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The
Oxidation States of the Elements
and their
Potentials in Aqueous Solutions

BY

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Preface

The most convenient method of ascertaining the relative heights of two mountains is generally by reference to a table of measured altitudes. In order to use the table, it is not necessary to understand the principles of triangulation by which the altitudes have been determined. So, also, a table of the energies of the elements in their various oxidation states may be used by one with a very elementary knowledge of thermodynamics to answer many of the qualitative questions involved in the interpretation of inorganic chemistry.

In making this summary of existing data, the author has adopted the point of view of one interested in the chemistry of the various elements, rather than the point of view of one whose interest is largely in thermodynamics as a science. The author hopes that readers of the latter class, who are disappointed at the frequent inclusion of approximate data, will find in these obvious shortcomings an incentive for careful investigations in the near future. Much of the older work should have been recalculated by modern methods, but the labor involved is beyond the capacity of a single author.

The free energies of the oxidation-reduction couples, taken with reference to the hydrogen couple, have been expressed as volts per equivalent, since this affords the simplest comparison of the relative driving power of the various couples. However, for completed oxidation-reduction reactions, the free energies have been given in calories, as the number of equivalents of electricity is sometimes ambiguous. Solubility products and the dissociation constants of weak acids, bases, and complex ions have been included whenever the data were available.

The author, in calculating many new free energies from reaction heats, has drawn largely upon his own experimental work on the entropies of solids and aqueous ions. Our present knowledge of the entropy values permits the estimation of many entropies from the values of similar substances, and these estimates have frequently been employed in third-law calculations to obtain approximate reaction potentials.

Potentials have been given for many couples which are not thermodynamically reversible. These values, of course, cannot be used in equilibrium reasoning. However, these potentials are of value in indicating the minimum energy which must be employed to accomplish the oxidation or reduction, and they often give considerable information regarding the possible reaction mechanisms and the cause of the slowness of the reactions.

In some cases it would be valuable to list potentials for couples at 1 *M* concentration, rather than list the E° values.* However, these molal potentials are not so useful as one might at first think. They can be used accurately only at 1 *M* concentration; and, if an approximate value is desired, the E° without corrections for the activity might as well be used.

References have been given for all values employed. These references may usually be consulted for additional references to older works. The author has endeavored to include in his references all works published up to 1938.

Some mention should be made of the author's attempt to avoid the confusion existing with regard to the use of the term *valence*. This term has been restricted to mean, in the organic chemistry sense, the number of bonds (electron pairs) which an atom shares with other atoms. Such a usage renders the terms *covalence* and *coördination number* unnecessary but requires additional nomenclature to designate the charge upon an atom. In many cases this charge is a readily determinable number as, for example, the charge of -1 on chloride ion. This charge will be called the *polar number*. In a large number of compounds the polar number of each atom cannot be readily determined experimentally, but a fair approximation is obtained by assuming that the two electrons of a bond are shared equally between the two atoms. On this basis the charge upon the sulfur atom in sulfate is $+2$ and that upon each oxygen is -1 . The term *formal polar number* has been suggested for the charge estimated in this manner.

However, for the purpose of classification, a still more arbitrary method of assigning values to the charges upon the atoms of a compound has proved extremely useful. As an example, we may again use the sulfate ion. This method assumes that each oxygen has a charge of -2 , which then gives a charge of $+6$ to the sulfur. These assumptions not only simplify the classification of compounds but are also valuable in the interpretation of oxidation-

reduction reactions. Thus, the +6 charge on the sulfur may be correlated with the six electrons involved in the half-reaction for the oxidation of sulfur to sulfate,



Similar half-reactions may be written for the oxidation (or reduction) of any free element to any of its compounds, and the number of electrons involved in the reaction may be used to define the oxidation number or oxidation state of the element.

To summarize the illustration of nomenclature for the sulfate example, we may state: the valence of the sulfur is four; the polar number is unknown, but the formal polar number is +2; and the oxidation state is +6.

The author owes much to the spirit of coöperation which has been so carefully fostered in this department by Professor Gilbert N. Lewis. In the author's opinion there is no man who has such a complete understanding of the mechanism of inorganic reactions as does Professor William C. Bray, and he is especially indebted to Professor Bray for the advice so willingly given on many problems. The author wishes to thank both the many graduate students who have read and criticized the manuscript and Dr. George G. Manov for his recalculation of many of the free energies.

