13 ± 3	115

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