TABLES OF
STANDARD ELECTRODE POTENTIALS

Guilio Milazzo
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Sergio Caroli

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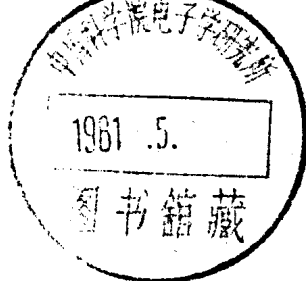**Guilio Milazzo**
and
Sergio Caroli

Istituto Superiore di Sanitá, Roma, Italy

with the cooperation of
V. K. Sharma
Department of Chemistry,
University of Rajasthan, Jaipur, India

Project of the IUPAC Electrochemistry Commission

A Wiley–Interscience Publication

5505990

$DR7S/12$

Introduction

The idea to collect all existing data on electrode potentials came to the mind of one of the authors (G.M.) when, needing the numerical value of a certain redox couple, he was unable to find it in any of the many tables published so far, and was therefore compelled to spend much time in searching for the value he needed in *Chemical Abstracts*. At the same time he realized once more that all available tables always reported the values of more or less the same electrode systems; for example Ag | AgCl | Cl⁻ or the calomel electrode, known practically by heart by every chemist.

All tables consulted constantly carried titles such as *Selected Tables* or *Critical Tables* or some other similar heading.

The reactions of this author were then:

1. Why collect always the values of the same electrode systems differing from one another by perhaps only a few tenths of millivolt (a difference which is negligible in common practice) and ignore a large number of investigated couples which can be of interest in many other cases?

2. What can be the unambiguous *logical* basis for the decision to accept in tables of so called 'critically selected' values the value given by a certain author for a particular electrode system in preference to all others published? For example, the Ag | AgCl | Cl⁻ electrode has been thoroughly investigated by Bates, Ives, Janz, and many others. Each paper of each one of these authors is scientifically an excellent paper giving all possible experimental details and a very good logical analysis of the errors. Nevertheless the results each author arrives at are somewhat different. On what logical basis should the value found, for example, by Bates be preferred to the one found by Ives, or vice versa?

3. On what *logical* basis should the value found by a less known investigator for a less familiar electrode system, such as lanthanide or actinide couple, be ignored? Even if a paper containing numerical data for less familiar systems investigated by less known scientists, were not, as a whole, as good as those quoted in point 2; these data, because of their usefulness (at least in first approximation) in specific cases still deserve inclusion in the collections of numerical data. Nevertheless they are practically never found in the collections of so-called 'selected values'.

Then, in view of the practical difficulty, if not of the impossibility, of giving really 'critically selected values' (i.e. *apparently* more reliable values), and in consideration also of the enormous amount of work and time required even for superficial criticism of all the papers read in order to compile these tables (more than 10,000), the decision was taken not to try any critical evaluation of the papers read and of the values given therein, unless they were evidently unreliable or they were found in a very incomplete abstract, the original paper being unavailable. In other words the present authors followed the philosophy that 'it is better to know something

than nothing' and adopted the practice of including in the tables all electrode systems and values found, accompanied by any useful information given in the original paper, and by the bibliographic reference, leaving it up to the reader to judge how far the value is reliable and how it answers his particular scientific needs.

At the time this work was started, one of the authors (G.M.) was a member of the Commission on Electrochemistry in the Division of Physical Chemistry of the International Union of Pure and Applied Chemistry (IUPAC). The idea of preparing this kind of table was brought up for discussion with the Colleagues on the Commission and it was accepted as one of its working projects.

Collecting all papers related to the subject and picking up the information required from all papers read, as well as the efforts to arrange such information into a single suitable scheme, as compact and clear as possible, took many years of painstaking work and many discussions at each meeting of the Commission. Criticism and suggestions brought forward at the end of each meeting, not only by colleagues in the Commission itself, but also by authoritative electrochemists outside the Commission, were taken into most serious consideration; their contributions led to consistent improvements in the usefulness of the tables. These tables were then presented in their near final form at the Brighton Meeting of the Commission held on September 20th and 21st, 1974. At the end of the meeting the statement, reproduced herewith in facsimile, was approved.