WENDELL M. LATIMER

Contents

CHAPTER	PAGE
I. UNITS, CONVENTIONS, AND GENERAL METHODS EMPLOYED IN THE DETERMINATION OF OXIDATION-REDUCTION POTENTIALS.....	1
Energy units. Temperature. E° values. Hydrogen reference couple. Conventions regarding sign. Addition or subtraction of half-reaction potentials. Potentials from galvanic cells: Cells without liquid junctions. Cells with liquid junctions. Potential values from free energies and equilibrium constants. Potential values from thermal data. Estimation of potential values from chemical evidence.	
II. IONIZATION POTENTIALS, ELECTRON AFFINITIES, LATTICE ENERGIES, AND THEIR RELATION TO STANDARD OXIDATION-REDUCTION POTENTIALS.....	13
Ionization potentials. Electron affinities. Reactions at 25° C. Lattice energies. Hydration energies. Absolute electrode potentials. Absolute hydration energies. Factors which determine the magnitude of oxidation-reduction potentials. Proton affinities. Acidic and basic oxides.	
III. HYDROGEN.....	26
Oxidation states. The H_2-H^+ couple. The second ionization constant of water. The hydride-hydrogen ion couple. The D_2-D^+ couple.	
IV. OXYGEN.....	34
Oxidation states. The water-oxygen couple. The water-oxygen atom couple. The peroxide-oxygen couple. The water-peroxide couple. The free energy of solid peroxides. The water, oxygen-ozone couple. Couples involving perhydroxl. Couples involving hydroxyl.	
V. THE HALOGENS.....	45
Flourine: The flouride-flourine couple. The flourine-oxide potential. Chlorine: Oxidation states. The chloride-chlorine couple. The chloride-hypochlorite couple. The chloride-chlorite couple. The chloride-chlorine dioxide couple. The chloride-chlorate couple. The chloride-perchlorate couple. Perchlorate radical. Additional chlorine half-reactions. Notes on the chlorine potentials. Bromine: Oxidation states. The bromide-bromine couple.	

V. THE HALOGENS (*Cont.*)

The bromide-hypobromite couple. The bromide-bromate couple. Bromine chloride as an oxidizing agent. Additional bromine half-reactions. Notes on the bromine potentials. Iodine: Oxidation states. The iodide-iodine couple. The iodide-triiodide couple. The iodide-hypoiodite couple. Iodine monochloride. Iodine monobromide. Iodine trichloride. The iodide-iodate couple. Periodic acid. Additional iodine half-reactions. Notes on the iodine couples. Notes on the potentials of the halogen group.

VI. SULFUR, SELENIUM, TELLURIUM, AND POLONIUM

64

Sulfur: Oxidation states. The sulfide-sulfur couple. The polysulfides. The sulfur-sulfurous acid couple. The sulfite-sulfate couple. Thiosulfate and tetrathionate. Sulfoxylic acid. Hyposulfurous acid. The thionic acids. Peroxydisulfate. Sulfur-halogen compounds. Reduction of sulfur compounds in steps. Selenium: Oxidation states. The selenide-selenium couple. The selenium-selenite couple. Selenite-selenate couple. Selenium halogen compounds. Tellurium: Oxidation states. The telluride-tellurium couple. The tellurium-tellurous acid couple. The tellurous acid-telluric acid couple. Halogen compounds of tellurium. Polonium: Oxidation states. Polonium couples. Summary of Group VI potentials.

VII. NITROGEN, PHOSPHORUS, ARSENIC, ANTIMONY, AND BISMUTH

82

Nitrogen: Oxidation states. Free energies from thermal data. Equilibria involving HNO_3 , HNO_2 , N_2O_4 , NO_2 , and NO . The reduction of nitric acid. The nitrite-nitrate couple. The reduction of nitrous acid. The hydroxylamine-ammonium couple. The reduction of nitrous acid with sulfite. The oxidation and reduction of hydrazine. Nitrite to ammonia in alkaline solution. The reduction of nitric and nitrous oxides. Hydrazoic acid. Nitrosyl chloride and nitrosyl bromide. Summary of nitrogen potentials. Phosphorus: Oxidation states. The free energies of phosphorus compounds. The phosphorous-phosphoric acid couple. Hypophosphoric acid. Hypophosphorus acid. Phosphine and other hydrogen phosphides. Phosphorus halogen compounds. Summary of phosphorus potentials. Arsenic: Oxidation states. Arsine. The arsenic-arsenious acid couple. The arsenious acid-arsenic acid couple. Arsenic sulfides. Arsenic trichloride. Summary of arsenic potentials. Antimony: Oxidation states. The stibine-antimony couple. The antimony-antimonous acid couple. The antimonous-antimonic acid couple. Antimony tetroxide. Antimony

CHAPTER

PAGE

VII. NITROGEN, PHOSPHORUS, ARSENIC, ANTIMONY,
AND BISMUTH (*Cont.*)

trichloride. The antimony sulfides. Summary of antimony potentials. Bismuth: Oxidation states. Bismuth hydrogen compounds. The bismuth-bismuthyl couple. Bismuth trichloride and oxychloride. Bismuth monoxide. Bismuth tetroxide and pentoxide. Trends in the Group V potentials.

