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**FORMATION OF METAL COMPLEXES
WITH ETHYLENEDIAMINE: A
CRITICAL SURVEY OF EQUILIBRIUM
CONSTANTS, ENTHALPY AND
ENTROPY VALUES**

Prepared for publication by

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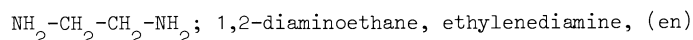
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FORMATION OF METAL COMPLEXES WITH ETHYLENEDIAMINE: A CRITICAL SURVEY OF EQUILIBRIUM CONSTANTS, ENTHALPY AND ENTROPY VALUES

Abstract - At present ethylenediamine is one of the more studied nitrogen-ligands. The main physico-chemical properties of this diamine are reported in this survey. The fundamental techniques for its purification and storage and its acid-base characteristics in aqueous solution are described. The formation constants of the complexes with various metal ion, the thermodynamic values relative to the reactions of formation of the complexes and their stereochemistry are presented. The protonation constants of the diamine and the corresponding enthalpic and entropic values obtained in various ionic media have been considered and a critical examination of the results is presented. The values of the stability constants of the complexes and the thermodynamic quantities relative to the present equilibria have been critically examined. Such values are recommended when the metallic systems, also in their proton- and hydroxide-form, are well determined and results by different authors are in agreement. For cases lacking accurate data tentative values are suggested or further investigations are recommended. Errors on the recommended values have been estimated.

1 - Physical and chemical properties of ethylenediamine



Ethylenediamine is colourless at room temperature having the characteristic smell of an amine. It has a melting point of 11.1 °C and a boiling point of 116.9 °C at 101325 Pa (1 atm.). Some physico-chemical constants of pure ethylenediamine are reported in Table 1.

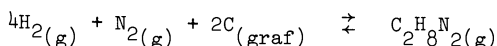
TABLE 1. Physico-chemical constants of ethylenediamine

		Ref.
1) Molecular weight	60.099	
2) Temperature of phase transition C(II) → C(I)	-84.2 °C	75M
3) Melting point	11.1 °C	75M
4) Boiling point	116.9 °C	75M
5) Enthalpy of transition	487 J mol ⁻¹	75M
6) Enthalpy of fusion	22.6 kJ mol ⁻¹	75M
7) Enthalpy of vaporization	45.69 kJ mol ⁻¹	69F
8) Heat capacity of crystal(II) at -40.4 °C	90.1 JK ⁻¹ mol ⁻¹	75M
9) Heat capacity of crystal(I) at -7.5 °C	102.3 JK ⁻¹ mol ⁻¹	75M
10) Heat capacity (liquid)	194.65-25.0800x10 ⁻² T+7.004x10 ⁻⁴ T ² -3.5970x10 ⁻⁷ T ³ JK ⁻¹ mol ⁻¹	75M

TABLE 1. (ctnd)

11) Density at 15 °C	0.900 g cm ⁻³	59T
at 30 °C	0.886 g cm ⁻³	59T
12) Refractive index n _D ¹⁵	1.45887	59T
13) Enthalpy of solution (infinite dilution at 25 °C)	31.8 kJ mol ⁻¹	76N
14) ΔC _p [∞] , aqueous solution process at 25 °C	12. JK ⁻¹ mol ⁻¹	76N
15) C _p [∞] (infinite dilution at 25 °C)	185.0 JK ⁻¹ mol ⁻¹	76N
16) log ₁₀ (p/101325)=A(1-390.069/T) (p is vapor pressure of liquid)		
	where: log ₁₀ A = 0.944370-8.35825x10 ⁻⁴ T+ +7.27655x10 ⁻⁷ T ²	75M
17) Entropy S ^o (298.15 K)	321.8 JK ⁻¹ mol ⁻¹	75M
18) ΔG _f ^o (298.15 K)	103.2 kJ mol ⁻¹	75M
19) ΔH _f ^o (298.15 K)	-17.3 kJ mol ⁻¹	75M
20) log K _f (298.15 K)	-18.08	75M

Subscript "f" refers to the reaction



With time the composition tends to change, especially in the presence of air. It absorbs both water and carbon dioxide from the atmosphere forming the carbonate, and it forms a stable monohydrate which can be distilled without decomposition, but fractional distillation does not normally lead to a very pure product. It can be improved by heating the amine under reflux over metallic sodium followed by fractional distillation. However, attention must be drawn to the fact that heating the amine in the presence of NaOH generally leads to decomposition and a yellow colouration. The best product, however, is obtained by preparing the acid salt of the amine, such as the ethylenediammonium(+2) dichloride, and recrystallising it repeatedly from a mixture of ethanol and water. This product can be stored indefinitely without decomposition. It is widely used in the study of complex formation to regenerate the amine when required. The crystal structure of ethylenediamine has been determined by X-ray analysis (73J) at -60 °C and is shown in Fig. 1