These tables collect all data published and abstracted in *Chemical Abstracts* from 1945 up to the end of 1973. An appendix contains some new data abstracted from the end of 1973 to the end of 1975 in *Chemical Abstracts* and in other relevant abstracting periodicals (*Analytical Abstracts* and *Electroanalytical Abstracts*).

The aim in presenting these tables is hence to offer a compilation of standard electrode potentials as complete as possible for all the elements, their compounds, and complexes.

By far the most important sources were original papers. A rather limited number of values, however, was taken from existing special compilations such as *The Standard Electrode Potentials and Temperature Coefficients at 25 °C* by A. J. de Bethune and N. A. Swendeman-Loud and the *Atlas d'Equilibres Electrochimiques* by M. Pourbaix, in which practically only standard potential values for some given systems are reported, without any indication of experimental conditions. A certain number of data taken from these special compilations are even calculated data. Finally, a very small number of data were calculated for the first time, following standard procedures, on the basis of other thermodynamically significant data (as in the case of equilibrium constants of complexes).

Not only data obtained using potentiometric procedures were collected, but also those derived using other electrochemical techniques (for example voltammetry), and even those obtained by non-electrochemical ones (for example spectrophotometry).

Some electrode and system compositions may appear strange or unusual, or even impossible. In such cases attention is drawn to the quoted method used to obtain the figure reported for the standard potential, which is in fact calculated theoretically (or obtained using very special procedures) concerning the hypothetical system considered. For instance, the standard potential given for the system $Na \mid (NaH_2 P_2 O_7)^-$ does not

International Union of Pure and Applied Chemistry

Division of Physical Chemistry
Commission on Electrochemistry

STATEMENT

Since 1967 the Commission on Electrochemistry of the IUPAC has followed with interest the important compilation on Standard Electrode Potentials carried out by Professor G. Milazzo within the frame of the activities of the Commission.

The author has taken into consideration the suggestions and the criticism which were presented on the occasion of the various meetings: Prague (1967), Cortina d'Ampezzo (1969), Paris (1970), Washington (1971), München (1973) and Brighton (1974).

The following set of extensive tables will certainly prove very useful for specialists in this field, because these data are widely scattered in the literature. In order to make these tables as comprehensive as possible Professor Milazzo has made no attempt to make a critical selection, but users can readily search in the numerous original contributions referenced for further information.

In view of this, the Commission encourages the publication of this work.

Brighton, Sept. 21st, 1974. The Chairman of the Commission

(Prof. R. Haase)

mean that it was really obtained by dipping a barrel of metallic sodium in a partially ionized acid pyrophosphate solution; it means, on the contrary, that this value was calculated theoretically for the given electrode reaction.

The term *potential* was adopted instead of *electromotive force*, since the latter (as usually employed by a number of electrochemists) is a thermodynamic quantity, not directly measurable, whereas the former is actually the quantity experimentally determined (which should be called much more correctly *electric tension*).[1]

The electrode reaction is always written in the sense of a reduction, according to the general scheme

$$Ox + e^- \rightleftharpoons Red$$
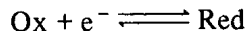
where Ox symbolizes the whole system in the oxidized state, while Red stands for the same system in the reduced state.

The convention used to obtain the sign of the potential is that of the *series of phases* in the galvanic half-element. This convention finally gives the same sign as results from the so-called *European Convention*, which in turn coincides also with the sign arising from the *Stockholm Convention*, but is more logical and of easier practical use.[2]

We hope that this set of extensive Tables will prove useful not only for specialists, but also for non-specialists in the field. The exhaustive character of this compilation together with the high number of references cited will give the reader a tool of practical use, which may encourage him and facilitate his task of retrieving in literature any couple of interest to him.

The achievement of such a goal will be for the authors of this compilation a more than satisfactory result.

Acknowledgements

1. G. Milazzo, *Anal. Quim.*, **70** (1974) 1214.
2. For more theoretical details on this point and on the practical advantages, see G. Milazzo, *Lehrbuch der Elektrochemie*, Vol. 1. Chap. III in course of publication, Birkhäuser Verlag, Basel.