VIII. CARBON, SILICON, GERMANIUM, TIN, AND
LEAD..... 117

Carbon: Oxidation states. The free energy of carbon compounds. The oxidation of hydrocarbons. Electrolytic reduction of acids, aldehydes, and alcohols. The electrolytic oxidation of alcohols, aldehydes, and acids. Peroxycarbonate. Carbon as an oxidizing agent. Unsaturated hydrocarbons. Aniline-nitrobenzene. Cyanide, cyanate, and cyanogen. Thiocyanate. Hydroquinone-quinone couples. Diphenylbenzidine and derivatives. Indophenols. Methylene blue. Indigo. Erioglaucine A. Nitroguanidine. Xanthines. Flavines, murexides, and porphyrexide. Safranine. Free energies of CS_2 , COS , $COCl_2$, CCl_4 , and $CO(NH_2)_2$. Silicon: Oxidation states. The free energies of some silicon compounds. Oxidation and reduction of silicon. Equilibria involving the silicon halides. Germanium: Oxidation states. Germanium potentials. Tin: Oxidation states. Tin-stannous potentials. Stannous-stannic potentials. Lead: Oxidation states. Lead-plumbous and lead-plumbite couples. Plumbous halides. Additional lead-plumbous couples. Plumbous-plumbic couples. The lead storage battery.

IX. GALLIUM, INDIUM, AND THALLIUM..... 147

Gallium: Oxidation states. The gallium-gallic ion couple. Gallous chloride. The +1 oxide. Indium: Oxidation states. The indium-indic ion couple. The +1 and +2 oxidation states. Thallium: Oxidation states. The thallium-thalious couple. The thalious-thallic couple. Summary of Group 3' potentials.

X. ZINC, CADMIUM, AND MERCURY..... 155

Zinc: Oxidation states. The zinc-zinc ion couple. Cadmium: Oxidation states. The cadmium-cadmium ion couple. Cadmium in the +1 state. Mercury: Oxidation states. The mercury-mercurous ion couple. The mercury-mercurous halide couples. Additional mercury-mercurous salt couples. The mercurous-mercuric couple. The mercury-mercuric oxide couple. The mercury-mercuric sulfide couple. The mercuric cyanide and halide complex ions. Additional mercuric couples. Summary of the Subgroup II potentials.

CHAPTER	PAGE
XI. COPPER, SILVER, AND GOLD.....	169
<p>Copper: Oxidation states. The copper-cuprous couple. The copper-cuprous oxide couple. The copper-cuprous halide couples. The copper-cuprous cyanide and thiocyanate couples. Copper-cuprous sulfide and other cuprous couples. The copper-cupric ion couple. The copper-cupric oxide or hydroxide couple. The copper-cupric sulfide couple. Other copper-cupric couples. Various cuprous-cupric couples. Copper in the +3 state. Silver: The oxidation states of silver. The silver-silver ion couple. The silver-silver oxide couple. The silver halide and cyanide couples. The complex silver ammonia, sulfite, and thiosulfate ions. The silver-silver sulfide couple. Additional silver-silver salt potentials. Silver in the +2 and +3 oxidation states. Gold: Oxidation states. Gold-auric couples. The gold-aurous couples. Gold in the +2 oxidation state. Summary of Subgroup I potentials.</p>	
XII. NICKEL, PALLADIUM, AND PLATINUM.....	187
<p>Nickel: Oxidation states. The nickel-nickelous couple. The nickel-nickel hydroxide couple. Complex nickelous ions. Nickel carbonate and sulfide. Nickelic oxide. Higher oxidation states of nickel. Palladium: Oxidation states. Palladium-palladous couples. Palladium in the +4 and +6 oxidation states. Platinum: Oxidation states. Platinum-platinous couples. Platinum in the +3 state. Platinous-platinic couples. Perplatinite. Summary of the group potentials.</p>	
XIII. COBALT, RHODIUM, AND IRIIDIUM.....	198
<p>Cobalt: Oxidation states. Cobalt-cobaltous couples. Cobaltous-cobaltic couples. Cobalt dioxide. Rhodium: Oxidation states. The free energies of some rhodium compounds. Rhodium in the +4 and +6 states. Iridium: Oxidation states. The free energy of a number of iridium compounds. The +3—+4 couples. Iridium in the +6 state. Summary of group potentials.</p>	
XIV. IRON, RUTHENIUM, AND OSMIUM.....	208
<p>Iron: Oxidation states. Iron-ferrous couples. Ferrous-ferric couples. Iron in the +4 and +6 states. Ruthenium: Oxidation states. Ruthenium potentials. Osmium: Oxidation states. The free energy of osmium tetroxide. Potentials of other osmium couples.</p>	