In the gas phase between 55 and 115 °C Yokozeki and Kuchitsu (71Y) have shown by electron diffraction studies that the ethylenediamine molecule has a gauche conformation and the dihedral angle is 64°. The difference in energy between trans and gauche was estimated to be about 4 kJ. As well as staggered configurations shown on Fig. 1 can exist three eclipsed configurations; two gauche with symmetry C₂ and one cis with symmetry C_{2v}. The infrared spectra were interpreted by Sabatini and Califano (60S) as a molecular symmetry C_{2v}. In water solution are present the staggered isomers: gauche for the 60% and trans for the 22% and an eclipsed cis isomer for the 18% (81B)

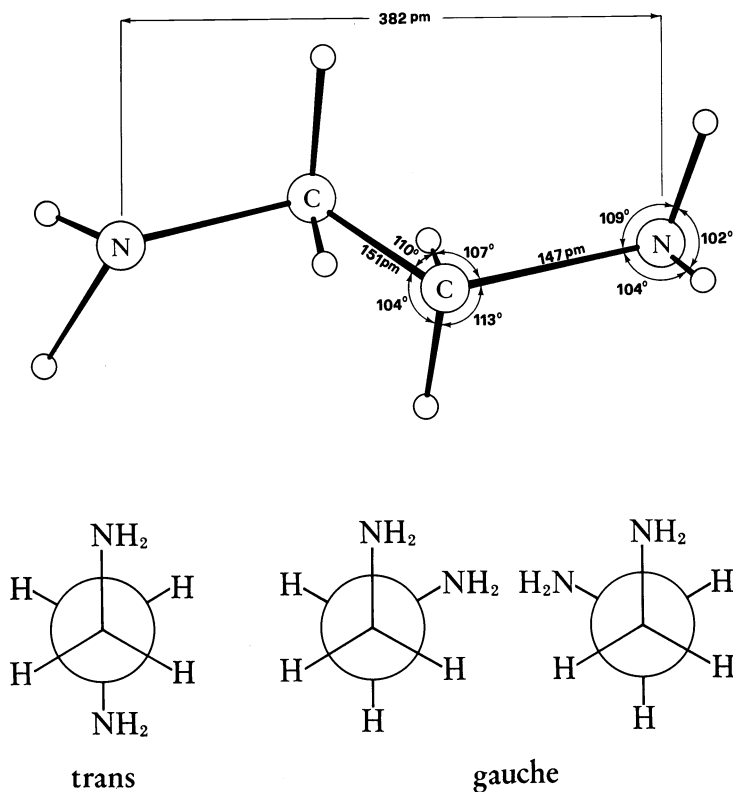
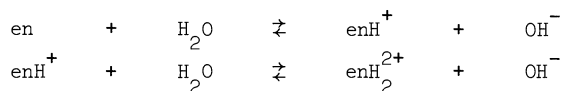


Fig. 1. The structure of pure ethylenediamine at -60°C . The molecule is in the trans conformation. The molecular symmetry is C_{2h} for trans and C_2 for gauche

2 - Acid-base properties of ethylenediamine

Ethylenediamine is extremely soluble in water and in the majority of organic solvents. In aqueous solution it reacts with water giving rise to the two equilibria



Nevertheless, ethylenediamine can, rarely, exhibit also acid properties. Thus, for example, with Pt(IV) it forms the complex $[\text{Pt}(\text{en})_3]^{4+}$ which is capable of loosing up to three protons (48G). This tendency to release hydrogen atoms in the form of protons can be enhanced by electrophilic substitution on the nitrogens.

3 - Coordinating properties of ethylenediamine

Ethylenediamine forms a large number of complexes with many different metal ions in the periodic table (Fig. 2). It usually acts as a bidentate ligand but examples are known in which ethylenediamine acts either as a monodentate or a bridging ligand. Finally, in a few rare cases, ethylenediamine forms monoprotonated complexes (730 and reference therein).

I A																				O									
H	II A																				He								
Li	Be											B	C	N	O	F	Ne												
Na	Mg											Al	Si	P	S	Cl	Ar												
		III A	IV A	V A	VI A	VII A	VIII			I B	II B																		
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr												
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe												
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn												
Fr	Ra	Ac	104	105																									

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Fig. 2. The marked elements form ethylenediamine complexes in solution and have been investigated thermodynamically.

The five-membered chelate ring in ethylenediamine complexes can exist in two different conformations: gauche symmetric, (Fig. 3(a)) or with an asymmetric conformation (Fig. 3(b)). The former is the most common and the bond angle $N-\hat{M}-N$ is almost always about 85° .

