

Reduction Potentials of One-electron Couples Involving Free Radicals in Aqueous Solution

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Reduction of an electron acceptor (oxidant), A, or oxidation of an electron donor (reductant), A²⁻, is often achieved stepwise *via* one-electron processes involving the couples A/A^{•-} or A^{•-}/A²⁻ (or corresponding prototropic conjugates such as A/AH[•] or AH[•]/AH₂). The intermediate A^{•-} (AH[•]) is a free radical. The reduction potentials of such one-electron couples are of value in predicting the direction or feasibility, and in some instances the rate constants, of many free-radical reactions. Electrochemical methods have limited applicability in measuring these properties of frequently unstable species, but fast, kinetic spectrophotometry (especially pulse radiolysis) has widespread application in this area. Tables of *ca.* 1200 values of reduction potentials of *ca.* 700 one-electron couples in aqueous solution are presented. The majority of organic oxidants listed are quinones, nitroaryl and bipyridinium compounds. Reductants include phenols, aromatic amines, indoles and pyrimidines, thiols and phenothiazines. Inorganic couples largely involve compounds of oxygen, sulfur, nitrogen and the halogens. Proteins, enzymes and metals and their complexes are excluded.

Key words: Aqueous solution; data compilation; electron transfer; equilibria; equilibrium constants; free radical; oxidation potential; radical; radiolysis; reduction potential; redox potential; review.

1. Introduction

Many reactions of free radicals involve one-electron transfer. If an electron acceptor, A is reduced to a radical, A^{•-} then the possibility of further or competing reactions involving other electron acceptors, B, C etc.:



can be calculated if the one-electron reduction potentials $E^\circ(A/A^{\bullet-})$, $E^\circ(B/B^{\bullet-})$ etc. are known. Thus the equilibrium constant, K_1 for reaction 1 is related to the difference ΔE_1 between the couples:

$$\Delta E_1^\circ = E^\circ(B/B^{\bullet-}) - E^\circ(A/A^{\bullet-}) \quad (1)$$

by the expression

$$\Delta G_1^\circ = -nF\Delta E_1^\circ = -RT\ln K_1 \quad (2)$$

where K_1 is the ratio of activities

$$K_1 = \frac{(a_A a_{B^{\bullet-}})}{(a_B a_{A^{\bullet-}})} \quad (3)$$

Except at high ionic strengths (see below, Sec. 3.8) we can replace activities by concentration so that

$$K_1 \approx \frac{[A][B^{\bullet-}]}{[B][A^{\bullet-}]} \quad (4)$$

At 298 K from Eq. (2) we have

$$\Delta E_1^\circ/\text{mV} \approx 59.1 \log K_1 \quad (5)$$

and differences of ca. 60 mV in reduction potential correspond to an order of magnitude change in equilibrium constant.

Even when reactions are irreversible and equilibria are not achieved, there are many instances where the rate constants for the reaction are reflected in the reduction potentials of electron donor or acceptor (see below, Sec. 7.2). Current interest in reactions of excited states with electron donors or acceptors, often involving electron transfer, is aided by the relative ease by which reduction potentials of many substances can be measured electrochemically in the aprotic solvents often used in such experiments. In water, however, free radicals are often too short-lived for conventional electrochemical methods to be used. The ability to observe directly the lifetimes and reactions of unstable intermediates using kinetic spectrophotometry offers obvious advantages. Detailed descriptions of electrochemical techniques can be readily found in the literature, and this introduction therefore concentrates on the more recent application of fast, kinetic methods to derive electrochemical potentials. As outlined below, pulse radiolysis and flash photolysis techniques can be used to measure equilibrium constants of redox reactions before transient species can decay. Neta¹ has summarized some early studies of redox properties of free radicals using the pulse radiolysis technique.

Dorfman and colleagues² used pulse radiolysis to observe electron-transfer equilibria of arene radicals in ethanol, and Patel and Willson³ measured equilibrium constants for electron transfer between semiquinones and oxygen in water. The latter data and approach enabled Wood,⁴ Ilan et al.⁵ and Meisel and Czapski⁶ to obtain the definitive value of the important couple $E^\circ(\text{O}_2/\text{O}_2^{\cdot-})$. Meisel and Neta⁷ extended the method to include reversible electron transfer between quinones and nitroaromatic compounds, and Steenken and Neta⁸ measured equilibria between phenoxyl radicals and hydroquinones or phenoxides at high pH. As a result of these pioneering studies, there are now many reliable values of thermodynamically-reversible one-electron reduction potentials of couples involving unstable free radicals in aqueous solution.

2. Reduction Potentials of Couples Involving Unstable Species

2.1. Stepwise Addition of Electrons

Many reactions formally involving two-electron couples A/A^{2-} are known to proceed in two one-electron steps, $\text{A}/\text{A}^{\cdot-}$ and $\text{A}^{\cdot-}/\text{A}^{2-}$. (*For simplicity we presently ignore protonation here*, but recognise that e.g. $\text{A}^{\cdot-}$ or A^{2-} may exist as conjugate acids at the pH of interest.) The intermediate $\text{A}^{\cdot-}$, generally a free radical in most of the cases tabulated here, may be produced *either* by reduction of A *or* by oxidation of A^{2-} (see below, Sec. 3.1, 3.2). The two-electron potential, $E^\circ(\text{A}/\text{A}^{2-})$ is related to the one-electron couples by

$$2 E^\circ(\text{A}/\text{A}^{2-}) = E^\circ(\text{A}/\text{A}^{\cdot-}) + E^\circ(\text{A}^{\cdot-}/\text{A}^{2-}). \quad (6)$$

Various alternative symbols are used for reduction potential, e.g. we can recognise the first- and second- one-electron potentials by denoting $E(\text{A}/\text{A}^{\cdot-})$ as E^1 and $E(\text{A}^{\cdot-}/\text{A}^{2-})$ as E^2 with subscripts for pH, e.g. E_7^1 , $E_{13.5}^2$. The standard reduction potential is usually denoted by E° . The distinction between standard potentials and measured quantities is not always clear, and is a particular problem where either ground state or radical species are protonated or dissociate in prototropic equilibria. A discussion of this point and recommendations for symbolism and description of reduction potentials is postponed to Sec. 4 when prototropic equilibria will have been considered in more detail.

2.2. Standard States, Reference Potentials and Sign Conventions⁹⁻¹¹

The standard states of unit activity (approximately 1 mol dm⁻³ concentration) for solids and liquids and unit fugacity (approximately 1 atmosphere partial pressure) for gases are used. *The latter convention frequently leads to errors in calculation*, particularly in reactions involving the important $\text{O}_2/\text{O}_2^{\cdot-}$ couple. Thus the standard potential is $E^\circ(\text{O}_2/\text{O}_2^{\cdot-}) \approx -325$ mV whereas the potential of the couple $E(\text{O}_2(1 \text{ mol dm}^{-3})/\text{O}_2^{\cdot-}) \approx -155$ mV.⁴⁻⁶ The difference can be appreciated by application of the Nernst equation (see Sec. 4.2, eq. (14), below) with the oxygen concentration of ~ 1.3 mmol dm⁻³. The standard state pressure was defined as 101.325 kPa; changing to a new standard state of 100 kPa = 1 bar alters potentials by only 0.17 mV, negligible in the present context. The convention of the standard state of pure elements being the normal physical state existing at 1 atmosphere and 298 K introduces another complication; thus the standard potential $E^\circ(\text{I}_2/\text{I}_2^{\cdot-})$ refers to solid elemental iodine and not ~ 1 mol dm⁻³ in aqueous solution.

The reference potential throughout these tables is the normal or standard hydrogen electrode (s.h.e.). Many electrochemical measurements are originally referred to the saturated calomel electrode (s.c.e.); these have been

The fraction of $\cdot\text{OH}$ attack on $-\text{CH}_3$ to yield a β -hydroxyalkyl radical, with similar properties to that produced in reaction 5 is $\sim 15\%$.¹⁶ Hence a fraction of $\text{A}^{\cdot-}$ may be lost via this unwanted reaction, albeit on a timescale often too slow to interfere with electron-transfer equilibration (see below, Sec. 3.5).

c. The $\cdot\text{OH}$ scavenger of choice when the longest 'natural' lifetime of $\text{A}^{\cdot-}$ is sought is formate (usually the sodium salt). The $\text{CO}_2^{\cdot-}$ radical formed upon scavenging $\cdot\text{OH}$ with HCO_2^- :



will *generally* produce the same species $\text{A}^{\cdot-}$ produced by reduction with e_{aq}^- :



although a high ionic strength usually results (see below, Sec. 3.8).

One aims to have the rate of reactions 5,6 or 8 much greater than the rate of reaction 4. Rate constants for reaction of $\cdot\text{OH}$ with many substances are known¹⁷ or can be estimated with sufficient accuracy for this inequality to be satisfied. Usually the $\cdot\text{OH}$ scavenger will be used at concentrations of 0.1-0.2 mol dm⁻³. Hydrogen atoms comprise ca. 10% of the total radicals and a fraction may react with e.g. $(\text{CH}_3)_2\text{CHOH}$ or HCO_2^- (*tert*-butyl alcohol is less reactive) depending on the solute reactivity. It cannot be assumed that H^\cdot will react with A to yield $\text{A}^{\cdot-}$. Especially with oxidants A of very low electron affinity it may not be safe to assume that reactions 7 and even 9 will yield $\text{A}^{\cdot-}$ and alternative (a) may be preferred in spite of the disadvantages noted.

3.2. Generating the Couple $\text{A}^{\cdot-}/\text{A}^{2-}$ by Oxidizing Radicals from Water Radiolysis¹²⁻¹⁵

Removing the reducing radical e_{aq}^- is simple:

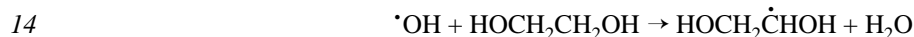


and saturation with N_2O ($[\text{N}_2\text{O}] \approx 25 \text{ mmol dm}^{-3}$) will prevent effectively the now unwanted reaction 10 if $k_{11}[\text{N}_2\text{O}] \gg k_{10}[\text{A}]$. Numerous values for k_{10} are tabulated.¹⁷ The H^\cdot atoms are usually ignored but could be a source of error if the product(s) of $\text{H}^\cdot + \text{A}^{2-}$ absorb significantly compared to $\text{A}^{\cdot-}$.