How to Read the Tables

The Tables are arranged by element in the order of the Mendeleev periodic table. As for Group I, for example, the elements Li, Na, K, Rb, Cs, Fr are followed by Cu, Ag, Au. Elements belonging to the lanthanides and actinides series (from La to Lu and from Ac to No, respectively) are collected in two special tables reported at the end of the elements of Group VIII. For each element an extended table, a reduced table, and tables with notes and bibliography are given. In the extended tables the different electrode-systems are arranged alphabetically according to the right-hand term of the electrode reaction. As a rule, inorganic systems are listed first, followed by systems involving at least one organic component. When a certain electrode-system has been investigated in different media, the standard potential value in water is given first and values in non-aqueous solvents follow. On the other hand, the reduced tables contain for each element only the standard potential values in order of increasing values, together with a reference number for the retrieval of the same electrode system in the extended tables. In these reduced tables, standard potential values for aqueous systems are listed first, followed by those in pure non-aqueous solvents.

The extended Tables contain the following information:

1. **Electrochemically conducting phase:** i.e. what is generally called the *electrode* in a restricted sense. Sometimes it is a composite object, for instance a *glass electrode*. The term Ind. stands for *indifferent* electrode, i.e. not participating chemically in the electrode reaction.
2. **Intermediate species:** The non-ionized or possibly not solute species are given under this heading. For example, AgCl in the Ag | AgCl | Cl⁻ electrode.
3. **Composition of the solution:** It is obviously reported only when given in the original paper. It is missing for values calculated on the basis of the thermodynamic quantities. The symbols M, m, and N. stand for moles/kg solvent, moles/liter solution, and equivalents/liter solution, respectively.
4. **Solvent:** This is indicated by an Arabic numeral. The complete list of the solvents with the corresponding numeral is given at the end of this introductory section.
5. **Temperature:** This is given in degrees Celsius. The uncertainty is reported whenever quoted in the original paper.
6. **Pressure:** This is given in Torr. When not otherwise specified, the pressure is the uncorrected atmospheric one.
7. **Measuring method:** This is given as a Roman numeral. The explanatory list is also given at the end of the introduction.

8. **Comparison electrode**: This is indicated by an Arabic numeral; the key is given at the end of the introduction*.

9. **Liquid junction**: This is reported whenever present and explicitly mentioned by the author. Otherwise, no indication is given.

10. **Electrode reaction**: This is written as an equilibrium reaction in the sense of a reduction. In the presence of a complex, the ligand, L, is always written in rouna brackets.

11. **Standard value**: Both for water and pure non-aqueous solvent, the standard value of the potential (in V) is referred to the standard hydrogen electrode in the same solvent. When more than a single value was available in the literature for a certain electrode, only that originating from the most complete set of experimental data is given. If the other values are in the same range of uncertainty their average is reported; if not, notice of all of them is given.

12. **Uncertainty**: This is given (in mV) whenever quoted in the original paper for the standard potential reported.

13. **Temperature coefficient**: This is obtained using isothermal cells and includes therefore the individual temperature coefficient of the potential of the standard hydrogen electrode. The temperature coefficients are reported in $\mu V/^\circ C$ and are considered positive in sign if an increase in temperature causes an increase in the standard potential value. Considering that the individual temperature coefficient of the potential of the standard hydrogen electrode (i.e. the so-called *non--isothermal* temperature coefficient of the electrode potential) is $+859$ $\mu V/^\circ C$, it is easy to obtain the individual (non-isothermal) temperature coefficient of the standard potential simply by adding this value to that quoted in this volume.[1]

14. **Notes**: Arabic numerals in this column refer to the list given at the end of the tables for each element. Therein useful details on the experimental conditions are given under which the standard potential values were determined, further information on the method employed, etc.

15. **References**: This column gives the bibliographic reference of the papers from which the quoted values were taken. The Arabic numerals refer to the bibliography list given at the end of each group of tables for each element.

16. **Electrode reference number**: This last column contains progressive numbers by which each electrode system is designated.

Each alphabetical table for a single element is followed, as already mentioned, by another condensed table for the same element. In the reduced tables the standard

*Attention is drawn to the fact that whenever concentrations in the composition of the comparison electrode quoted are missing, they were missing in the original paper and the numerical value of the standard potential of the electrode under consideration (vs. the hydrogen standard electrode) were given directly by the author(s) of the paper.