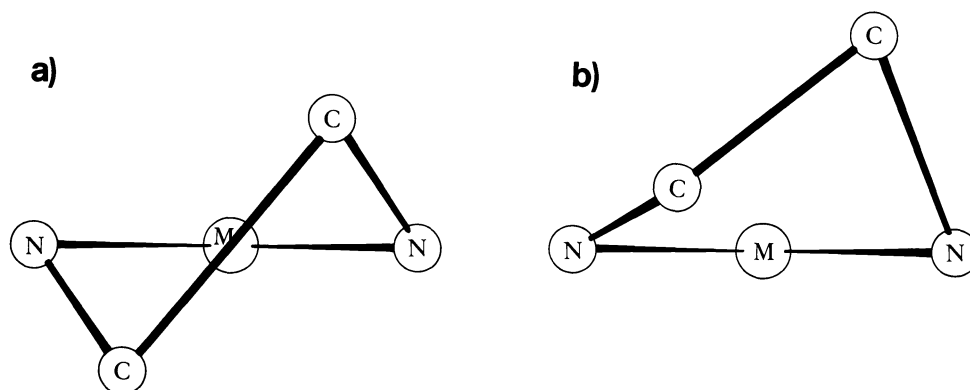


Fig. 3. Symmetric (a) and asymmetric (b) conformations of the five-membered chelate ring in ethylenediamine complexes

In aqueous solutions the most common complexes are octahedral, with a metal/ligand ratio of 1:1, 1:2 or 1:3. The remaining coordination sites are occupied by water molecules.

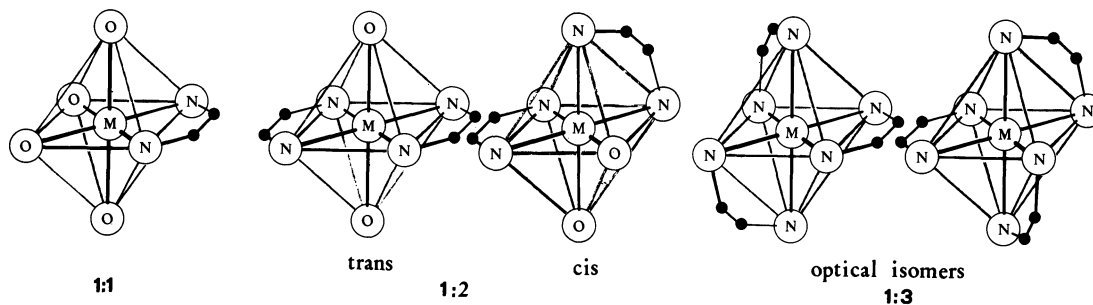


Fig. 4. Some octahedral ethylenediamine complexes.

$[\text{Zn en}_2]^{2+}$ (79F) and $[\text{Cden}_2]^{2+}$ (80F) were found to be tetrahedral by X-ray diffraction studies on solutions. Complexes with a metal/ligand ratio of 1:4 are formed with particularly "hard" metals, such as lanthanides (69Fa). As we have seen, ethylenediamine can occasionally act as a monodentate ligand and the Ag^+ -en system in aqueous solution is an interesting example. When considering protonated complexes a good example can be found in Ag^+ complexes of the type $[\text{AgHen}]^{2+}$ (52S). Although this review will be limited to a discussion of non mixed complexes of ethylenediamine, the hydroxide complexes will also be included. Ethylenediamine forms such hydroxide complexes with a number of metals in aqueous solution and one of the most comprehensively studied systems is that of Cu^{2+} . Of these copper hydroxo complexes, the two $[\text{Cu}_2(\text{OH})_2\text{en}]^{2+}$ and $[\text{Cu}_2(\text{OH})_2(\text{en})_2]^{2+}$ probably have polynuclear structures of the type (66Pa) shown in Fig. 5.

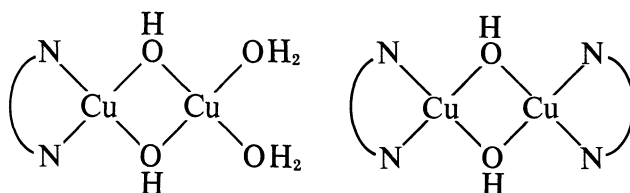


Fig. 5. Possible polynuclear structures of $[\text{Cu}_2(\text{OH})_2\text{en}]^{2+}$ and $[\text{Cu}_2(\text{OH})_2(\text{en})_2]^{2+}$.

4 - The equilibria of complex formation

Ethylenediamine strongly interacts with water molecules and each nitrogen atom binds a water molecule by means of a hydrogen bond of the type $\text{N} \cdots \text{H}-\text{O}-\text{H}$. During the formation of the metal complexes, these water molecules together with others from the first and second hydration spheres of the metal are removed. Although little is known about the hydration of the complexes of ethylenediamine, it has been shown that the two hydrogen atoms bonded to the nitrogen carry a partial positive charge in the complex and are, therefore, able to form bonds of the type:



The formation of complexes with ethylenediamine leads, especially in the first step, to the liberation of some water molecules so that an increase in entropy (ΔS° positive) would be expected to be associated with this process. In general, this compensates for the decrease in entropy translational, rotational and vibrational, which accompanies the formation of the chelate ring. The formation of the first complex is always characterized by a positive entropy term. This term is larger, the more stable the complex. This is due to an extensive liberation of water molecules. This process becomes less pronounced in the following steps and the entropy of formation therefore diminishes until it finally becomes negative.