With $\text{A}^{2-} = \text{phenoxide ion}$, reaction 13 rapidly follows reaction 12 to yield the desired phenoxyl radical $\text{A}^{\cdot-}$ in basic solution:



However, the lack of selectivity in reactions of $\cdot\text{OH}$ has led to the practice of converting it to a more selective oxidizing radical, e.g. $\dot{\text{C}}\text{H}_2\text{CHO}$:¹⁸



Alternative oxidizing systems more selective than $\cdot\text{OH}$ are the halogen or pseudohalogen radicals $\text{X}_2^{\cdot-}$ (X = halogen or thiocyanate etc.) and N_3^\cdot :



Rate constants of many one-electron oxidation reactions of these species have been tabulated:¹⁹



Another useful system involves $SO_4^{\bullet-}$ (via $e_{aq}^- + S_2O_8^{2-}$)¹⁹



Since $k_4 \approx k_{14} \approx k_{17} \approx k_{18}$ we use [glycol], $[X^-]$, $[N_3^-]$ etc. \gg $[A]$, e.g. 1 mol dm⁻³ glycol or 0.1 mol dm⁻³ Br⁻.

3.3. Generating Radicals by Flash Photolysis

The triplet state A^* (e.g. of nitroaromatic compounds)^{20,21} may be quenched by electron donors, D to yield radical-anions:



although little application of this method to measuring reduction potentials has been reported.²⁰

3.4. Electrochemical Measurements of Reduction Potentials in Aqueous Solution

Clark's classical text²² includes methods by which one-electron potentials may be derived from electrochemical measurements, and Bard²³ has described general electrochemical methods. Some electrochemical methods require the intermediate $A^{\bullet-}$ to be relatively stable; this condition is easily met for $A =$ bipyridinium dication²² (viologens), some quinones at high pH²⁴, etc., and for $A^{2-} =$ some phenylenediamines, and phenothiazines in acidic solution. Polarography with a time resolution compatible with pulse radiolysis²⁵ offers obvious advantages over conventional methods, but protonation of radicals is frequently accompanied by irreversibility of the reduction process. More recently, cyclic voltammetry has had some success²⁶⁻²⁹ in determining reduction potentials involving both inorganic and organic radicals in aqueous solution; in this case, the theoretical treatment requires rapid loss of the radical^{26,30,31}.

3.5. Establishing a Redox Equilibrium: Kinetic Constraints

Many of the radiolytic reactions useful for generating radicals $A^{\bullet-}$ (7,9,10,16,19-21) are so rapid that at practical concentrations of A of the order 10 μ mol dm⁻³ - 10 mmol dm⁻³, the production of radicals $A^{\bullet-}$ and/or $B^{\bullet-}$ for the desired equilibrium 1 is complete a few microseconds after a radiation pulse. The rate of approach to equilibrium 1 is then controlled by k_I and k_{-I} :

$$k_{I,obs} \approx k_I[B] + k_{-I}[A]. \quad (7)$$

This approximation is usually valid if pulse radiolysis or flash photolysis involves generation of ca. 1 - 10 μ mol dm⁻³ $A^{\bullet-}$ and/or $B^{\bullet-}$ and $[A^{\bullet-}]$, $[B^{\bullet-}] \ll [A]$, $[B]$. Here $k_{I,obs}$ is the first-order rate constant (units s⁻¹) obtained by plotting the appropriate function of absorbance vs. time. As equilibrium 1 is approached, significant loss of $A^{\bullet-}$, $B^{\bullet-}$ (e.g. by disproportionation):



must be negligible if K_I is to be estimated reliably. While k_I and/or k_{-I} may be of the order of 10⁸ dm³ mol⁻¹ s⁻¹ for many electron-transfer reactions, it is frequently observed that protonation of A, $A^{\bullet-}$, or A^{2-} slows down electron-transfer rate constants by orders of magnitude, and then equilibrium 1 may not be achieved in competition with reaction 24 etc. Thus deprotonation of hydroquinones, phenols, ascorbate etc. is often necessary to observe reversible electron-transfer reactions of these substrates.⁸

3.6. Calculation of Reduction Potentials from Concentrations at Equilibrium

By making the assumption that as [A], [B] is varied the radiolytic yield ($[A^{\bullet-}] + [B^{\bullet-}]$) remains constant, then⁷

$$K_I \approx \frac{(A_{\text{obs}} - A_{A^{\bullet-}})}{(A_{B^{\bullet-}} - A_{\text{obs}})} \cdot \frac{[A]}{[B]} \quad (8)$$

A_{obs} is the absorbance at a constant dose (constant total radical concentration) in the solution containing A and B, and $A_{A^{\bullet-}}, A_{B^{\bullet-}}$ are the absorbances at the selected wavelength of $A^{\bullet-}$ and $B^{\bullet-}$ alone. Alternative algebraic routes to K_I have been used.^{3,6} Under some circumstances a significant fraction of A, B may be converted to $A^{\bullet-}, B^{\bullet-}$ and calculation by an iterative procedure for the concentrations of A, B at equilibrium may be necessary.

3.7. Calculation of Reduction Potential from the Kinetics of the Approach to Equilibrium

From Eq. (7) we have:

$$\frac{k_{I,\text{obs}}}{[B]} \approx k_I + k_{-I} \frac{[A]}{[B]} \quad (9)$$

A plot of $k_{I,\text{obs}}/[B]$ vs. $[A]/[B]$ yields an estimate of K_I from the ratio (intercept/slope). Again, the kinetics must reflect only the approach to equilibrium I and there must be insignificant loss of $A^{\bullet-}, B^{\bullet-}$ by other routes.

3.8. Effects of Ionic Strength, Temperature and Solvent

If *either* both reactants *or* both products of reaction I are charged then K_I defined by Eq. (4) will vary with ionic strength, I . We can either plot several measured values of ΔE_I against (say) $I^{1/2}$ to extrapolate to zero ionic strength or use the Debye–Hückel equation to calculate activity coefficient ratios.³² The limitations of such treatments to ionic strengths much lower than those used in many radiolysis experiments are well known. An alternative approach uses the Debye–Hückel–Brønsted–Davies expression for the primary kinetic salt effect:³³

$$\log k = \log k^0 + 2z_A z_B A (I^{1/2}(1 + I^{1/2})^{-1} - BI) \quad (10)$$

where the constants A, B vary with solvent and ions but are close to 0.5 and 0.2 respectively for water and typical ions. If for simplicity we abbreviate z_A, z_B to a, b (the charges on A, B) then reaction I may be written:



It is readily shown that

$$\Delta E_0 = \Delta E_I + \Delta E_{\text{corr}} \quad (11)$$

where the correction term to be added to the value ΔE_I measured at an ionic strength I is:

$$\Delta E_{\text{corr}}/\text{mV} \approx 59.1(b-a)f(I) \quad (12)$$

The function $f(I)$ appropriate for many reactions in water at 298 K can be approximated to:

$$f(I) \approx 1.02(I^{1/2}(1 + I^{1/2})^{-1} - 0.2I) \quad (13)$$

If e.g. A = a bipyridinium dication and B = a quinone sulfonate monoanion then $(b - a) = -3$ and $\Delta E_{\text{corr}} \approx -16$ and -49 mV at $I = 0.01$ and 0.2 respectively. At a given pH we may see $A^{\bullet-}$ protonated but A not and the salt effect then requires more careful consideration; with complex molecules the effective charge may differ from the nominal net charge,³⁴ and experiments at several ionic strengths are desirable. Some other effects of ionic strength are considered in Sec. 5.

Little work has been done on the effects of temperature and solvent. The author has used data³⁵ for the temperature-variation of the reduction potential of 1,1'-dimethyl-4,4'-bipyridinium dication and its benzyl analogue to show that $E(A/A^{\bullet-})$ for A = the 2-nitroimidazole, misonidazole varies with temperature at pH 7 in aqueous solution with $dE/dT \approx -1.1$ to -1.8 mV K^{-1} depending on the viologen data used (unpublished work). Solvent effects (mixed aqueous: organic solutions) will vary widely, depending especially upon the net charges involved; illustrations of these effects have been presented.^{36,37} Entropy changes can, of course, be estimated from dE/dT .

Typical values of dE/dT for viologen reference compounds are -0.4 to -0.9 mV K^{-1} ,³⁵ and for simple nitroaryl compounds are -1 to -2 mV K^{-1} . Thus the common practice of ignoring variations in experimental temperatures may introduce systematic errors in estimates of E° of several mV, aside from other uncertainties noted below.

3.9. Relative and Absolute Uncertainties Associated with Measurements

From Eq. (5) an uncertainty of $\pm 10\%$ in K_f corresponds to ca. ± 2.6 mV in ΔE_1° . The lack of, or uncertainties in ionic strength corrections (where needed) may be *at least* of this order and in general values of ΔE_1° are unlikely to be more accurate than ± 5 mV. The potentials of most redox indicators (see below, Sec. 5,6) are certainly not known to better than ± 5 -10 mV and a realistic uncertainty in $E^\circ(\text{A}/\text{A}^{\bullet-})$ of ± 10 mV is probably the *minimum* associated with the data given in Tables 1-4. For couples of the form $\text{A}^{\bullet-}/\text{A}^{2-}$ (Tables 5-8) ΔE_1° may often be measurable to ± 10 mV or so⁸ but ionic strength effects, where present (either $a \neq 0$, $b \neq 0$ or $a \neq b$) in e.g. 0.5 mol dm^{-3} KOH may lead to treble this uncertainty in values of reduction potentials.

The potentials in the Tables are presented in integer millivolts mainly to minimize rounding errors where several values may be coupled together to facilitate calculations, or to facilitate calculation of equilibrium constants from which the potentials were derived. The *absolute* values of the potentials are seldom reliable to better than ± 10 mV, and many may be uncertain by ± 20 mV.

Couples involving protons (see below) introduce further uncertainties since thermodynamic $\text{p}K_a$'s are frequently unavailable. The effects of these possible systematic errors are discussed further below.