XV. MANGANESE, MASURIUM, AND RHENIUM..... 219

Manganese: Oxidation states. Manganous ion and its compounds. Manganic potentials. Complex manganese cyanides. Manganese dioxide, manganate, and permanganate. Manganese dioxide electrode in dry cells. Summary of manganese potentials. Rhenium: Oxidation states. Rhenium potentials. Summary of rhenium potentials.

XVI. CHROMIUM, MOLYBDENUM, TUNGSTEN, AND URANIUM..... 228

Chromium: Oxidation states. The free energy of chromic ion. Chromic hydroxide. Chromous ion. Chromate and dichromate. Chromyl chloride. Molybdenum: Oxidation states. The free energy of molybdate and molybdic acid. The reduction of molybdic acid to the +5 and +3 states. Molybdenum cyanides. Molybdenum dioxide. Molybdenum peroxide. Tungsten: Oxidation states. Free energies of the oxides. The free energy of tungstate. The reduction of tungstate in hydrochloric acid. Uranium: Oxidation states. Free energy of uranyl ion. Uranium dioxide. Uranium in the +3 state. Summary of group potentials.

XVII. VANADIUM, COLUMBIUM, TANTALUM, AND PROTOACTINIUM..... 241

Vanadium: Oxidation states. Vanadic acid and the vanadates. The vanadyl-pervanadyl couple. The $V^{++}-VO^{++}$ and $V^{++}-V^{+++}$ couples. The free energy of the vanadium oxides. The metal- V^{++} couple. Vanadium peroxyacids. Columbium: Oxidation states. Columbic oxide. Columbium potentials. Tantalum: Oxidation states. Tantalic oxide and fluoride. Tantalum potentials. Protoactinium: Summary of group potentials.

XVIII. TITANIUM, ZIRCONIUM, HAFNIUM, AND THORIUM..... 249

Titanium: Oxidation states. Titanium dioxide. The $Ti^{+3}-TiO^{++}$ couple. The $Ti^{++}-Ti^{+3}$ couple. The $Ti-Ti^{++}$ potential. Fluotitanate. Summary of titanium potentials. Zirconium: Oxidation states. The free energy of zirconium dioxide. Hafnium: Oxidation states. The free energy of hafnium oxide. Thorium: Oxidation states. Free energy of thorium dioxide. Summary of group potentials.

CHAPTER	PAGE
XIX. BORON, ALUMINUM, SCANDIUM, YTTRIUM, LANTHANUM, RARE EARTH ELEMENTS, AND ACTINIUM.....	258
<p>Boron: Oxidation states. Boric acids and their salts. Boron potentials. Heteroboric acids. Aluminum: Oxidation states. Aluminum potentials. Scandium: Oxidation states. Scandium potentials. Yttrium: Oxidation states. Yttrium potentials. Lanthanum and the rare earth elements: Oxidation states. Properties of the +3 state. The dioxides. Properties of the +2 ions. Actinium.</p>	
XX. BERYLLIUM, MAGNESIUM, CALCIUM, STRONTIUM, BARIUM, AND RADIUM.....	270
<p>Beryllium: Oxidation states. Beryllium free energies. Magnesium: Oxidation states. Free energy of Mg^{++} and its compounds. The free energy of Mg^+. Calcium: Oxidation states. Calcium free energies. Calcium in the +1 state. Strontium: Oxidation states. Strontium free energies. Barium: Oxidation states. Barium free energies. Radium: Summary of group potentials.</p>	
XXI. LITHIUM, SODIUM, POTASSIUM, RUBIDIUM, AND CESIUM.....	283
<p>Oxidation states. The metal-metal ion potentials. Free energies of solution of alkali salts. Trends in the solubilities of the alkali compounds.</p>	