The formation of an ethylenediamine complex requires the breaking of an $\text{M}-\text{O}$ bond and the formation of an $\text{M}-\text{N}$ bond; since this process is exothermic (ΔH° negative), the enthalpy term will always contribute in a favourable way to the complex formation. The enthalpy of formation (ΔH°) does not vary very much, between the consecutive steps, with only a slight tendency to become more negative; however the decrease in ΔS° prevails over the variation in ΔH° with the result that the formation constants become smaller for each successive step in the complex formation. Although the decrease of the stepwise formation constants was predicted long ago on the basis of a statistical model (41B) (entropy effect), the actual values found for ethylenediamine complexes are much larger than those predicted.

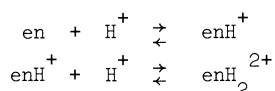
5 - Determination of equilibrium constants

Many different methods have been employed for the determination of stability constants and in the case of ethylenediamine complexes the potentiometric method has been extensively used. As seen in the second section, ethylenediamine liberates hydroxide ions in the presence of water, thereby changing the concentration of the free hydrogen ions. It is thus possible to follow the reaction of ethylenediamine with metal ions by means of a hydrogen or glass electrode whose potential depends on the activity of hydrogen ions.

Two main pH-metric techniques have been used in the study of ethylenediamine complexes. In the first of these, a solution containing ethylenediamine is added to a solution containing acid or both acid and metal ions; in the second, a solution of sodium or potassium hydroxide is added to a solution which contains the metal ion and the chloride or other stable acid salt of ethylenediammonium(+2) and subsequently to a solution containing both the acid salt and the metal ion. We believe that the latter technique gives more reliable results since the reagent can be obtained in a more pure form and can be analysed more accurately.

The following symbols will be used throughout this review.

The formation constants of ethylenediammonium ions refer to the equilibria:



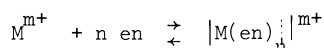
The constant K_1 relates to the first of these equilibria

$$K_1 = \frac{|\text{enH}^+|}{|\text{en}| |\text{H}^+|}$$

and K_2 to the second

$$K_2 = \frac{|\text{enH}^+|}{|\text{enH}^+| |\text{H}^+|}$$

For the complex formation equilibrium



the overall constant β_n is stated as follows:

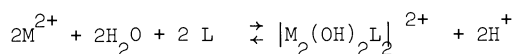
$$\beta_n = \frac{|\text{M(en)}_n|^{m+}}{|\text{M}^{m+}| |\text{en}|^n} = \prod_{i=1}^n K_i$$

where K_i is the stepwise formation constant.

For polynuclear, protonated or hydroxo-species the following symbolism will be used:

$$\beta_{pqr} = \frac{|M_p H_q L_r|}{|M|^p |H|^q |L|^r}$$

The value of q is negative for hydroxo-species. Thus for



the equilibrium constant is:

$$\beta_{2-22} = \frac{|M_2(\text{OH})_2\text{L}_2|}{|M|^2 |H|^{-2} |L|^2}$$

Furthermore, the determination of the error associated with an equilibrium constant for a system containing ethylenediamine depends upon, i.e., the number and type of complex species formed; in some cases only a few species are present as, for example, Ni^{2+} where only the simple species $|\text{Ni(en)}|^{2+}$, $|\text{Ni(en)}_2|^{2+}$ and $|\text{Ni(en)}_3|^{2+}$ are formed. In others, such as the Ag^+ system, may different species are present, having a range of stoichiometries.

The stabilities of ethylenediamine complexes vary remarkably, $\log K_1$ can range from 0.37 for $[\text{Mgen}]^{2+}$ (41B) to >20 for $[\text{Pden}]^{2+}$ (68R). As we have already seen, the determination of stability constants involves a wide range of different experimental conditions and techniques as well as different methods of calculation. However, some authors do not supply sufficient information to make it possible to establish if a mixed or a thermodynamic constant is calculated (78M).

In case in which different authors have investigated the same system, a comparison of the results obtained can provide a useful indication for the evaluation of reliability; in this connection, we can draw readers' attention to the work carried out by the Italian Group on the study of the Thermodynamics of Complexes (70M): six different research groups have separately determined, in different laboratories, the equilibrium constants for the Ni^{2+} /glycinate ion and H^+ /glycinate ion systems. In particular, the first protonation constant, which refers to the protonation of an $-\text{NH}_2$ group, has been determined with a standard deviation of 0.011 log units. This value can also be considered to be the lower limit for the error connected with the basicity constants of an $-\text{NH}_2$ group. Nevertheless, even in these cases some difficulties arise because different authors, although adopting the same technique, have used different temperatures and/or different media. Provided the enthalpy change has been determined with a sufficient accuracy, it is possible to correct the various constants determined to the same temperature, so that the results can be compared. Wherever possible in this review, account has also been taken of corrections due to the influence of medium salts.