4. Effects of Prototropic Equilibria upon Reduction Potentials

4.1. Introduction

Reduction potentials refer to reactions of the form:



The couples A/A^{2-} , $\text{A}/\text{A}^{\bullet-}$ and $\text{A}^{\bullet-}/\text{A}^{2-}$ may represent the reactions involved in the two-electron reduction of A to A^{2-} , or the two individual one-electron steps, as described above. In the latter case, the radical species $\text{A}^{\bullet-}$ is involved as reductant in the couple $\text{A}/\text{A}^{\bullet-}$, and as oxidant in the couple $\text{A}^{\bullet-}/\text{A}^{2-}$. If protons are involved in the reaction:



then the reduction potential of the 'half-cell' describing the reaction varies with pH. However, the *standard potential* does *not* vary with pH, since it is defined as the potential referred to the hydrogen standard when each species in the reaction, including H^+ if present, is at unit activity. This obviously includes the condition $\text{pH} = 0$ if H^+ is a reactant, and leads to considerable confusion. Symbols for standard potentials include E^\ominus and E° ; the latter is often typeset as E^0 and frequently also expressed as E_0 even though the subscripted symbol does not refer to a standard potential. Obviously, in verbal discussion the opportunities for confusion of E° and E_0 are even greater.

The symbol E_0 is best restricted to denote a *formal* rather than *standard* potential; this distinction should become clear later. Unfortunately, such formal potentials can have rather variable definitions, and care needs to be taken to ascertain just which constants are included in E_0 . This point is not always clear even in well-known texts, e.g. Clark's book,²² and is discussed further below.

4.2. Coupling of Electrons and Protons in the Reaction

Suppose the reductant, formally represented by A^{2-} previously, can be involved in prototropic equilibria, e.g.:



as can the radical intermediate, $\text{A}^{\bullet-}$ or the oxidant, A:



(It is important to recognise that free radicals may have dissociation constants for such equilibria which differ by several orders of magnitude from the corresponding dissociation in the ground state; thus for simple benzoquinones, $pK_{29} \gg pK_{30}$.^{3,38}) The two-electron reduction of A to A^{2-} can be represented *either* as 31a, excluding protons in the equation, *or* as 31b, which includes protons:



The *standard* potentials, $E^\circ(\text{A}/\text{A}^{2-})$ and $E^\circ(\text{A}, 2\text{H}^+/\text{AH}_2)$ have quite distinct definitions and values, and when discussing the reduction of A to A^{2-} or its protonated conjugates AH^\bullet , AH_2 we should take care always to qualify E° as shown above with the oxidant/reductant couple in parentheses.

The electrode potential (reduction potential) of a system or couple is the e.m.f. of a cell in which the couple forms the right-hand electrode and the standard hydrogen electrode (s.h.e.) forms the left.⁹ If A^{2-} is involved in prototropic equilibria (reactions 27,28) of any significance over the pH range of practical interest - say 0 to 14 - then the potential of the half-cell in which A is reduced can be assigned the symbol E_h . This is defined in the Nernst relationship:

$$E_h = E^\circ + \frac{RT}{nF} \ln \left\{ \frac{\text{(product of activities of oxidant)}}{\text{(product of activities of reductant)}} \right\} \quad (14)$$

where E° is the standard potential of the oxidant/reductant couple *as defined in the half-cell equation*. The relationship can be expressed *either* using the half-cell reaction 31a:

$$E_h = E^\circ(\text{A}/\text{A}^{2-}) + \frac{RT}{nF} \ln \frac{(\text{A})}{(\text{A}^{2-})} \quad (15)$$

or in terms of the half-cell reaction 31b, including protons:

$$E_h = E^\circ(\text{A}, 2\text{H}^+/\text{AH}_2) + \frac{RT}{nF} \ln \frac{(\text{A})(\text{H}^+)^2}{(\text{AH}_2)} \quad (16)$$

whichever is most convenient (see below). (We generally follow the symbols used by Clark,²² except in the more restrictive use of E_0 as shown below; activities are denoted by parentheses, (A) etc., while concentrations are represented by square brackets, [A] etc.) For simplicity we ignore, for the present, protonation of oxidant (reaction 30), i.e. $pK_{30} \ll 0$. E_h is *not* a standard potential, but merely the potential of a half-cell in which A is being reduced (in this case by two electrons, ignoring the individual one-electron couples). We *could* use the symbol $E_h(\text{A}, 2\text{H}^+/\text{AH}_2)$ to remind ourselves that the reduction is coupled to protons at some pH values of interest, but the reductant is really a mixture of all three prototropic conjugates.

4.3. General Approach to Describing the pH-Dependence of Reduction Potentials

As noted above, the standard potential $E^\circ(\text{A}, 2\text{H}^+/\text{AH}_2)$ is pH-invariant since the condition $(\text{H}^+) = 1$ applies. However, E_h will vary with pH since in Eq. (15) the activity of A^{2-} will depend on equilibrium 28 conjugating A^{2-} with H^+ . In Eq. (16) not only will (AH_2) be controlled by equilibrium 27, but (H^+) is also incorporated in the Nernst relationship. The general approach to deriving an expression relating E_h to (H^+) may be summarized: (i) Write down the reaction as a reduction of an oxidant to a reductant, reading left to right, in any form in which protons and electrons balance (e.g. reactions 25 or 26; 31a or 31b). (ii) Write down the Nernst expression for the reaction as written, with E° clearly defined in parentheses after the symbol (e.g. Eqs. (15) or (16)). (iii) Derive expressions for the fraction of total oxidant and/or total reductant which are in the prototropic forms shown in the reaction as written, i.e. in the definition of E° . (iv) Substitute these terms in the Nernst expression, and separate out the term for the ratio of total activities (or concentrations, see below) of oxidants and reductants to define a mid-point potential, E_m when this ratio is unity. (v) A formal (*not* standard) potential, E_0 can then be defined to separate out the constants

and present a relationship between E_m and pH which includes the dissociation constants for the prototropic equilibria involved. The standard potential E° is included in the constant E_0 but the latter may, or may not, approximate to E° , as discussed below.

Restricting ourselves for the present to defining E_h for the two-electron reduction of the oxidant A, and ignoring prototropic equilibria such as 30 involving the oxidant, we have already accomplished steps (i) and (ii) above to arrive at Eqs. (15) and (16). Using Eq. (16), for step (iii) we have to derive the proportion of total reductant in the form AH_2 . Following Clark,²² we define the symbol S_r to denote the sum of reductants:

$$S_r = AH_2 + AH^- + A^{2-} \quad (17)$$

and define equilibrium constants for the dissociation of the reductant in decreasing numerical value:

$$K_{r1} = \frac{(AH^-)(H^+)}{(AH_2)} \quad (= K_{27}) \quad (18)$$

$$K_{r2} = \frac{(A^{2-})(H^+)}{(AH^-)} \quad (= K_{28}). \quad (19)$$

We can then express (AH_2) in terms of (S_r) , K_{r1} and K_{r2} :

$$(S_r) = (AH_2) + (AH^-) + (A^{2-}) \quad (20)$$

$$(S_r) = (AH_2) \left[1 + \frac{K_{r1}}{(H^+)} + \frac{K_{r2}}{(H^+)^2} \right] \quad (21)$$

$$(AH_2) = (S_r) \left[\frac{(H^+)^2}{K_{r1}K_{r2} + K_{r1}(H^+) + (H^+)^2} \right]. \quad (22)$$

To progress to step (iv) we define, for consistency, S_o as the sum of the oxidants (only A if we ignore AH^+ formation, reaction 30). Eq. (16) then becomes:

$$E_h = E^\circ(A, 2H^+/AH_2) + \frac{RT}{2F} \ln \frac{(S_o)}{(S_r)} + \frac{RT}{2F} \ln \frac{(K_{r1}K_{r2} + K_{r1}(H^+) + (H^+)^2)(H^+)^2}{(H^+)^2} \quad (23)$$

if we separate out the term with $(S_o)/(S_r)$ since $(S_o) = (A)$. When $(S_o) = (S_r)$, E_h can be described as a 'mid-point' potential with symbol E_m :

$$E_m = E^\circ(A, 2H^+/AH_2) + \frac{RT}{2F} \ln (K_{r1}K_{r2} + K_{r1}(H^+) + (H^+)^2). \quad (24)$$

Beginning with the alternative 'orienting reaction' 31a and its corresponding Nernst relationship Eq. (15), we have to derive an expression for (A^{2-}) analogous to Eq. (22), in a similar fashion:

$$(A^{2-}) = (S_r) \left[\frac{K_{r1}K_{r2}}{K_{r1}K_{r2} + K_{r1}(H^+) + (H^+)^2} \right]. \quad (25)$$

We then obtain the alternative expression for E_m :

$$E_m = E^\circ(A/A^{2-}) + \frac{RT}{2F} \ln \frac{(K_{r1}K_{r2} + K_{r1}(H^+) + (H^+)^2)}{K_{r1}K_{r2}}. \quad (26)$$

Equations (24) and (26) describe the same parameter, E_m , the potential of the half-cell in which A is reduced by 2 electrons when the sum of the activities of the oxidant equals the sum of the activities of the reductant. Equating these expressions, the relationship between the two standard potentials is:

$$E^\circ(A, 2H^+/AH_2) = E^\circ(A/A^{2-}) - \frac{RT}{2F} \ln (K_{r1}K_{r2}). \quad (27)$$

If potentials are in mV and $T \approx 298$ K:

$$E^\circ(A, 2H^+/AH_2) \approx E^\circ(A/A^{2-}) + 29.6(pK_{r1} + pK_{r2}). \quad (28)$$

To obtain a more convenient expression for fitting data of E_m vs. pH to the appropriate function, Eq. (26) could be modified by incorporating the pH-independent term, $K_{r1}K_{r2}$ in the denominator, with the standard potential to yield a new constant, E_0 :

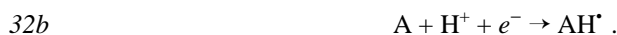
$$E_0 = E^\circ(A/A^{2-}) - \frac{RT}{2F} \ln (K_{r1}K_{r2}) \quad (29)$$

$$E_m = E_0 + \frac{RT}{2F} \ln (K_{r1}K_{r2} + K_{r1}(H^+) + (H^+)^2). \quad (30)$$

Clark²² uses this procedure extensively. However, the definition of E_0 is often not immediately apparent in some more complex situations, and the symbol is very frequently used for a formal potential with a specific definition; this introduces an ambiguity which is discussed below.

