

Short Communication

Studies on Gold Complexes. III. The Standard Electrode Potentials of Aqua Gold Ions

L. H. SKIBSTED^a and JANNIK BJERRUM^b^a Chemistry Dept., Royal Veterinary and Agricultural University, DK-1871 Copenhagen V, Denmark and ^b Chemistry Dept. I, Inorganic Chemistry, H.C. Ørsted Institute, University of Copenhagen, DK-2100 Copenhagen Ø, Denmark

The hypothetical diaquagold(I) and tetraaqua-gold(III) ions do not exist even in strong perchloric acid solution, and their standard electrode potentials are therefore not accessible to direct measurements. However, information about these potentials can be obtained by utilizing the knowledge of the standard potentials for a series of gold(I) and gold(III) complexes. A number of such potentials are tabulated in Table 1.

Some authors have assumed that linear relationships exist between these potentials and analogous potentials for other d^{10} and d^8 metal ions for which the potentials of the aqua ions are known.¹⁻³ However, standard potentials obtained by such correlations are open to criticism.⁴ More reliable results might be expected with the use of Edward's four-parameter equation⁵

$$(1/N) \log \beta_N' = \alpha E_n + \beta H$$

In this equation α and β are parameters for the metal ion and E_n and H parameters for the ligand. E_n is related to the oxidation potential of the ligand: $E_n = E^\circ(X^r, \frac{1}{2}X_2^{(2r-2)-}) - E^\circ(\text{ref.})$, and H is related to $\text{p}K_a$ for the corresponding Brønsted acid: $H = \text{p}K_a - \text{p}K_a(\text{ref.})$. Both of these parameters as well as the relative overall stability constants β_N' are usually defined with water and the aqua complex as reference. It then follows that: $\log \beta_N' = \log \beta_N + N \log 55$. In order to use the equation for Au(I) and Au(III) complexes β_N' were defined relative to the relevant chlorido complexes and E_n and H relative to $E^\circ(\text{Cl}^-, \frac{1}{2}\text{Cl}_2) = -1.36$ V and $\text{p}K_a(\text{HCl}) = -6.1$.⁶ The necessary ligand parameters were estimated from literature data⁵ and are tabulated in Table 2. A certain arbitrariness in the choice of the E_n and H parameters is apparent. The lack of spread in the Edwards plots, shown in Fig. 1, which is based partly on parameters resulting from accurate experiments and partly on rough estimates, provides some justification for the E_n and H values proposed in Table 2. Values for $\log \beta_N'$ are given in Table 1. The upper part in Fig. 1 is a plot of $\frac{1}{2} \log \beta_2'/H$ versus E_n/H for Au(I), and the lower part a plot of $\frac{1}{4} \log \beta_4'/H$ versus E_n/H for Au(III). Straight lines are obtained in both cases, α being equal to the slope of the lines. E_n/H for water has the value -0.28 (see Table 2), corresponding to $\frac{1}{2} \log \beta_2'/H = -1.70$ for Au(I) and $\frac{1}{4} \log \beta_4'/H = -1.90$ for Au(III). Inserting $H = 4.40$ for water, one calculates on this basis $\log \beta_2 \cong 11.5$ for Au(I),

Table 1. Standard electrode potentials at 25 °C of Au(I) and Au(III) complexes and their stability constants in aqueous solution.^a

Ligand	$E^\circ_{1,0}$	$\log \beta_2'$	$\log \beta_2^a$	$E^\circ_{3,0}$	$\log \beta_4'$	$\log \beta_4^b$
Cl ⁻	+1.154	0	11	+1.002	0	26
Br ⁻	+0.959	3.29	15	+0.854	7.50	34
SCN ⁻	+0.662	8.31	20	+0.636	18.55	45
I ⁻	+0.578	9.73	21	(+0.56)	22.4	49
NH ₃	+0.563	10.0	21	+0.325	34.3	60
(NH ₂) ₂ CS	+0.380	13.1	24			
S ₂ O ₃ ²⁻	+0.153	16.9	28			
Dpm ^c	+0.053	18.6	30			
CN ⁻	-0.48	27.6	39	(-0.10)	56	82
OH ⁻				(+0.48)	26.4	53

^a Calculated with $E^\circ[\text{Au}(\text{H}_2\text{O})_2^+, \text{Au}] = +1.83$ V. ^b Calculated with $E^\circ[\text{Au}(\text{H}_2\text{O})_4^{3+}, \text{Au}] = +1.52$ V.

^c Diphenylphosphinobenzene-*m*-sulfonate.

Table 2. Ligand parameters to Edwards' equation defined relative to the chloride ion.