6 - Determination of the enthalpy and entropy contributions to the equilibrium constants

If the stability constants and the enthalpy change associated with a particular reaction are known, it is possible to determine the entropy change from the Gibbs expression. However, the enthalpy change, ΔH° , for systems containing ethylenediamine, has very often been obtained from van't Hoff relationship:

$$\frac{d \log K}{dT} = \frac{\Delta H^\circ}{2.3RT^2}$$

It is well recognised that reliable values of ΔH° can only be obtained, by this method, by using accurate values of stability constants, over a sufficiently wide temperature range, which calls for a considerable sophistication in experimental techniques. On the other hand, the direct calorimetric method, in general, is much more precise. In some cases, however, a good agreement between values obtained by the two methods has been obtained (52E). Although only a few data exist, it is clear that the enthalpies of protonation and of complex formation of ethylenediamine vary with the ionic strength and hence differences in the enthalpy values which have been obtained in different ionic media will, likewise, be taken into account. A difficulty in this connection is that ΔH° varies with the temperature. To correct for this by means of the Kirchhoff equation it is necessary to know ΔC_p° . Only rarely, however, are such values, available for systems containing ethylenediamine. In general, the change in ΔH° with temperature is much less significant than the change in $\log K$. It is clear, however, that any errors in either $\log K$ or ΔH° are both reflected in the value of ΔS° . The notations ΔH_{1-n}° is referred to the total enthalpy of the reactions, that is the sum of the partial enthalpies:

$$\Delta H_1^\circ + \Delta H_2^\circ + \dots + \Delta H_n^\circ$$

7 - Critical examination of Data

In this review the enthalpy and entropy values are given in kJoule mol^{-1} and $\text{joule deg}^{-1}\text{mol}^{-1}$, respectively. Evaluation criteria of stability constants and thermodynamic quantities associated with these shall be as below:

- 1) The uncertainties given by authors, when available
- 2) Evaluation of experimental methods and calculation techniques used by authors
- 3) Comparison between results independently obtained in different investigations

On the basis of these criteria selected values will be distinguished in:

- 1) recommended (R)
- 2) tentative (T)

3) further investigations are needed

H⁺

Protonation constants of ethylenediamine

Bjerrum (41B): hydrogen electrode at 30 °C in 1 KCl
 $\log K_1 = 10.05$ $\log K_2 = 7.31$

Bjerrum (45B): glass electrode at 25 °C in 1 KNO₃
 $\log K_1 = 10.18$ $\log K_2 = 7.49$

Carlson et al. (45C): glass electrode at 30 °C in 0.5 KNO₃
 $\log K_1 = 9.87$ $\log K_2 = 7.23$

Carlson et al. (45C): glass electrode at 30 °C in 1 KCl
 $\log K_1 = 9.92$ $\log K_2 = 7.19$

Bjerrum (50B): glass electrode at 25 °C in 1 KNO₃
 $\log K_1 = 10.05$ $\log K_2 = 7.49$

Edwards (50E): glass electrode at 25 °C in 1 KCl
 $\log K_1 = 10.17$ $\log K_2 = 7.44$

Basolo and Murmann (52B): glass electrode at 0 - 25 °C in 0.5 KNO₃

t	0 + °C	25 °C
$\log K_1$	10.73	10.18
$\log K_2$	7.98	7.47

Schwarzenbach et al. (52S): glass electrode at 20 °C in 0.1 NaNO₃
 $\log K_1 = 10.03$ $\log K_2 = 7.22$

Everett and Pinsent (52E): hydrogen electrode at 0-60 °C in I=0.

t/°C	$\log K_1$	$\log K_2$
0	10.712	7.564
10	10.383	7.266
20	10.075	6.985
25	9.928	6.848
30	9.784	6.718
40	9.510	6.463
50	9.252	6.221
60	9.005	5.990

McIntyre et al. (53M): glass electrode at 0 - 30 °C in I = 0

t	0 °C	30 °C
$\log K_1$	10.65	9.81
$\log K_2$	7.52	6.73

Cotton and Harris (55C): glass electrode at 0 - 49.1 °C in I = 0.15, using activity scale

t	0 °C	49.1 °C
$\log K_1$	10.80	9.40
$\log K_2$	7.86	6.66

Poulsen and Bjerrum (55P): glass electrode at 25 °C in 1 KNO₃.

$\log K_1 = 10.17$ $\log K_2 = 7.49$

Nyman et al. (55N): glass electrode at 25 °C in I = 0.2

$\log K_1 = 9.96$ $\log K_2 = 7.18$

Nyman et al. (55Na): glass electrode at 25 °C in 0.5 KNO₃

$\log K_1 = 10.14$ $\log K_2 = 7.40$

Bennet (57B): glass electrode at 30 °C in I = 0.1

$$\log K_1 = 10.18 \qquad \log K_2 = 7.47$$

Martell et al. (57M): glass electrode at 25 °C in 0.1 KNO₃

$$\log K_2 = 7.1$$

Pecsok and Bjerrum (57P): glass electrode at 25 °C in I = 1.4

$$\log K_1 = 10.06 \qquad \log K_2 = 7.44$$

McIntyre et al. (59M): glass electrode at 10 - 40 °C in I → 0.