APPENDIXES

I. SUMMARY OF OXIDATION-REDUCTION POTENTIALS.....	293
II. SUMMARY OF FREE ENERGIES OF FORMATION...	302
III. SUMMARY OF EQUILIBRIUM CONSTANTS.....	309
IV. THE ACTIVITY OF STRONG ELECTROLYTES.....	318
V. ENTROPY VALUES.....	328
INDEX.....	337

CHAPTER I

Units, Conventions, and General Methods Employed in the Determination of Oxidation-Reduction Potentials

As stated in the Preface, the primary object of this work is to gather together the large mass of free-energy data which is scattered throughout the literature and to present it in a simple form as an aid in the interpretation of inorganic chemistry. Although the author does not wish to stress in detail the methods by which these data have been obtained, it seems desirable, for the sake of clarity, to discuss in a preliminary chapter general methods and to give references to more detailed treatments.

The potentials have been derived from four sources: (1) the direct measurement of cells, (2) equilibrium data, (3) thermal data, and (4) approximate limiting values based upon the chemical behavior of a couple with respect to known oxidizing and reducing agents. Before outlining these methods, a statement of the energy units employed and the general conventions in nomenclature will be given.

Energy units. The unit of potential employed is the international volt. This is related to the absolute volt by the equation,

$$1 \text{ volt (international)} = 1.0004 \text{ volts (absolute)}.$$

The international joule, defined by the international units for the volt, ampere, and ohm, is the unit of energy. When it is desired to express energies in calories, the defined calorie used by Bichowsky and Rossini¹ has been employed.

$$1 \text{ calorie (defined)} = 4.1833 \text{ joules}.$$

Other units which enter into various calculations are:

$$0^\circ \text{ Centigrade} = 273.15^\circ \text{ Absolute or Kelvin},$$

$$1 \text{ Faraday} = 1 \text{ equivalent} = 96,494 \text{ coulombs (international)},$$

$$1 \text{ volt equivalent} = 23,066 \text{ calories (defined)},$$

$$R \text{ (gas constant)} = 8.3118 \text{ joules (international) per degree per mole}.$$

¹ Bichowsky, F. R., and Rossini, F. D., *Thermochemistry of the Chemical Substances* (Reinhold, New York, 1936), p. 9.

Temperature. Unless otherwise stated, all potentials are given for the temperature of 25° C. or 298.15° K. The choice of the best value for 0° C. on the absolute scale is difficult. The value 273.1 is certainly too low. It is to be hoped that some definite agreement on the value to be used will be reached in the near future.

E° values. A potential is referred to as an E° value if all gases involved in the reaction are at a fugacity (thermodynamic pressure) of 1 atmosphere and all dissolved substances at an activity (thermodynamic concentration) of 1 molal, *i.e.*, 1 mole per 1000 grams of water.

The potential, E , at other concentration and pressures at 25° C. is given by the expression:

$$E = E^\circ - \frac{0.05914}{n} \log_{10} Q, \quad (1)$$

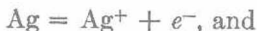
where Q is the product of the activities (or fugacities) of the resulting substances divided by the product of the activities of the reacting substances, each activity raised to that power whose exponent is the coefficient of the substance in the chemical equation; and n is the number of Faradays of electricity involved in the reaction as written. Thus Q has the same general form as the equilibrium constant, but it differs in that the activities refer not to the equilibrium state but to the actual activities of the reacting substances and their products. Activities of pure solids and liquids are taken as unity. For the equilibrium state, Q becomes the equilibrium constant, K , and since E for a reaction at equilibrium is zero,

$$E^\circ = \frac{0.05914}{n} \log K. \quad (2)$$

Hydrogen reference couple. Any oxidation-reduction reaction may be broken up into two "half-reactions" or "couples" that indicate the mechanism by which the electrons are transferred from the reducing agent to the oxidizing agent. For example, in the reaction,



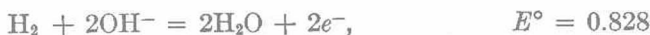
the two half-reactions, or couples, are:



The experimental determination of the absolute potential of any couple is a different problem (cf. p. 21), but since any chemical reaction involves only the difference in potential between two couples, the absolute values are unnecessary. For this reason the procedure has come into general use of choosing the potential of some one couple as an arbitrary zero and using this as a reference couple for potentials of all other couples. The reference couple so chosen is the hydrogen gas-hydrogen ion couple:



Reactions which involve hydroxide ion will also be referred to the hydrogen couple, but in such solutions this couple has the form (cf. p. 28),



The E° values of half-reactions in alkaline solution will be designated as E_B° to indicate that this basic potential of the hydrogen couple must be used to obtain the completed reaction potential against hydrogen.