4.4. Practical Application to One-Electron Reduction Potentials

Both equilibrium constants and mid-point potentials are usually measurable only in terms of *concentrations* rather than activities, and the expressions for the pH-dependence of E_m for one-electron couples will be derived in terms of these measurable quantities. Consider first the one-electron reduction of A, which can be represented by the two alternative equations:



These are linked by the prototropic equilibrium 29. The *practical* ionization constant for dissociation of AH^{\cdot} will mix concentrations and activities:

$$K'_r = \frac{[A^{\cdot-}](H^+)}{[AH^{\cdot}]} \quad (= K'_{29}). \quad (31)$$

The use of K' rather than K denotes the use of concentrations for all species except H^+ (activities of H^+ are measured with the glass electrode or calculated using standard buffers). The subscript r with K' is used since A is the oxidant and $AH^{\cdot}/A^{\cdot-}$ the reductant. Since there is only one ionization of the reductant considered, K'_r rather than K'_{r1} can be used.

The Nernst expression corresponding to the simpler alternative reaction 32a is:

$$E_h = E^\circ(A/A^{\cdot-}) + \frac{RT}{F} \ln \frac{(A)}{(A^{\cdot-})}. \quad (32)$$

When modified to include activity coefficients, f defined by:

$$(A) = f_A[A] \quad (33)$$

etc., this yields:

$$E_h = E^\circ(A/A^{\cdot-}) + \frac{RT}{F} \ln \frac{f_A}{f_{A^{\cdot-}}} + \frac{RT}{F} \ln \frac{[A]}{[A^{\cdot-}]}. \quad (34)$$

Representing A by S_o and the sum of $A^{\cdot-}$ and AH^{\cdot} by S_r as before, and following the general approach described above:

$$[A^{\cdot-}] = [S_r] \left[\frac{K'_r}{K'_r + (H^+)} \right] \quad (35)$$

$$E_h = E^\circ(A/A^{\cdot-}) + \frac{RT}{F} \ln \frac{f_A}{f_{A^{\cdot-}}} + \frac{RT}{F} \ln \frac{[S_o]}{[S_r]} + \frac{RT}{F} \ln \left[\frac{K'_r + (H^+)}{K'_r} \right]. \quad (36)$$

If a *formal potential*, E_0 is now defined as the mid-point potential when the ratio of the total concentrations of oxidized and reduced species is unity, and H^+ is at unit activity ($pH = 0$), then from Eq. (36):

$$E_0 = E^\circ(A/A^{\cdot-}) + \frac{RT}{F} \ln \frac{f_A}{f_{A^{\cdot-}}} + \frac{RT}{F} \ln \left[\frac{K'_r + 1}{K'_r} \right] \quad (37)$$

$$E_m = E_0 + \frac{RT}{F} \ln \left[\frac{K'_r + (H^+)}{K'_r + 1} \right]. \quad (38)$$

For many species of interest, such as semiquinones, $K'_r \ll 1$ so that:

$$E_0 \approx E^\circ(A/A^{\cdot-}) + \frac{RT}{F} \ln \frac{f_A}{f_{A^{\cdot-}}} - \frac{RT}{F} \ln K'_r \quad (39)$$

$$E_m \approx E_0 + \frac{RT}{F} \ln (K'_r + (H^+)). \quad (40)$$

The latter two equations also result if E_0 has no specific definition but merely represents taking out the pH-independent terms in the expressions for E_h or E_m . The values of E_0 calculated from Eq. (39) rather than Eq. (37) may differ by negligibly small amounts, e.g. by < 0.3 mV if $pK'_r > 2$; however, it is recommended that E_0 is defined clearly as the formal potential described above even though it introduces extra terms such as $(K'_r + 1)$ in the equations. We can then use consistently subscripts with E_m to denote pH and by definition, $E_{m0} = E_0$.

Equation (38) may also be derived starting from the alternative Nernst relationship corresponding to reaction 32b:

$$E_h = E^\circ(A, H^+/AH\cdot) + \frac{RT}{F} \ln \frac{(A)(H^+)}{(AH\cdot)}. \quad (41)$$

An expression is derived for $[AH^*]$ in terms of $[S_r]$, etc., except that E_0 in Eq. (38) now becomes (using the defined formal potential as before):

$$E_0 = E^\circ(A, H^+/AH\cdot) + \frac{RT}{F} \ln \frac{f_A}{f_{AH\cdot}} + \frac{RT}{F} \ln (K'_r + 1). \quad (42)$$

At constant ionic strength, Eqs. (37) and (42) equate, so that

$$E^\circ(A/A^{\cdot-}) = E^\circ(A, H^+/AH\cdot) + \frac{RT}{F} \ln \frac{f_{A^{\cdot-}}}{f_{AH\cdot}} + \frac{RT}{F} \ln K'_r. \quad (43)$$

Since:

$$K'_r = K_r \frac{f_{A^{\cdot-}}}{f_{AH\cdot}}, \quad (44)$$

$$E^\circ(A/A^{\cdot-}) = E^\circ(A, H^+/AH\cdot) + \frac{RT}{F} \ln K_r. \quad (45)$$

This relationship may be re-arranged in the same form as Eq. (28):

$$E^\circ(A, H^+/AH\cdot) \approx E^\circ(A/A^{\cdot-}) + 59.2 pK_r. \quad (46)$$

Obviously, Eq. (45) may also be derived more directly in the same way as was Eq. (27), using activities rather than concentrations, or by simply considering the free-energy changes in the reactions concerned.

Note that E_0 as defined by Eq. (42) does not equate to $E^\circ(A, H^+/AH^*)$, but if $K'_r \ll 1$ it *approximates* to it at low ionic strength. These formal potentials may be defined to include not only activity coefficients, but also e.g. complexation with counter-ions in the supporting electrolyte. Thus for the Fe(III)/Fe(II) couple, E_0 is dependent upon the nature of the acid as well as ionic strength. An extension of this approach is to define the formal potential

to have some other ‘standard’ condition (really, non-standard!). For example, in biochemical systems (H^+) may be redefined with $pH = 7$ as the ‘standard’ state; a symbol such as E'_0 may then be used.

Regardless of the definition of E_0 , at any two pH values, i and j , Eq. (38) yields:

$$E_{mi} = E_{mj} + \frac{RT}{F} \ln \left[\frac{K'_i + 10^{-i}}{K'_i + 10^{-j}} \right]. \quad (47)$$

For the radical/reductant one-electron couple, the half-cell may be written in several forms:



The Nernst expression for reaction 33a is:

$$E_h = E^\circ(A^{\cdot-}/A^{2-}) + \frac{RT}{F} \ln \frac{[A^{\cdot-}]}{[A^{2-}]} \quad (48)$$

The radical species $AH^{\cdot}/A^{\cdot-}$ is now the oxidant, rather than the reductant as in the example immediately preceding. Thus we denote:

$$K'_o = \frac{[A^{\cdot-}][H^+]}{[AH^{\cdot}]} \quad (= K'_{29}) \quad (49)$$

(cf. (Eq. 31)), and

$$[A^{\cdot-}] = [S_o] \left[\frac{K'_o}{K'_o + (H^+)} \right] \quad (50)$$

(cf. (Eq. 35)). The reductant concentration, $[A^{2-}]$ is defined by Eq. (22) except that concentrations replace activities and practical ionization constants K'_{r1} , K'_{r2} are used. We then obtain:

$$E_m = E^\circ(A^{\cdot-}/A^{2-}) + \frac{RT}{F} \ln \frac{f_{A^{\cdot-}}}{f_{A^{2-}}} + \frac{RT}{F} \ln \left[\frac{K'_o}{K'_o + (H^+)} \right] + \frac{RT}{F} \ln \left[\frac{K'_{r1}K'_{r2} + K'_{r1}(H^+) + (H^+)^2}{K'_{r1}K'_{r2}} \right]. \quad (51)$$

If the formal potential, E_0 is defined strictly as before, with unit ratio of total concentrations of oxidant to reductant, and $(H^+) = 1$, then:

$$E_0 = E^\circ(A^{\cdot-}/A^{2-}) + \frac{RT}{F} \ln \frac{f_{A^{\cdot-}}}{f_{A^{2-}}} + \frac{RT}{F} \ln \left[\frac{K'_o}{K'_o + 1} \right] + \frac{RT}{F} \ln \left[\frac{K'_{r1}K'_{r2} + K'_{r1} + 1}{K'_{r1}K'_{r2}} \right] \quad (52)$$

$$E_m = E_0 + \frac{RT}{F} \ln \left[\frac{K'_{r1}K'_{r2} + K'_{r1}(H^+) + (H^+)^2}{K'_o + (H^+)} \right] + \frac{RT}{F} \ln \left[\frac{K'_o + 1}{K'_{r1}K'_{r2} + K'_{r1} + 1} \right]. \quad (53)$$

The last term in Eq. (53) will be negligible if $K'_o, K'_{r1}, K'_{r2} \ll 1$. Indeed, as noted above, it would be omitted if E_o was simply defined by combining the pH-independent terms in Eq. (51).

Corresponding pairs of expressions for E_o and E_m are derived setting out from the alternative orienteering reactions 33b-d. The standard potentials are related by:

$$E^\circ(\text{A}^{\cdot-}/\text{A}^{2-}) = E^\circ(\text{A}^{\cdot-}, \text{H}^+/\text{AH}^-) + \frac{RT}{F} \ln K_{r2} \quad (54a)$$

$$= E^\circ(\text{A}^{\cdot-}, 2\text{H}^+/\text{AH}_2) + \frac{RT}{F} \ln K_{r1}K_{r2} \quad (54b)$$

$$= E^\circ(\text{AH}^{\cdot}, \text{H}^+/\text{AH}_2) + \frac{RT}{F} \ln \frac{K_{r1}K_{r2}}{K_o}. \quad (54c)$$

These relationships, and also Eqs. (27) and (45) can be most simply obtained by writing down the appropriate equations and summing the free energy changes involved.