t/°C	10	20	30	40
log K ₁	10.39 ± 0.01	10.09 ± 0.01	9.81 ± 0.01	9.53 ± 0.01
log K ₂	7.28 ± 0.04	7.00 ± 0.02	6.79 ± 0.03	6.50 ± 0.02

James and Williams (61J): glass electrode at 25 °C in 0.1 K₂SO₄

$$\log K_1 = 9.83 \pm 0.03 \qquad \log K_2 = 7.30 \pm 0.05$$

Näsänen et al. (63N, 65N, 67N): glass electrode at 25 °C in I < 2(NaClO₄).

$$\log K_1 = 9.93 + 0.308 I$$

$$\log K_2 = 6.84 + 1.018 \sqrt{I}/(1 + 1.381 \sqrt{I}) + 0.209 I$$

Fischer and Bye (64F): glass electrode at 25 °C in several ionic media

$$\log K_2 = 7.213 + 0.226c \text{ for } c \geq 1$$

$$\log K_2 = 7.00 + A \sqrt{c} + Bc \text{ for } c < 1$$

where c = concentration of the anion and A and B depend on the salt

(e.g. A = 0.332 ; B = 0.137 for NaClO₄ solution).

Bjerrum and Larsen (64B): glass electrode at 25 °C in 1 KNO₃

$$\log K_1 = 10.03 \qquad \log K_2 = 7.22$$

Perrin and Sharma (66Pa): glass electrode at 20 °C in I = 0

$$\log K_1 = 10.27 \qquad \log K_2 = 6.17$$

Holmes and Williams (67H): glass electrode at 25 °C in 0.3 NaClO₄

$$\log K_1 = 9.90 \qquad \log K_2 = 7.32$$

Kanemura and Watters (67K): glass electrode at 25 °C in 1 KNO₃

$$\log K_1 = 10.22 \qquad \log K_2 = 7.54$$

Kanemura and Watters (67K): glass electrode at 25 °C in (0.85 KNO₃ + 0.20 K₂C₂O₄)

$$\log K_1 = 10.31 \qquad \log K_2 = 7.63$$

Perrin et al. (67P, 68P): glass electrode at 37 °C in 0.15 KNO₃

$$\log K_1 = 9.696 \qquad \log K_2 = 6.928$$

Scharf and Paris (67S): glass electrode at 25 °C in 0.5 NaNO₃

$$\log K_1 = 10.18 \qquad \log K_2 = 7.39$$

Vacca and Arenare (67V): glass electrode at 25 °C in 0.5 KNO₃

$$\log K_1 = 9.98 \pm 0.01 \qquad \log K_2 = 7.28 \pm 0.01$$

Faraglia et al. (70Fa): glass electrode at 25 °C and 0.5 (Li)ClO₄

$$\log K_1 = 10.01 \pm 0.02 \qquad \log K_2 = 7.31 \pm 0.01$$

Griesser and Sigel (71G): glass electrode at 25 °C and 0.1 (NaClO₄)

$$\log K_1 = 9.89 \pm 0.03 \qquad \log K_2 = 7.10 \pm 0.03$$

Hauer et al. (71H): glass electrode at 25 °C and 0.1 (NaClO₄)

$$\log K_1 = 9.83 \pm 0.05 \qquad \log K_2 = 7.05$$

Hall et al. (72H): glass electrode at 25 °C and 0.5 KNO₃
 $\log K_1 = 10.13$ $\log K_2 = 7.47$

Newman et al. (72Na): glass electrode at 25 °C and I → 0
 $\log K_1 = 9.86$ $\log K_2 = 6.96$

Hall (76H): glass electrode at 25 °C in 0.5 KNO₃
 $\log K_1 = 10.13$ $\log K_2 = 7.47$

Ohtaki and Ito (730): glass electrode at 25 °C in 3(LiClO₄)
 $\log K_1 = 10.65 \pm 0.01$ $\log K_2 = 8.04 \pm 0.01$

Evaluation of selected values:

(R) $\log K_1 = 9.94 \pm 0.01$ (52E, 59M) I = 0, t = 25 °C

(R) $\log K_2 = 6.86 \pm 0.02$ (52E, 59M) I = 0; t = 25 °C

(R) $\log K_1 = 10.65 \pm 0.01$ (730) I = 3(LiClO₄) t = 25 °C

(R) $\log K_2 = 8.04 \pm 0.01$ (730) I = 3(LiClO₄) t = 25 °C

(T) $\log K_1 = 9.93 + 0.308I$ (63N, 65N, 67N) I = 2(NaClO₄) t = 25 °C

(T) $\log K_2 = 6.84 + 1.018 \sqrt{I} / (1 + 1.381 \sqrt{I}) + 0.209I$ (63N, 65N, 67N),
 I < 2(NaClO₄), t = 25 °C

Both (T) constants ± 0.04 log units

Enthalpy and entropy of protonation of ethylenediamine

Everett and Pinset (52E): calculated from stability constants at 25 °C and I → 0.