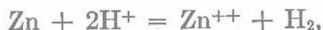
EXAMPLE



Conventions regarding sign. All couples will be written with the electrons on the right hand side of the equation. A positive value for E° will mean that the reduced form of the couple is a better reducing agent than H_2 . For example,



will mean that the reaction,



goes as written with a potential of 0.762 volts. And similarly a negative E° will mean that the oxidized form of the couple is a better oxidizing agent than H^+ . For example,



will mean that the reaction,

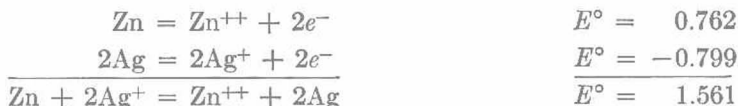


goes as written with a potential of 0.345 volts.

The convention, illustrated in these examples, of giving a positive sign to the potential of any complete reaction, which goes spontaneously in the direction as written, will be followed.

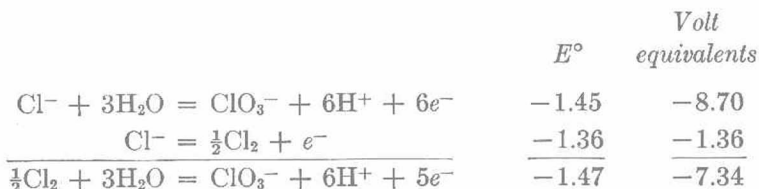
Addition or subtraction of half-reaction potentials. When one half-reaction is subtracted from another to give a complete reaction, the potential of the complete reaction is the algebraic difference in the potentials of the two half-reactions.

EXAMPLE



However, in the addition or subtraction of two half-reactions to give a third half-reaction, the free energies, *i.e.*, volt equivalents of the two half-reactions must be added or subtracted to give the free energies of the third half-reaction.

EXAMPLE

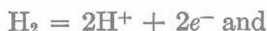


Potentials from Galvanic Cells

Cells without liquid junctions. The potential of a fairly large number of reactions may be measured directly in cells having a single electrolyte. Thus, for the reaction



having as half-reactions,



a cell may be constructed, using as one electrode metallic silver in contact with silver chloride, and as the other electrode hydrogen gas in contact with hydrogen ion on a platinum surface. The electrolyte throughout the cell may then be hydrochloric acid and is uniform except for the slight solubility of silver chloride. The two electrode reactions must be reversible and reasonably rapid. On many surfaces the hydrogen couple does not meet this requirement, but the reaction is sufficiently catalyzed by a platinized platinum surface. In the construction of any cell, the reducing and oxidizing agents must not come into direct contact with each other. Moreover the reducing agent must be the strongest reducing agent present at the anode and the oxidizing agent must be the strongest oxidizing agent present at the cathode. These requirements are met by the above cell with the exception that, if air is not excluded, the oxygen is a stronger oxidizing agent than silver chloride. However, its action is slow under these conditions and its exclusion from the cathode is therefore not necessary in this case.

From the electromotive force of this cell at any given concentration of hydrochloric acid and pressure of hydrogen, the E° value may be calculated from equation (1), if the activities of the hydrogen and chloride ions are known. Strictly speaking, it is not possible to measure the activity of an ion of one sign independently of the ion of opposite sign, so the information required is the *mean activity*, a_{\pm} , of the two ions. By definition, the *activity coefficient*, γ , is the ratio of the mean activity to the mean molality, m_{\pm} . That is,

$$\gamma = \frac{a_{\pm}}{m_{\pm}}. \quad (3)$$

At infinite dilution, the activity equals the molality and γ equals 1; and for each type of salt, the mean molality is defined in such a way that the ratio approaches unity at infinite dilution (cf. Appendix IV). If the potential measurements are carried out in dilute solutions, one may assume the concentration equal to the activity and calculate approximate E° values. However for the highest accuracy it is necessary to determine the γ values, and Appendix IV should be consulted for general references dealing with these experimental procedures. Fairly complete values of γ for various types of salts are also given in this appendix, and the following example illustrates their use in calculating E° values.