1. For a deeper understanding of this very important point, see G. Milazzo, Ref. 2 of Introduction, or for more details the series of papers by G. Milazzo *et al., J. Electroanal. Chem.*, 2 (1961) 419; *Z. Phys. Chem. N.F.*, 52 (1967) 293; 54 (1967) 1, 13, 27; *J. Res. Inst. Catalysis Hokkaido Univ.*, 16 (1968) 387; *Z. Phys. Chem. N.F.*, 62 (1968) 47; 68 (1969) 250; 76 (1971) 127; 79 (1972) 41; *Anal. Quim.*, 71 (1975) 1033; *Electrochim. Acta*, 21 (1976) 349.

potentials of the electrode systems of each element considered are arranged according to the increasing values, listing aqueous systems first and then those in non-aqueous pure solvents. These condensed tables consist of three columns, with the headings 'Standard Values (V)', 'Solvent', and 'Electrode Reference Number'. This last indication leads the reader, who selected a system on the basis of the value of its standard potential in a given solvent, to locate it immediately in the alphabetical tables and to find all other information requested for the same system.

As already mentioned, at the end of this double series of tables for each element, explanatory notes as well as the related bibliography are given.

Keys and Explanatory Notes for Tables

(a) Ind = indifferent electrode, not participating chemically in the electrode reaction; composite terminal electrodes are given by name.

(b) Species not ionized, or not in solution.

(c) m = mol/kg; M = mol/liter.

(d) See list.

(e) When the value of the pressure is not specifically given, the pressure is the uncorrected atmospheric one.

(f) When more than one reference is given, the standard potential is the mean value of the potentials given by each author, all in the same range of uncertainty.

(g) The values include the temperature coefficient of the potential of the standard hydrogen electrode.

(h) Notes at the end of each group of tables.

Numerical Key for Solvents

1. Water
2. Ammonia
3. Hydrazine
4. Ethane bromide
5. Nitromethane
6. Ethylenediamine
7. Methyl alcohol (methanol)
8. Ethyl alcohol (ethanol)
9. Isopropyl alcohol (isopropanol)
10. n-Propyl alcohol
11. n-Butyl alcohol
12. n-Pentyl alcohol (n-Amyl alcohol)
13. Ethylene glycol
14. Propylene glycol
15. Acetone
16. Formic acid
17. Acetic acid
18. Formamide
19. N-Methylformamide
20. N,N-Dimethylformamide (DMF)
21. N-Methylacetamide
22. N,N-Dimethylacetamide
23. Acetonitrile
24. Dimethylsulfoxide
25. Toluene
26. Nitrobenzene
27. Pyridine
28. Hydrofluoric acid
29. Propylene carbonate
30. 1,2-Dimethoxyethane
31. Tetrahydrofurane
32. Glycerol
33. Trifluoroacetic acid
34. Acetamide
35. Deuterium oxide (heavy water)
36. N-Methylpyrrolidone
37. n-Hexanol
38. Phosphorous oxychloride
39. Benzonitrile
40. Phenylphosphoxydifluoride
41. Ethylacetate
42. Ethylpropionate
43. Phenylphosphoxydichloride
44. Diethylether
45. Trimethylphosphate
46. Hexamethylphosphoramide

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Measuring Methods

(I)   Potentiometric.

(II)   Polarographic.

(III)   Other: voltammetric,
conductometric, rotating disk, etc.

(IV)   Calculated.

(V)   Non-electrochemical method.

Numerical Key for Electrodes*

(1) $Pt-H_2$

(2)   N.C.E. (Normal Calomel Electrode)

(3)   S.C.E. (Saturated Calomel
Electrode)

(4)   Ag, AgCl

(5)   Ag, AgBr

(6) $Ag \mid Ag^+$ (0.1 M)

(7) $Ag \mid Ag^+$ (0.01 M)

(8) $Ag-AgCl_2$ (s) | LiCl·

(9) $Ag \mid Ag_2O$

(10) $Ag \mid Ag_4 [Fe(CN)_6]$

(11)   Ag, Ag_2MoO_4 $\left| \begin{array}{l} AgNO_3 \\ NaNO_3 \end{array} \right.$

(12)   Ag, Ag_2WO_4 $\left| \begin{array}{l} AgNO_3 \\ NaNO_3 \end{array} \right.$

(13) $Ag \mid Ag_2$ (oxalate)

(14)   Ag | Ag picrate 0.01 N

(15) $Cu-H_2$

(16)   Cu | CuCl

(17) $Cu \mid CuSO_4$ (0.01 M)

(18)   Hg, Hg_2Br_2

(19) $Hg \mid Hg_2SO_4, H_2SO_4$ (1 M)

(20) $Hg \mid Hg_x^{2+}$ (0.01 M)

(21) $(HCOO)_2$ Hg (checked vs. S.C.E.)