$-\Delta H_1^\circ = 49.46$ $-\Delta H_2^\circ = 45.48$

$\Delta S_1^\circ = 24.3$ $\Delta S_2^\circ = 21.3$

Davies et al. (54D): calorimetry at 25 °C in 0.1 KCl

$-\Delta H_1^\circ = 49.8 \pm 0.4$ $-\Delta H_2^\circ = 45.6 \pm 0.4$

McIntyre et al. (59M): calculated from stability constants at different temperatures and I=0

$-\Delta H_1^\circ = 48.1$ $-\Delta H_2^\circ = 43.1$

$\Delta S_1^\circ = 29$ $\Delta S_2^\circ = -13$

Ciampolini and Paoletti (61C): calorimetry at 25 °C in 1 KCl

$-\Delta H_1^\circ = 51.0$ $-\Delta H_2^\circ = 44.4$

$\Delta S_1^\circ = 24$ $\Delta S_2^\circ = -6$

Holmes and Williams (67H): calorimetry at 25 °C in 0.3 NaClO₄

$-\Delta H_1^\circ = 50.2$ $-\Delta H_2^\circ = 45.6$

Vacca and Arenare (67V): calorimetry at 25 °C in 0.5 KNO₃

$-\Delta H_1^\circ = 51.0 \pm 0.2$ $-\Delta H_2^\circ = 45.6 \pm 0.4$

$\Delta S_1^\circ = 20$ $\Delta S_2^\circ = -14$

Evaluation of selected values

(R)	$-\Delta H_1^{\circ} = 50.0 \pm 0.4$	(54D, 67H)	$t = 25^{\circ}\text{C}$,	$I = 0.1 - 0.3$
(R)	$-\Delta H_2^{\circ} = 45.6 \pm 0.4$	(54D, 67H)	$t = 25^{\circ}\text{C}$,	$I = 0.1 - 0.3$
(R)	$-\Delta H_1^{\circ} = 51.0 \pm 0.2$	(61C, 67V)	$t = 25^{\circ}\text{C}$,	$I = 0.5 - 1$
(R)	$-\Delta H_2^{\circ} = 45.2 \pm 0.4$	(61C, 67V)	$t = 25^{\circ}\text{C}$,	$I = 0.5 - 1$
(T)	$\Delta S_1^{\circ} = 22 \pm 2$	(61C, 67V)	$t = 25^{\circ}\text{C}$,	$I = 0.5 - 1$
(T)	$\Delta S_2^{\circ} = -10 \pm 4$	(61C, 67V)	$t = 25^{\circ}\text{C}$,	$I = 0.5 - 1$

Mg²⁺Stability constants

Bjerrum (41B): hydrogen electrode at 30 °C in 1 KCl

$$\log K_1 = 0.37$$

Van Uitert and Fernelius (54V): glass electrode in 75% dioxane at 30 °C

$$\log K_1 = 1.8$$

Evaluation of selected values

Further investigations are needed

Lanthanides(III)

Stability constants

Forsberg and Moeller (69Fa): calorimetric titration with ethylenediamine of lanthanide(III) perchlorate solutions (0.03M) in anhydrous acetonitrile at 23 °C gave both the ΔH_i and $\log K_i$ values for the four steps; $\log K_i$ values reported only for La³⁺, Tb³⁺ and Yb³⁺. For the other lanthanide chelates values¹ of $\log K_1$ lie between those for the lanthanum-ytterbium species.

	$\log K_1$	$\log K_2$	$\log K_3$	$\log K_4$
La ³⁺	9.5	7.5	6.2	3.3
Tb ³⁺	10.4	8.4	6.2	3.2
Yb ³⁺	11.5	9.3	6.5	3.8

All values ± 0.5 log unitsEvaluation of selected values

In absence of other values these ones may be considered as tentative (T) values, although the uncertainties given very large.

Enthalpy values

Forsberg and Moeller (69Fa): calorimetric titration with ethylenediamine solutions (0.03M) of Ln(III) perchlorate in anhydrous acetonitrile at 23 °C

Ln ³⁺	$-\Delta H_1$	$-\Delta H_2$	$-\Delta H_3$	$-\Delta H_4$
La	72	65	58	46
Pr	78	70	57	45
Nd	79	71	58	46
Sm	81	75	56	41
Eu	83	77	58	41

Gd	82	75	58	40
Tb	83	78	55	38
Dy	83	77	53	38
Ho	83	76	53	42
Er	84	78	55	48
Yb	84	79	60	54
Lu	84	78	60	54
Y	84	78	54	44

All values $\pm 1 \text{ kJ mol}^{-1}$

Evaluation of selected values

These values can be considered as tentative (T)

Ti^{IV}

Stability constants

Bains and Bradley (62B): stability constants for the system $\text{Ti}(\text{isopropoxide})_4 - \text{en}$ were obtained from freezing point measurements in benzene and cyclohexane.