Again, for any two pH values, i and j , Eq. (51) or Eq. (53) yields:

$$E_{mi} = E_{mj} + \frac{RT}{F} \ln \left[\frac{K'_{r1}K'_{r2} + K'_{r1}(10^{-i}) + 10^{-2i}}{K'_{r1}K'_{r2} + K'_{r1}(10^{-j}) + 10^{-2j}} \right] + \frac{RT}{F} \ln \left[\frac{K'_o + 10^{-j}}{K'_o + 10^{-i}} \right]. \quad (55)$$

We neglected earlier the possibility of protonation of the oxidant, A as in equilibrium 30. Returning to the one-electron reduction of A, to incorporate this equilibrium we define:

$$K'_o = \frac{[\text{A}](\text{H}^+)}{[\text{AH}^+]} \quad (= K'_{30}). \quad (56)$$

Following the usual approach we obtain, for example:

$$E_i = E_j + \frac{RT}{F} \ln \left[\frac{K'_r + 10^{-i}}{K'_r + 10^{-j}} \right] \left[\frac{K'_o + 10^{-j}}{K'_o + 10^{-i}} \right]. \quad (57)$$

This describes the variation with pH of the mid-point potential of the oxidant/radical one-electron couple, in place of Eq. (47).

4.5. Examples of the pH-Dependence of One-Electron Reduction Potentials and Suggestions for Symbols

The quinone/semiquinone and semiquinone/hydroquinone one-electron couples are illustrated in Figs. 1 and 2 respectively. The mid-point potentials, E_m are plotted vs. pH for 1,4-benzoquinone. (The numerical values used are those calculated in Sec. 5.5, below). The pH range 0-14 is separated into regions with pK values defining the 'break points'. In each region, the prototropic forms of the species *predominating* as shown in a box: oxidant, upper species; reductant, lower. The positions of the various standard potentials, E° are also given. It should be stressed that the apparent coincidence of some standard potentials with intercepts (pH 0) or asymptotes (pH \approx 14) in the curves of E_m vs. pH arises because of the identity: $0 \ll (pK_s, pK_{r1}, pK_{r2}) \ll 14$ *in this example*, and not by definition ($pK_s = pK_a$ for dissociation of the semiquinone species, QH^\cdot).

It has been stressed already that E° should always be qualified with the half-cell reaction in parenthesis, as shown in Figs. 1 and 2, and that E_o is to be preferred as a defined, formal potential rather than a collection of constants. However, convenient abbreviations to qualify E_m are not so simply defined; perhaps it is reasonable to use the prototropic forms predominating over the pH range of most interest. Thus the abscissae in Figs. 1 and 2 might be labeled: $E_m(\text{A}/\text{A}^{\cdot-})$ and $E_m(\text{Q}^{\cdot-}, 2\text{H}^+/\text{QH}_2)$ respectively. We stress again that E° does *not* vary with pH.

It has been common practice to use superscripts to qualify symbols for first and second one-electron reduction potentials, with subscripts for pH, e.g. $E_7^1(\text{A}/\text{A}^{\cdot-})$ or $E_{13.5}^2(\text{A}^{\cdot-}/\text{A}^{2-})$. This now seems superfluous and possibly confusing. On the other hand, if results are described as mid-point potentials throughout (except where standard

potentials are clearly denoted), it seems reasonable to use E_i for simplicity rather than E_{mi} , where the subscript i is the pH.

The variation of E_m with pH may be influenced by prototropic functions not closely associated with the redox center, if the pK_a of the function differs in oxidant and reductant. Figure 3 shows an example of the effect of a basic function in the substituent in a nitroaryl compound. The unsubstituted imidazolyl nitrogen has $pK_a \leq 0$ in the ground state and may be ignored. However, this site is protonated in the electron adduct (radical), with $pK'_1 \approx 5.0$. The piperidino nitrogen in the substituent protonates with $pK'_0 \approx 7.6$ in the ground state, but the inductive effect of the nitroaryl group is reduced in the electron-adduct: $pK'_2 \approx 8.5$ fits the experimental data. This shift in pK_a of ~ 0.9 is observed in spite of an 'insulating' saturated carbon chain separating the basic site and the redox center. (In this example, the nitro group will be protonated in the radical, but this occurs at pH values lower than those shown.)

Similarly, other unpublished work by the author indicates the carboxylate function in 4-nitrobenzoic acid dissociates with a pK_a about 0.9 higher in the radical-ion than the ground state. Such effects, if ignored, result in significant errors in extrapolating to lower pH values. They may be present to some extent, although as yet undetected, in biologically-important redox couples involving tryptophan and tyrosine, for example.

4.6. The Use of Mid-Point Potentials in Calculating Equilibrium Constants

The Introduction (Sec. 1) showed how reduction potentials were related to electron-transfer equilibria such as I :



If A, B and/or the radicals, $A^{\cdot-}$, $B^{\cdot-}$ are involved in prototropic equilibria, then the measured mid-point potentials E_{mi} will yield, *via* Eq. (5), an apparent or *effective* equilibrium constant, K_i where:

$$K_i \approx \left[\frac{[S_A][S_{B^{\cdot-}}]}{[S_B][S_{A^{\cdot-}}]} \right]. \quad (4')$$

This is a modification of Eq. (4) where, following previous use, we replace $[A]$, $[A^{\cdot-}]$, etc. by the sums of the concentrations of related prototropic conjugates: $[S_{A^{\cdot-}}] = ([A^{\cdot-}] + [AH^{\cdot}])$, etc. Such an effective equilibrium constant is most useful in predicting the overall equilibrium, or direction of electron flow, as illustrated in Fig. 4.

This figure represents an equilibrium I in which, like semiquinones for example, the reductant species $A^{\cdot-}$, $B^{\cdot-}$ participate in prototropic equilibria, with $E^\circ(A/A^{\cdot-})$ and $E^\circ(B/B^{\cdot-}) = -400$ and -300 mV respectively but with pK_a for the dissociation of the protonated conjugates, AH^{\cdot} and $BH^{\cdot} = 8$ and 5 respectively. At $pH \geq 9$, K_i can be calculated from Eqs. (1) and (5) to be ≈ 49 . However, because E_{mi} increases more rapidly with decreasing pH for the oxidant A compared to B, the *effective* position of the equilibrium reverses at $pH \leq 6$. At $pH \leq 4$, K_i is approximately constant at ≈ 0.05 .

It is preferable to treat such pH-dependent equilibria in this way rather than add protons to equilibrium I and work with complex equilibrium expressions. There is, however, an important *kinetic* consequence of these prototropic equilibria in many instances. It is commonly observed that protonation (or absence of ionization) of basic (or acidic) functions slows down the rates of electron transfer reactions, often dramatically, as noted in Sec. 3.5. The *rate* of approach to equilibrium I may depend, for example, on the fraction of radicals from A present in the form $A^{\cdot-}$ rather than the much less reactive AH^{\cdot} . Thus the electron-transfer equilibrium I may not be kinetically achievable under practicable conditions even though calculation readily establishes the thermodynamic feasibility. In general, prototropic equilibria are established so rapidly that the kinetics of proton transfer are seldom rate-determining.

Other, some more complex, illustrations of the effects of prototropic equilibria on reduction potentials have been discussed, e.g. for quinones,^{6,39-42} nitroaromatic compounds,⁷ flavins,⁴³ phenoxyl radicals,⁸ etc. The principles of the calculations are simply as outlined above in Sec. 4.3. In some instances, however, the formulae given represent approximations to those derived herein. In almost every case the practical implications of such differences are negligible.

5. Calculation of One-Electron Reduction Potentials Using Radical Formation Constants

5.1 Introduction

Radicals, e.g. $A^{\cdot-}$ may be present in equilibrium with oxidant, A and reductant, A^{2-} or their protonated conjugates:



and a radical formation constant can be defined:

$$K_f = \frac{(A^{\cdot-})^2}{(A)(A^{2-})}. \quad (58)$$

The value of K_f is obviously a measure of the steady-state concentrations of radicals, $A^{\cdot-}$ obtained on mixing oxidant A with reductant, A^{2-} . When experimental conditions result in sufficiently high concentrations of radicals to be measured, estimates of K_f can be used in conjunction with the two-electron potentials, $E^\circ(A/A^{2-})$ or $E^\circ(A, 2H^+/AH_2)$ to obtain estimates of the one-electron couples, $E^\circ(A/A^{\cdot-})$, etc.

5.2. Derivation of Expressions

Reaction 34 (above) can be obtained by subtracting 33a from 32a:



Eq. (59) is obtained by subtracting the corresponding free-energy changes:

$$E^\circ(A/A^{\cdot-}) - E^\circ(A^{\cdot-}/A^{2-}) = \frac{RT}{F} \ln K_f. \quad (59)$$

If we add reaction 32a to reaction 33a we obtain reaction 31a. Noting that $n = 2$ in the conversion of free energy to potential, Eq. (2), in the latter reaction:

$$E^\circ(A/A^{\cdot-}) + E^\circ(A^{\cdot-}/A^{2-}) = 2 E^\circ(A/A^{2-}) \quad (60)$$

(cf. Eq. (6)). Adding Eqs. (59) and (60) yields:

$$E^\circ(A/A^{\cdot-}) = E^\circ(A/A^{2-}) + \frac{RT}{2F} \ln K_f \quad (61)$$

while subtraction gives:

$$E^\circ(A^{\cdot-}/A^{2-}) = E^\circ(A/A^{2-}) - \frac{RT}{2F} \ln K_f. \quad (62)$$

Using Eq. (28) with potentials in mV and $T \approx 298$ K:

$$E^\circ(A/A^{\cdot-}) \approx E^\circ(A, 2H^+/AH_2) - 29.6(pK_{r1} + pK_{r2} + pK_f) \quad (63)$$

$$E^\circ(A^{\cdot-}/A^{2-}) \approx E^\circ(A, 2H^+/AH_2) - 29.6(pK_{r1} + pK_{r2} - pK_f) \quad (64)$$

where K_{r1} , K_{r2} are the dissociation constants for AH_2 and AH^- respectively as defined in Eqs. (18) and (19).

It may be difficult to measure K_f directly, e.g. because very high pH values may be required to ionize completely the reductant to A^{2-} . It is much more convenient to define an apparent formation constant, K_{fi} at an experimentally accessible pH, i :

$$K_{fi} = \frac{(S_s)^2}{(S_o)(S_r)}. \quad (65)$$

We follow previous symbolism and define S_o and S_r as the sums of the oxidant (only A) and reductant ($AH_2 + AH^\cdot + A^{2-}$) respectively, as before, and use S_s to represent the sum of the radical intermediate species. The subscript s is convenient because the radical will be a semiquinone in many examples. It is easily shown, using the approach already used in Sec. 4.3, that:

$$K_f = K_{fi} \left[\frac{K_s}{K_s + (H^+)} \right] \left[\frac{K_{r1}K_{r2} + K_{r1}(H^+) + (H^+)^2}{K_{r1}K_{r2}} \right] \quad (66)$$

where K_{r1} , K_{r2} are defined in Eqs. (18) and (19) as before and $K_s = K_{29}$.

