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STANDARD POTENTIAL OF THE SILVER–SILVER CHLORIDE ELECTRODE

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Abstract - Presumably as a result of variations in preparative
techniques, silver-silver chloride electrodes prepared in dif-
ferent laboratories may vary in potential by as much as 0.2 mV.
The specific causes of this variability have not yet been
identified. The routine standardization of this electrode as
recommended 22 years ago should therefore be continued.

The silver-silver chloride electrode is widely used in cells without
transference to determine precise values of the electrochemical and thermo-
dynamic properties of chemical systems; hence, a knowledge of its standard
potential is of unique importance. It was therefore disturbing to discover,
some 22 years ago, that studies of the emf of the cell

$$Pt;H_2(g,1\ atm)\,|\,HCl\,(molality\ m)\,|\,AgCl;Ag \qquad\qquad A$$
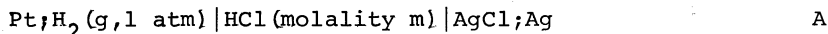
apparently performed with equal care, led to values of the standard potential
($E°$) that differed by nearly 0.2 mV. The data obtained in the extensive
investigations of Harned and Ehlers (1, recalculated) lead to values near
0.22250V for $E°$ at 25°C, while the value derived from equally extensive
measurements of Bates and Bower (2) is 0.22234V. An analysis by Ahluwalia
and Cobble (3) in terms of third-law entropies nonetheless led to a common
value of 0.22238V from both sets of data.

Despite this uncertainty in the value of $E°$, mean molal activity coefficients
($\gamma_\pm$) of hydrochloric acid derived from these separate studies were in sub-
stantial agreement, suggesting that the thermodynamic state of the Ag;AgCl
electrodes, for some preparative reason not then identified, differed from
one laboratory to another. It was therefore recommended (4) that Ag;AgCl
electrodes should be standardized routinely in each laboratory through
measurement of the emf (E) of cell A with m=0.01 mol kg^{-1}. Then

$$E° = E + (2RT/F)\ ln\ (0.01\gamma_\pm) \qquad\qquad (1)$$

where $\gamma_\pm$ is assigned the value 0.904 at 25°C and 0.908 at 0°C; the corres-
ponding values of the Nernst slopes 2RT/F are 0.051383 and 0.047075, respect-
ively. This procedure could be abandoned, it was expected, when the causes
of the variability had been identified and eliminated.

In 1973, a questionnaire was prepared and sent to 60 investigators in the
field of solution electrochemistry, in an effort to determine whether the
values of $E°$ now display a greater consistency than was the case 22 years
ago. Additional information concerning methods of electrode preparation and
cell design was also solicited.

Table 1 summarizes the data for $E°$ calculated by equation (1) from the emf
of cell A at 25°C, m=0.01 mol/kg. All but two of the entries in the table
refer to electrodes of the thermal-electrolytic variety, prepared by the
thermal decomposition of well-washed silver oxide, with subsequent electrol-
ysis in a solution of hydrochloric acid. The values reported by Etz (Nation-
al Bureau of Standards, 1971-72) and by Lietzke (Oak Ridge National Labora-
tory) were obtained with electrodes prepared by thermal decomposition of a
mixture of silver oxide and silver chlorate or perchlorate.

TABLE 1.   Values of E° at 25°C derived from the emf of cell A
(molality of HCl, 0.01 mol/kg; $\gamma_{\pm}$ = 0.904)

Laboratory	Reporter or Investigator	Year	No. of Cells	E°/V	Std. dev. (mV.)	Remarks	Ref.[a]
Argonne National Laboratory	A. J. Zielen	1963	3	0.22234	0.03		5
Baas Becking Laboratory (Canberra)	C. J. Downes	1972	6	0.22231	0.03		6
Barnard College (Columbia University)	E. J. King	1953		0.22248		From emf for HCl (0.01m)+ taurine (m_1), extrapolated to m_1=0.	7
		1956		0.22258			8
Drury College	R. N. Roy	1973	2	0.22279		Emf at 0.05m and 0.1m leads to lower E°, near 0.22255V.	PC
University of Florida	S. Goldman	1971		0.22264			9
	A. Y. W. Ho	1972	3	0.22260	0.03		PC
	R. N. Roy	1972	9	0.22263	0.10		PC
	R. A. Butler	1975	10	0.22235	0.03		PC
	J. B. Macaskill	1975	20	0.22242	0.02		PC
	C. A. Vega	1975	4	0.22240	0.03		PC
	K. H. Khoo	1976	22	0.22249	0.03		PC
	R. W. Ramette	1976	6	0.22243	0.02		PC
University of Helsinki	E. Tommila, I. Belinskij	1969	20	0.22244	0.01		10
Jadavpur University	K. K. Kundu	1973	10	0.22270	0.11		PC
University of Malaya (Kuala Lumpur)	K. H. Khoo, C. Y. Chan, T. K. Lim	1977		0.22253			11
	K. H. Khoo	1977		0.22251			PC
National Bureau of Standards	R. Gary	1964		0.22244			12,13
	V. E. Bower, R. Gary, H. B. Hetzer, M. Paabo	1965	4	0.22247	0.06		14
	E. S. Etz	1967	4	0.22261	0.07		PC
		1972	9	0.22272	0.03		PC
	M. Paabo	1970	3	0.22265	0.04		PC
		1970	3	0.22265	0.03	Ag_2O prepared at the University of Florida	
University of Newcastle upon Tyne	A. K. Covington	1965		0.22237	0.02		PC
		1968		0.2223			15
		1973		0.22236			16
University of New England	R. H. Stokes	1963		0.22237	0.13	E at m=0.01 obtained by interpolation	17
Oak Ridge National Laboratory	M. H. Lietzke	1960	3	0.22230	0.05		18

University of Otago	R. F. Smith	1962		0.22236			19
	C. J. Downes	1965		0.22258			20
	P. Morrison	1966		0.22248			21
	C. Y. Chan	1970		0.22251			22
University of Reading	A. J. Read	1966		0.22248	0.03		23
	G. Romeo	1971		0.22232		Reported by J. E. Prue	24
	J. B. Macas-kill	1972	15	0.22240	0.02		25

[a] PC = personal communication.

In addition to these values of E° calculated by equation (1), D. F. Swinehart of the University of Oregon has reported approximately 100 measurements made by five investigators at molalities near 0.1 mol/kg. If these results are corrected to a molality of exactly 0.1 mol/kg and $\gamma_\pm$ is taken to be 0.797 at this molality, one obtains E° = 0.22249V, with a standard deviation of 0.09 mV. Likewise, a value of 0.22243V can be derived from the measurements of Evans and Monk (26) at four molalities less than 0.01 mol/kg.

The mean of the 35 entries in the column headed "E°" in Table 1 is 0.22249V, with a standard deviation of 0.13 mV. There is no strong evidence that cell design, the interposition of a stopcock between the electrode compartments, or sensitivity to light has a significant bearing on the emf of the cell. Furthermore, the method of precipitating and washing the silver oxide has been varied in important particulars without apparent effect on the properties of the electrodes. The observed variations are too great to be attributed to the "depth effect" described by Hills and Ives (27).

The factors influencing the potentials of silver-silver chloride electrodes are still under study. Until the causes of variability are clearly identified, the practical routine standardization through measurements of cell A at m=0.01 mol/kg, as recommended in 1956, should be continued.

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