Ligand	H	E_n	E_n/H
Br^-	-1.1	+0.27	-0.25
SCN^-	+5.3	+0.59	+0.11
I^-	-3	+0.82	-0.27
NH_3	+15.3	+0.60	+0.04
$(\text{NH}_3)_2\text{CS}$	+5.2	+0.94	+0.18
$\text{S}_2\text{O}_3^{2-}$	+7.8	+1.28	+0.16
CN^-	+15.5	+1.56	+0.10
OH^-	+21.9	+0.36	+0.02
H_2O	+4.4	-1.24	-0.28

Table 3. Softness parameter for some heavy metals.

	α	σ_K
Cd(II)	2.2	2.0
Cu(I)	3.4	2.3
Ag(I)	3.5	2.8
Tl(III)	4.6	3.4
Au(I)	6.5	4.4
Hg(II)	6.8	4.6
Au(III)	7.4	-

and $\log \beta_4 \approx 26.4$ for Au(III). These values combined with the standard electrode potentials for the relevant chlorido complexes yield the following estimate for the two aqua gold potentials: $E^\circ[\text{Au}(\text{H}_2\text{O})_2^+, \text{Au}] = 1.83$ V and $E^\circ[\text{Au}(\text{H}_2\text{O})_4^{3+}, \text{Au}] = 1.52$ V.

Previous estimates of the aqua gold(I) electrode potential range from 1.67 to 2.12 V.^{1,3,7,8} The present value of 1.83 V is further supported by other evidence which will be discussed in a forthcoming paper.⁹ The value of 1.52 V found for the aqua gold(III) electrode potential deviates less from values in the literature^{7,10} and is in good agreement with Latimer's⁷ estimate of 1.50 V. We therefore suggest that the stability constants given in Table 1 calculated on the basis of the present new values should replace constants already published by one of the present authors.⁸

The α coefficient in Edwards' equation is a measure of the softness¹¹ of the metal; in Table 3 the values for Au(I) and Au(III) obtained from Fig. 1 are compared with values of α for other metals¹¹ as well as with Klopman's¹² softness parameter σ_K which is derived from polyelectronic perturbation theory. The most remarkable result is that Au(III) is softer than Au(I) with Hg(II) having an intermediate softness.

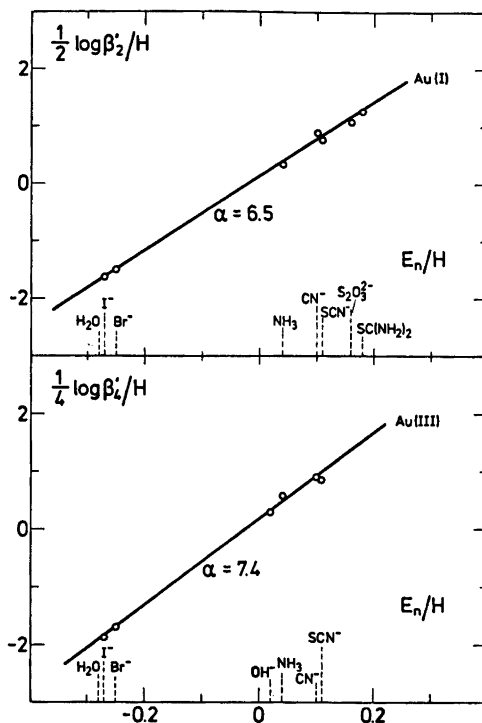


Fig. 1. Edwards' plots for Au(I) and Au(III).

- Ehrenburg, A. M. and Peshchevitskii, B. I. *Russ. J. Inorg. Chem.* 14 (1969) 1429.
- Jørgensen, C. K. and Pouradier, J. *J. Chim. Phys.* 67 (1970) 124.
- Hancock, R. D., Finkelstein, N. P. and Evers, A. *J. Inorg. Nucl. Chem.* 36 (1974) 2539.
- Pearson, R. G. *J. Chem. Educ.* 45 (1968) 581.
- Edwards, J. O. *J. Am. Chem. Soc.* 76 (1954) 1540.
- Robinson, R. A. *Trans. Faraday Soc.* 32 (1936) 743.
- Latimer, W. M. *The Oxidation Potentials*, 2nd Ed., Prentice-Hall, New York 1952, p. 192.
- Hawkins, C. J., Mønsted, O. and Bjerrum, J. *Acta Chem. Scand.* 24 (1970) 1059.
- Skibsted, L. H. and Bjerrum, J. *Indian J. Chem.* 54 (1977) *In press*.
- Finkelstein, N. P. and Hancock, R. D. *Gold Bull.* 7 (1974) 72.
- Bjerrum, J. *Essays on Analytical Chemistry. In Memory of Professor Anders Ringbom*, Pergamon, Oxford 1976.
- Klopman, G. *J. Am. Chem. Soc.* 90 (1968) 223.

Received November 26, 1976.