As noted earlier, in practice, concentrations rather than activities are generally measured. We will usually obtain an estimate of K_f or K_{fi} at some ionic strength, I . Using K'_f , K'_{fi} as before to denote the apparent formation constants thus defined in *concentration* terms except for (H^+) , together with the mid-point potentials E_{mi} measured at the same ionic strength, it can be shown that:

$$E_{mi}(A/A^\cdot) = E_{mi}(A/A^{2-}) + \frac{RT}{2F} \ln K'_{fi} \quad (67)$$

$$E_{mi}(A^\cdot/A^{2-}) = E_{mi}(A/A^{2-}) - \frac{RT}{2F} \ln K'_{fi} \quad (68)$$

The mid-point condition now refers to the sum of the *concentrations* of oxidant being equal to the sum of the concentrations of reductant. (The activity coefficient terms in Eqs. (36) and (51) cancel out the terms in Eq. (69)).

$$K'_f = K_f \frac{f_{A^\cdot}^2}{f_A f_{A^{2-}}} \quad (69)$$

5.3. Examples of Calculations

The one-electron reduction potential of the oxidant, duroquinone (DQ) can be *estimated* using electrochemical data for the reduction potential of the two-electron couple: duroquinone/durohydroquinone, and spectrophotometric measurement of the semiquinone concentration present in mixtures of the quinone and hydroquinone at high pH. Interpolating Baxendale and Hardy's data^{44,45} to yield values at 298 K give: $pK'_{r1} = 11.24$, $pK'_{r2} = 12.83$ and $pK'_f = 0.11$ at $I = 0.65$. Conant and Fieser⁴⁷ indicate $E^\circ(DQ, 2H^+/DQH_2) = 480$ mV (but used 50% ethanol). Equation (63) then yields an *estimate* of $E^\circ(DQ/DQ^\cdot) = -236$ mV, ignoring the use of practical rather than thermodynamic equilibrium constants. Alternatively, Michaelis *et al.*⁴⁸ estimated E_{mi} (duroquinone/durohydroquinone) using 20% pyridine in water at 303 K, for pH (i) = 7.4 to 13.5; a value of $E_{m7} = 41$ mV is interpolated. Baxendale and Hardy's data,^{44,45} and $pK'_s = 5.1$ from pulse radiolysis,³ yields $K'_{r7} = 1.1 \times 10^{-10}$. Using Eq. (67), $E_7(DQ/DQ^\cdot) = -254$ mV is *estimated*. These values are similar to those obtained quite independently by Wardman and Clarke³² using pulse radiolysis.

(A number of authors have used $pK'_{r2} = 13.2$ for duroquinone, as tabulated from Bishop and Tong⁴⁶ from Baxendale and Hardy's measurements. The original data⁴⁴ clearly show pK'_{r2} varying between 13.17 at 14.9 °C to 12.70 at 29.8 °C, from which the present author interpolates a value of 12.83 at 298 K).

Electron spin resonance measurements⁴⁹ of the steady-state concentrations of ascorbyl radicals produced on mixing the reductant, ascorbic acid with the corresponding oxidant, dehydroascorbic acid gave estimates of K_{fi} between pH 4.0 and 6.4. An *estimate* of $K_f = 1.2 \times 10^{-3}$ is obtained using Eq. (66) and $pK'_{r1} = 4.21$, $pK'_{r2} = 11.52$ (representative literature values) and $pK'_s = -0.45$.⁵⁰ A value of $E_{m0} = 400$ mV for the two-electron reduction (see Clark,²² p.470), will be close to $E^\circ(A, 2H^+/AH_2)$, from Eq. (24). Eq. (64) yields $E^\circ(A^\cdot/A^{2-}) \approx 19$ mV for $A^{2-} =$ ascorbic acid. Steenken and Neta,⁸ using the pulse radiolysis redox equilibrium method, estimated $E_{13.5}(A^\cdot/A^{2-}) = 15$ mV. This is well within the uncertainty of the independent calculation. (Because $pK'_{r2} \approx 11.5$, $E_{13.5}(A^\cdot/A^{2-}) \approx E^\circ(A^\cdot/A^{2-})$).

5.4. Uncertainties in the Calculations

As an example, consider the calculation for $E^\circ(A/A^\cdot)$ for A = simple quinones. Clark's tables²² of values of E_0 for the two-electron reduction of many quinones indicate random uncertainties of 5-15 mV, the higher values including measurements in partly non-aqueous solvents. In these cases E_0 approximates to $E^\circ(A, 2H^+/AH_2)$. To calculate the uncertainty in the estimate of $E^\circ(A/A^\cdot)$, for example, we also need to consider the uncertainty in the

sum: $pK_{r1} + pK_{r2} + pK_f$, as indicated in Eq. (63). Estimates⁴⁴⁻⁴⁶ of pK'_{r1} , pK'_{r2} and pK'_f refer to ionic strengths of 0.65 or 0.375, and the substitution of these practical constants for the thermodynamic constants required in Eq. (63) introduces *systematic* errors.

Perrin *et al.*⁵¹ derived a formula to correct practical ionization constants. For dissociation of the weak acid $HA^{(n-1)-}$:

$$35 \quad HA^{(n-1)-} \rightleftharpoons A^{n-} + H^+$$

$$pK \approx pK' + [(2n-1)/2]f(I). \quad (70)$$

We have adapted his formula to use the ionic strength function, $f(I)$ previously defined:

$$f(I) \approx 1.02(I^{1/2}[1 + I^{1/2}]^{-1} - 0.2I). \quad (13)$$

At high ionic strengths, $I \approx 0.4-0.6$, reliable use of Eq. (70) is doubtful. However, we see that for uncharged quinones (e.g. duroquinone), pK'_{r1} and pK'_{r2} may *underestimate* the thermodynamic values by *ca.* 0.1-0.2 and 0.5 respectively. It can be shown that

$$pK_f \approx pK'_f - f(I) \quad (71)$$

for uncharged oxidants A, i.e. for uncharged quinones. The semiquinone formation constant decreases with increasing I so that pK'_f *overestimates* pK_f by *ca.* 0.3 at $I \approx 0.4-0.6$. There is thus partial canceling-out of these systematic errors in the application of Eq. (63). The systematic error introduced into the calculation of $E^\circ(A/A^{\cdot-})$ will still amount to the estimate being *ca.* 10 mV more positive than the true value.

Even for these simple quinones, generally only one estimate⁴⁴⁻⁴⁶ of the ionization and formation constants required is available. *Even discounting random errors* in their determination, the calculations of one-electron reduction potential as described in this section must involve uncertainties of *at least* 10-20 mV is general. Similar consideration may be given to other applications of the formulae derived.

These illustrations may be used, in turn, to refine calculations of standard potentials using experimental measurements of ionization and formation constants. Thus the literature data^{44,46} for 1,4-benzoquinone may be corrected to yield estimates of the thermodynamic constants: pK_{r1} , pK_{r2} , pK_s and pK_f of 10.0, 11.9, 4.0 and -0.92 respectively. Using the well-established²² $E^\circ(Q, 2H^+/QH_2) = 699$ mV yields estimates of $E^\circ(Q, Q^{\cdot-}) = 78$ mV and $E^\circ(Q^{\cdot-}, Q^{2-}) = 24$ mV, the former some 20 mV lower than previous estimates.⁴² In fact, such corrections are not so straight-forward, since Baxendale and Hardy⁴⁴ included some activity coefficients (of the buffers used) in defining K'_{r1} , K'_{r2} . The simple application of Eqs. (70) or (71) may be inappropriate in some instances.

6. Recommended Redox Indicators and their Potentials

The choice of redox indicators B with which to establish and measure the position of the desired equilibrium I with the unknown A is influenced by several factors. Ideally, determinations of K_I with two indicators - one higher than the unknown by (say) 50-100 mV, one lower - will lead to the most reliable value. In practice, the choice depends on solubilities, absorption spectra of reactants and products, pK_a 's, kinetic constraints, (especially the need for fast electron transfer, see above, Sec. 3.5) and ready availability with adequate purity.

6.1. Oxygen

Oxygen is an important reactant with many radicals, although electron-transfer rather than radical-addition is a pre-requisite and it is somewhat inconvenient to vary the concentration of oxygen over a wide range. It is useful to draw attention again to the standard definition: $E^\circ(O_2(1 \text{ atm.})/O_2^{\cdot-}) = -325$ mV whereas $E(O_2(1 \text{ mol dm}^{-3})/O_2^{\cdot-}) = -155$ mV.

6.2. Quinones

Reduction potentials for the couples $A/A^{\cdot-}$ and $A^{\cdot-}/A^{2-}$ for A = quinones may be calculated^{4,5,6,42} from the ionization constants of AH_2 and the semiquinone formation constants, as described above (Sec. 5). Completely independent estimates of $E^\circ(A/A^{\cdot-})$ for A = *duroquinone* are provided by the measurements of ΔE_1 corrected to $I = 0$ for A = duroquinone and B = 1,1'-dibenzyl-4,4'-bipyridinium dication.³² Values of ΔE_1 of 110 ± 4^{32} , 113 ± 4^{52} , and 107 ± 3^{53} mV together with $E^\circ(B/B^{\cdot-}) = -354$ mV (but see below, Sec. 6.3) yield $E^\circ(A/A^{\cdot-}) = -244$ mV for

duroquinone, in good agreement with the values calculated^{4,5,6,42} from dissociation constants (see also Sec. 5.3). A value of $E^\circ(\text{A}/\text{A}^{\cdot-}) = -375$ mV for *9,10-anthraquinone-2-sulfonate* is a reasonable mean of estimates based on equilibria involving duroquinone^{7,32,52}, and two bipyridinium indicators^{32,52,53} and is quite close to the value -360 mV obtained polarographically at high pH.²⁴ The more negative potential now recommended for benzyl viologen (see below) will result in corresponding alterations to the values for the quinone couples, e.g. to -260 mV for duroquinone and -390 mV for *9,10-anthraquinone-2-sulfonate*.