(22)   Hg | HgO

(23) $Hg \mid (Hg_2)_3 [Co(CN)_6]_2$

(24)   Zn(Hg) | $ZnCl_2$

(25)   Cd | $CdCl_2$, KCl (satd)

(26)   Cd(Hg) | Cd^{2+}

(27)   Tl(Hg)(l)−TlCl(s)

(28)   Pb

(29)   Pb | $PbNO_3$ (0.1 N in NH_3)

(30)   Pb(5% wt in Hg) | $Pb_2 [Fe(CN)_6]$

(31)   Pb(Hg), $PbSO_4$ $\left| \begin{array}{l} K_2SO_4 \\ KNO_3 \end{array} \right.$

(32)   Na(Hg) | NaF

(33)   Pt $\left| \begin{array}{l} \text{Ferricinium} \\ \text{Ferrocene} \end{array} \right.$

(34)   Glass electrode

(35)   Ag, AgCl | $AgClO_4$ (0.01 m)

(36)   Fe

(37)   Quinhydrone

(38) $Pt-D_2$

(39) K_2SO_4 (satd), Hg_2SO_4 (satd)

(40)   Hg pool

*See footnote on page xii.

Contents

Group I

Electronically conducting phase	Intermediate species	Composition of the solution	Solvent	Temperature °C	Pressure Torr	Measuring method
a	b	c	d		e	d
Li(Hg)		LiOH: 0.026 up to 2.669 m	1	25 ± 0.02		I
Li			7	25		I
Li(Hg)		Li: 0.035 % wt in Hg; LiHCOO: 0.01 N	16	25 ± 0.01		I
Li		LiCl: 0.01 N	23	25		I
Li		LiCl: 0.01 N	24	25		I
Li		LiCl or LiClO$_4$	29	25		I
Li		LiNO$_3$	8	25		V
Li	LiH		1	25		IV
Ind.	LiH		1	25		IV
Pt,H$_2$		Li (glycolate)$^-$: 0.003765 up to 0.06515 m; HCl: 0.0001958 up to 0.03388 m	1	25		I
Pt,H$_2$		Li (lactate)$^-$: 0.004724 up to 0.09660 m; HCl: 0.002367 up to 0.04827 m	1	25		I

Comparison electrode	Liquid junction	Electrode reaction	Standard value V	Uncertainty mV	Temperature Coefficient $\mu V/^oC$	Notes	Reference	Electrode Reference Number
d			f		g	h		
1	no	$Li^+ + e^- \rightleftharpoons Li$	-3.0401	± 1.6	-534		1, 11	1
		$Li^+ + e^- \rightleftharpoons Li$	-3.095				2	2
14	no	$Li^+ + e^- \rightleftharpoons Li$	-3.48	± 2	850		3	3
7	no	$Li^+ + e^- \rightleftharpoons Li$	-3.23		750		4	4
27	no	$Li^+ + e^- \rightleftharpoons Li$	-2.4212			3	5	5
1		$Li^+ + e^- \rightleftharpoons Li$	-2.8874		877		6	6
1		$Li(H_2O)^+ + e^- \rightleftharpoons Li + (H_2O)$	-3.022			2	7	7
		$Li + H^+ + e^- \rightleftharpoons LiH$	0.726				8	8
		$Li^+ + H^+ + 2e^- \rightleftharpoons LiH$	-1.161				8	9
4		$Li(glycolate)^- + e^- \rightleftharpoons Li + (glycolate)^{2-}$	-3.033			1	9	10
4		$Li(lactate)^- + e^- \rightleftharpoons Li + (lactate)^{2-}$	-3.052			1	10	11