Reduction potentials for other quinone couples have been calculated^{4,5,6,42} from literature data and experimentally derived⁴³ from equilibrium measurements. They can be relied upon when confirmed by independent routes, e.g. when the values are consistent with measurements of the $\text{A}^{\cdot-}/\text{O}_2$ equilibrium.^{5,6,43} 1,4-Benzoquinone (Q) is a recommended standard, with $E^\circ(\text{Q}/\text{Q}^{\cdot-}) = 78$ mV and $E^\circ(\text{Q}^{\cdot-}/\text{Q}^{2-}) = 24$ mV, as calculated in Sec. 5.4.

6.3. Bipyridinium Compounds (Viologens)

While these viologens are, in principle, excellent redox indicators because the radicals $\text{A}^{\cdot-}$ are essentially stable in aqueous solution and have a high extinction coefficient at wavelengths where interfering absorptions are seldom a problem, a note of caution is appropriate. Not only is variable water of hydration a problem (relatively minor in this context) with the dimethyl derivative (paraquat), but variable purity of commercial samples of both viologens has been noted. Note, however, that the spectra of the viologen radical cations are concentration-, temperature- and time-dependent^{32,54-59} and that electrochemical measurements may involve higher concentrations of these cations than are utilized in pulse radiolysis measurements. The spectral changes arise because the radical cations $\text{V}^{\cdot+}$ obtained on one-electron reduction of viologens, V^{2+} dimerize:



Estimates of the apparent dimer dissociation constant, K'_D have been made. These vary from $\sim 1.5 \times 10^{-3}$ mol dm⁻³ for methyl viologen⁵⁵⁻⁵⁷ to $\sim 2.7 \times 10^{-3}$ (ethyl viologen)⁵⁸ and 2×10^{-5} mol dm⁻³ (benzyl viologen),⁵⁹ *under the experimental conditions used* (K'_D is ionic strength dependent). If x is the fraction of radicals in the monomeric form and S_r is the total concentration of reductant ($[\text{V}^{\cdot+}] + 2[(\text{V}^{\cdot+})_2]$), then:

$$K'_D = \frac{2S_r x^2}{(1-x)}. \quad (72)$$

The ~ 100 -fold lower value of K_D for benzyl viologen compared to its methyl analogue has serious implications in using the former as a redox indicator, since it is seen that if e.g. $S_r = 10^{-5}$ mol dm⁻³, $x \approx 0.6$ with benzyl viologen. By application of the Nernst relationship in a similar manner to that used in Sec. 4, it can be shown that:

$$E_m = E^\circ(\text{V}^{2+}/\text{V}^{\cdot+}) - \frac{RT}{F} \ln \left\{ \frac{K_D}{4S_r} ([1 + (8S_r/K_D)]^{1/2} - 1) \right\}. \quad (73)$$

If, e.g. $K_D = 5 \times 10^{-5}$ mol dm⁻³ and $S_r = 2.5 \times 10^{-4}$ mol dm⁻³, E_m is *ca.* 30 mV more positive than $E^\circ(\text{V}^{2+}/\text{V}^{\cdot+})$.

Concentration-dependent mid-point potentials for benzyl viologen (BV^{2+}) have been reported⁶⁰⁻⁶¹ and it seems likely that the value of this reference potential is more negative than the electrochemical data suggest.⁶¹ A provisional value of -370 mV would be reasonable, pending further investigation; such a value is also consistent with unpublished work by the author with Mr. E.D. Clarke. Experiments determining ΔE for nitroaryl compounds *vs.* both benzyl and methyl viologen indicated *either* $E^\circ(\text{V}^{2+}/\text{V}^{\cdot+})$ for the benzyl analogue was lower than -354 mV (previously assumed) *or* the value for methyl viologen was higher than the well-established value of -448 mV. The apparent correction necessary was usually ~ 16 mV, in agreement with the new recommendation for $E^\circ(\text{BV}^{2+}/\text{BV}^{\cdot+}) = -370$ mV.

This problem of dimerization of viologen radical-cations has serious implications in estimating the value of $E^\circ(\text{BV}^{2+}/\text{BV}^{\cdot+})$ from electrochemical measurements. It is much less of a problem when electron-transfer equilibria with $\text{BV}^{\cdot+}$ as reactant are studied by pulse radiolysis, since $[\text{BV}^{\cdot+}]$ is typically ≤ 1 $\mu\text{mol dm}^{-3}$ at equilibrium, and the equilibrium point may well be established before significant dimerization (reverse of reaction 36) can occur. Dimerization is also much less of a problem with methyl viologen (MV^{2+}), and there are so many values published (see Table 3, compound 3.8.2) that outliers can be clearly identified. A value of $E^\circ(\text{MV}^{2+}/\text{MV}^{\cdot+}) = -448$ mV is recommended. The usefulness of low potential viologens in particular, outweigh these uncertainties. The reported⁶²

protonation of the methyl viologen radical cation with $pK_a = 1$ seems more likely ascribable to other reactions⁶³, and the pH-independence of these couples is a further advantage.

6.4. Hydroquinones and Phenols

The studies of Steenken and Neta^{8,64} of equilibria of the form:



with A^{2-} , B^{2-} = hydroxy- and amino-phenols, phenylenediamines, etc. have provided values of $E_{13,5}(A^{\cdot-}/A^{2-}) = 23, 43$ and 174 mV for A^{2-} = hydroquinone, 1,2-dihydroxybenzene (catechol) and 4-(*N,N*-dimethylamino)phenol respectively. These are supported by internal consistency of measured values of K_{37} . Their value of $E_{13,5}(A^{\cdot-}/A^{2-}) = 266$ mV for A^{2-} = *N,N,N',N'*-tetramethyl-*p*-phenylenediamine is similarly supported by other redox equilibria,⁶⁴ and by earlier electrochemical measurements⁶⁵ so that an estimate⁸ of 88 mV may be discounted. All the equilibria were measured at $I \approx 0.5$. It is worth stressing again that values of reduction potentials enable the *thermodynamic feasibility* of reactions to be calculated, not the *likelihood*; deprotonation of reactants may be necessary before the *rates* of reaction become sufficiently fast for the reaction to proceed. The lack of reversibility of the NAD⁺/NADH couple for nicotinamide adenine dinucleotide has been discussed.⁶⁶

6.5. Inorganic Indicators other than Oxygen

Reference to Table 9 indicates the high reliability of $E^\circ(\text{ClO}_2^{\cdot-}/\text{ClO}_2^-) = 934$ mV. More powerful oxidants include halogen- and pseudohalogen radical-anions, e.g. $(\text{SCN})_2^{\cdot-}$ or $\text{Br}_2^{\cdot-}$; the reduction potentials of these radicals are established to *ca.* ± 30 mV; values of $E^\circ((\text{SCN})_2^{\cdot-}/2\text{SCN}^-) = 1330$ mV and $E^\circ(\text{Br}_2^{\cdot-}/2\text{Br}^-) = 1660$ mV are presently recommended.

A useful, very low potential inorganic oxidant is Ti^+ , the reduced form of which is in equilibrium with Ti_2^+ :



The equilibrium constant $K_{38} = 140 \text{ dm}^3 \text{ mol}^{-1}$ and under certain conditions equilibrium 38 may be attained faster than electron transfer between Ti^+ and reductants.⁶⁷ Hence providing account is taken of the equilibrium 38, the reduction potential of very low potential oxidants may be derived using Ti^+ as indicator and $E^\circ(\text{Ti}^+/\text{Ti}_{\text{aq}}^0) = -1.94$ V.⁶⁷

7. Prediction of Reduction Potentials for Unknown Couples

7.1. Use of Polarographic and Cyclic Voltammetric Data Obtained Using Non-aqueous Solvents

The literature of electrochemical measurements of $E(A/A^{\cdot-})$, $E(A^{\cdot-}/A^{2-})$ in aprotic solvents is voluminous. Such measurements will generally differ considerably in absolute terms (when corrected to s.h.e., see above, Sec. 2.2) from corresponding values for water. However, relative effects in aprotic solvents, e.g. the influence of substituents⁶⁸ in a molecule of known potential in aqueous solution, may be useful. Measurements in water using cyclic voltammetry correlate⁶⁹ but do not necessarily equate with the reversible potentials $E(A/A^{\cdot-})$ (but see Sec. 3.4, above). The greatest discrepancies will be where molecules have substituents with prototropic functions.

7.2. Correlations Between Reduction Potentials and Rate Constants

There are several correlations of k_f , k_{-f} with ΔE_1 of the form based upon the Marcus theory (e.g. with radiation-produced radicals^{64,70,71}). Values of $E(A/A^{\cdot-})$, for example, may sometimes be estimated from other rate constants providing they are well below the diffusion-controlled limits. Values of k_f were correlated with the e.s.r. characteristics (see below) of $A^{\cdot-}$ for A = nitrobenzenes,⁷² and are therefore linked to reduction potentials.

7.3. Correlations Between Reduction Potential and Other Physico-chemical Parameters

The correlations well established for polarographic potentials⁶⁸ provide a guide to other useful parameters which may be used to predict values for unknown couples. Hammett substituent constants (σ values) are the most useful, e.g. for 5-substitution of 1-methyl-2-nitroimidazole we have:⁷³

$$E(A/A^{\cdot-})/mV = -(406 \pm 5) + (146 \pm 8)\sigma_p^- \quad (74)$$

Hammett constants are well known to correlate with hyperfine splittings (h.f.s.) in the electron spin resonance spectra of radical-anions of series of derivatives and a useful correlation between the N (NO₂) h.f.s. and $E(A/A^{\cdot-})$ has been made.⁷ Variations between mono- and di-nitrosubstituted series were noted.⁷⁴ Of course, relationships such as Eq. (74) will only be reliable predictors *either* when prototropic functions which could modulate E_m are absent, *or* when the pH is sufficiently high that E_m is unaffected by further increases in pH (all groups ionized or deprotonated). Since σ values are a measure of pK_a shifts, it would be theoretically possible to modify relationships between E_m and pH to incorporate σ as a predictor, but the relationships would be complex.

8. Arrangement of the Data Tables and Indexes

8.1. Content of the Tables

The Tables fall into 3 distinct groups. Tables 1 to 4 present reduction potentials of organic oxidants, in the form $E(A/A^{\cdot-})$ where A is a stable ground state and $A^{\cdot-}$ the radical produced on one-electron reduction. Tables 5 to 8 present reduction potentials of the radicals obtained upon one-electron oxidation of organic reductants, in the form $E(A^{\cdot-}/A^{2-})$ where A^{2-} represents a stable reductant and $A^{\cdot-}$ the radical (disregarding prototropic state, of course). Table 9 presents reduction potentials of inorganic species, but without separation into groups where the radical is either reductant or oxidant.

The systematic names for many of the compounds are complex, and (except for inorganic couples) rather than arrange alphabetically, compounds in Tables 1 to 8 are subdivided into related groups. Within each group, compounds are generally listed in related sub-groups with increasing element count (C,H,N etc.) in substituents defining order where appropriate. With the structures at the foot of appropriate pages, the various groupings should be reasonably clear. Multiple entries for any one couple appear in order of publication year.

Each Table contains 10 main columns: (1) A compound reference number. (2) The reduction potential of ground state or radical, as appropriate, all referring to one-electron reduction and all vs. the standard hydrogen electrode. These potentials are all mid-point potentials, E_m and in many, although not all cases, may be used as estimates for standard potentials, E° . Whether a measured or calculated value for E as tabulated equates or approximates to a standard potential depends largely upon the possible or known occurrence of prototropic equilibria involving either reductant, or oxidant, as discussed in Sec. 4. Column (3) gives the pH of measurement (or to which the calculation refers, where appropriate). Except where electrochemical methods were used most of the values were obtained by measurement of the concentrations of radicals and ground states at equilibrium, as outlined in Secs. 1 and 3. These have the symbol C (for concentrations) in column (9). A minority were determined from the kinetics of approach to equilibrium (Sec. 3.7). In this case K (for kinetics) appears in column (9). Either C or K may appear in parentheses where the data were secondary to, i.e. merely supported, the calculation of ΔE . Column (4) gives the reference compound used in the electron-transfer equilibrium, and (5) the reference potential *assumed* in the calculation of E (see below).

Since many values were derived from radiation-chemical experiments in which *either* one-electron oxidation *or* reduction was selected by using scavengers as described in Secs. 3.1, 3.2, in column (6) the co-solute (scavenger) is given, to help describe the experiment. As described in Sec. 3.8, ionic strength frequently influences measured equilibrium constants or kinetics, and column (7) gives an approximate ionic strength to which the experiments relate. The expression: $\rightarrow 0$ appears in column (7) if the experimental values were extrapolated to zero ionic strength. Column (8) notes the experimental method used: if only C and/or K appears, as described above, then the method involved monitoring fast electron-transfer equilibria following generation of radicals by pulse radiolysis, before the radical species disappear by other routes. The final column, (10) gives the reference number of the study, using the number assigned by the Radiation Chemistry Data Center of the University of Notre Dame and is common to the many publications of the Center and its online databases.

8.2. Alterations to Published Values

In general, only correction to s.h.e. (where appropriate) has been made to the original data. Where a value seems questionable, this is indicated by a dagger alongside the value, usually with an explanatory note in the Comments/method column. A recommended value is indicated by an asterisk. Many of the values may be immediately corrected by the reader using new recommendations or new values for reference potentials as they become available, since the Table indicates the reference couple and value assumed in the original work. Such corrections will be relatively minor and presentation of original data seemed preferable to making minor changes which will themselves be subject to revision as refinements to reference potentials are published.

8.3. Inorganic Couples: Standard States

The user is reminded that the standard state for a substance is that existing in its normal state at standard temperature and pressure (Sec. 2.2.), i.e. for gases such as oxygen it is 1 atmosphere partial pressure. For calculations of equilibrium constants where concentrations are appropriate, the Nernst equation should be used to calculate a reduction potential corresponding to unit concentration. More detailed discussion of numerous inorganic couples is given in Stanbury's recent compilation,⁷⁵ but the reader is warned that the latter author presents data uniformly using a standard state of 1 mol dm⁻³, including couples involving gases.

9. Some other Compilations of Reduction Potentials

Clark's classical text²² includes compilations of many reduction potentials of organic substances. The volume by Bard *et al.*¹¹ supersedes an earlier compilation¹⁰ of reduction potentials of inorganic substances in aqueous solution. Stanbury's review⁷⁵ discusses inorganic couples involving free radicals in more detail (note the comment about standard states in Sec. 8.3). Steenken⁷⁶ presents comprehensive information concerning electron transfer equilibria involving radicals and radical ions in aqueous solution. This includes values of reduction potentials as well as data characterizing the kinetics of electron-transfer equilibria involving radicals. Koppenol and Butler have discussed the energetics of interconversion of oxyradicals.⁷⁷

10. List of Abbreviations and Symbols

A	General symbol for oxidant or electron acceptor
A*	Triplet excited state of species A
A ²⁻	General symbol for fully dissociated form of reductant AH ₂
A _i	Absorbance of species <i>i</i>
a _A	Activity of species A
AcOH	Acetic acid
AH ⁻	General symbol for partially dissociated form of reductant AH ₂
AH ₂	General symbol for reductant or electron donor
Approx.	Approximate
AQS ⁻	9,10-Anthraquinone-2-sulfonate (Tables, 1.3.1)
Au.	This author (PW)
bpy	2,2'-Bipyridine
<i>t</i> -BuOH	<i>tert</i> -Butyl alcohol (2-Methyl-propan-2-ol)
BV ²⁺	Benzyl viologen (1,1'-Dibenzyl-4,4'-bipyridinium) (Tables, 3.8.39)
C (in Methods column)	Concentrations used to estimate equilibrium constant (Introduction, Sec. 8.1)
CAT	Catechol (1,2-Dihydroxybenzene) (Tables, 5.2.1)
Calc.	Calculated
Calc. data	Calculated by the present author from data in reference shown
Calc. lit.	Calculated by the authors in the reference shown from literature data
Calc.	Calculation
Consts.	Constants
Cyc. v.	Cyclic voltammetry
Diff. pulse volt.	Differential pulse voltammetry
DMAP	4-(Dimethylamino)phenol (Tables, 5.1.8)
DQ	Duroquinone (2,3,5,6-Tetramethyl-1,4-benzoquinone) (Tables 1.1.7)

E	General symbol for reduction potential
E°	Standard reduction potential (Introduction, Sec. 4.2)
E_0	Formal reduction potential (Introduction, Secs. 4.3, 4.4)
E_h	Reduction potential of half-cell relative to s.h.e. (Introduction, Sec. 4.2)
E_m	Mid-point potential of half-cell (Introduction, Sec. 4.3)
E_{mi}	Mid-point potential of half-cell at pH = i (Introduction, Sec. 4.4)
Eq.	Equation
Extrap.	Extrapolated
F	The Faraday constant = $9.649 \times 10^4 \text{ C mol}^{-1}$
f_A	Activity coefficient of species A
$f(I)$	Ionic strength function (Introduction, Sec. 3.8)
Fp	Flash photolysis
Glycol	Ethylene glycol (1,2-Ethandiol)
GlyTyr	Glycyl-L-tyrosine
h	Planck's constant = $6.626 \times 10^{-34} \text{ J s}$
HQ	Hydroquinone (1,4-Dihydroxybenzene) (Tables, 5.4.1)
I	Ionic strength
k	Rate constant
K	Equilibrium constant (expressed in terms of activities)
K'	Equilibrium constant (expressed in terms of concentrations)
K_a	Dissociation constant of an acid or the conjugate acid of a base
K_D	Equilibrium constant for dissociation of dimer (Introduction, Sec. 6.3)
K_f	Equilibrium constant of semiquinone formation equilibrium (Introduction, Sec. 5.1)
K_{fi}	Apparent semiquinone formation constant at pH = i (Introduction, Sec. 5.2)
K (in Methods column)	Kinetics used to estimate equilibrium constant (Introduction, Sec. 8.1)
Kin.	Kinetics
MV^{2+}	Methyl viologen (1,1'-Dimethyl-4,4'-bipyridinium) (Tables, 3.8.2)
n	Number of electrons transferred in the oxidant/reductant couple
NAD^+	Nicotinamide-adenine dinucleotide (Tables, 4.4.6)
$NADH$	Nicotinamide-adenine dinucleotide, reduced form (Tables, 8.2.1)
n.c.e.	Normal calomel electrode ($1 \text{ mol dm}^{-3} \text{ KCl}$)
Pol.	Polarography
Pot.	Potentiometry
Potl.	Potential
2-PrOH	<i>iso</i> Propyl alcohol (Propan-2-ol)
Q	General symbol for quinones
QH_2	General symbol for hydroquinones
R	The gas constant = $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$
Rad.	Radiolysis
Rec.	Recommended
Reduct.	Reduction
Ref.	Reference
S_o	Sum of all oxidant species (Introduction, Sec. 4.3)
S_r	Sum of all reductant species (Introduction, Sec. 4.3)
s.c.e.	Saturated calomel electrode
Sec.	Section
s.h.e.	Standard (normal) hydrogen electrode
Spect.	Spectrophotometry
T	Absolute temperature
TMP	3,4,7,8-Tetramethylphenanthroline
TMPD	<i>N,N,N',N'</i> -Tetramethyl- <i>p</i> -phenylenediamine (Tables, 6.1.5)
TQ^{2+}	Triquat (7,8-Dihydro-6 <i>H</i> -dipyrido[1,2- <i>a</i> :2',1'- <i>c</i>]diazapinediium) (Tables, 3.4.1)
v/v	Parts by volume
z_A	Net charge (valency) on ion A

ν	Frequency
σ_p^-	Hammett sigma substituent constant (from <i>para</i> substituted phenols)
ΔE	Difference in reduction potentials (Introduction, Sec. 1)
ΔG	Free energy change accompanying reaction

11. Acknowledgements

The Radiation Laboratory at the University of Notre Dame is operated under contract DE-AC02-76ER0038 with the Department of Energy. The Radiation Chemistry Data Center is supported jointly by the Office of Basic Energy Sciences of the Department of Energy and the National Bureau of Standards, Office of Standard Reference Data. This is Radiation Laboratory Document No. NDRL-3098. Peter Wardman is supported by the Cancer Research Campaign. The author would like to acknowledge the continual assistance and encouragement of Dr. Alberta B. Ross during this project, Dr. W. Phillip Helman and Ms. Christa Wardlow for help with the text processing, and all their colleagues in the Data Center for invaluable assistance: their help is gratefully acknowledged.

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