$\log K = 2.8$ at 5.4°C in benzene

$\log K = 3.7$ at 6.2°C in cyclohexane referred to the equilibrium

$\text{Ti}(\text{O iso-Pr})_4 + \text{en} \rightleftharpoons \text{Ti}(\text{O iso-Pr})_4 \text{en}$

$\log K = 5.3$ at 6.2°C in cyclohexane referred to the equilibrium

$|\text{Ti}(\text{O iso-Pr})_4 \text{en}| + |\text{Ti}(\text{O iso-Pr})_4| \rightleftharpoons |\text{Ti}_2(\text{O iso-Pr})_8 \text{en}|$

Evaluation of selected values

Further investigation are needed

Zr^{IV}

Stability constants

Bains and Bradley (62B): the complex $|\text{Zn}_2(\text{O iso-Pr})_8 \text{en}|$ was isolated

Evaluation of selected values

Further investigations are needed

V²⁺

Stability constants

Crabtree et al. (61Ca): glass electrode at 25°C in $I = 1.4$

$\log K_1 = 4.63$ $\log K_2 = 2.95$ $\log K_3 = 1.33$

Evaluation of selected values

Authors do not furnish standard deviations. An error of ± 0.1 log units may be drawn considering the facile oxidizability of the ion and the procedure used.

VO²⁺

Stability constants

Bhattacharya and Saxena (61B): spectrophotometry and Job's conductometry at 20 °C in 0.017 (VOSO₄).

$$\log \beta_2 = 5.7$$

Evaluation of selected values

Further investigations are needed

Ta^V

The complex Ta₂(isopropoxide)₁₀⁻ en was isolated by Bains and Bradley (62B)

Evaluation of selected values

Further investigations are needed

Cr²⁺

Stability constants

Pecsok and Bjerrum (57P): glass electrode at 25 °C in I = 1.4

$$\log K_1 = 5.15 \quad \log K_2 = 4.04$$

Evaluation of selected values

Authors do not furnish standard deviations. An error of ± 0.1 log units may be inferred considering the facile oxidizability of the ion and the procedure used.

Cr³⁺

Stability constants

Hoyer (56H): at 4 °C in I = 0.1

$$K = \frac{|ML_2|}{|M(OH)L_2| |H|} \quad \log K = 4.86$$

$$K = \frac{|M(OH)L_2|}{|M(OH)_2L_2| |H|} \quad \log K = 7.34$$

Ohta and Matsukowa (64O): spectrophotometry at 25 °C in I = 0.1

$$\log K_1 = 16.5 \quad \log K_2 < 14$$

Evaluation of selected values

Further investigations are needed

Mn²⁺Stability constants

Bjerrum (41B): hydrogen electrode at 30 °C in 1 KCl

$$\log \beta_1 = 2.73 \quad \log \beta_2 = 4.79 \quad \log \beta_3 = 5.67$$

These values corrected to 25 °C using subsequent enthalpy values (60C) gave the following values:

$$\log \beta_1 = 2.76 \quad \log \beta_2 = 4.86 \quad \log \beta_3 = 5.80$$

Pecsok and Bjerrum (57P): glass electrode at 25 °C in I = 1.4

$$\log \beta_1 = 2.77 \quad \log \beta_2 = 4.87 \quad \log \beta_3 = 5.79$$

Pool and Sandberg (69Pa) potentiometric measurements in DMSO at 25 °C in I = 0.1

$$\log \beta_1 = 3.7 \pm 0.2 \quad \log \beta_2 = 6.9 \pm 0.2 \quad \log \beta_3 = 10.1 \pm 0.2$$

Evaluations of selected values

$$(R) \log \beta_1 = 2.77 \pm 0.04 \quad (41B, 57P) \quad t = 25^\circ\text{C}, \quad I = 1 - 1.4$$

$$(R) \log \beta_2 = 4.87 \pm 0.04 \quad (41B, 57P) \quad t = 25^\circ\text{C}, \quad I = 1 - 1.4$$

$$(R) \log \beta_3 = 5.79 \pm 0.04 \quad (41B, 57P) \quad t = 25^\circ\text{C}, \quad I = 1 - 1.4$$

Enthalpy and entropy valuesCiampolini et al. (60C) calorimetry at 25 °C in I = 1(KCl)

$$\begin{array}{lll} -\Delta H_1^\circ = 11.7 \pm 0.8 & -\Delta H_{1-2}^\circ = 25.1 \pm 0.8 & -\Delta H_{1-3}^\circ = 46.2 \pm 0.6 \\ -\Delta S_1^\circ = 13 & \Delta S_{1-2}^\circ = 8 & \Delta S_{1-3}^\circ = -44 \end{array}$$

Values obtained from enthalpies and stability constants (57P)

Evaluation of selected values

$$(T) -\Delta H_1^\circ = 11.7 \pm 0.8 \quad (60C) \quad t = 25^\circ\text{C} \quad I = 1(\text{KCl})$$

$$(T) -\Delta H_{1-2}^\circ = 25.1 \pm 0.8 \quad (60C) \quad t = 25^\circ\text{C}, \quad I = 1(\text{KCl})$$

$$(T) -\Delta H_{1-3}^\circ = 46.2 \pm 0.6 \quad (60C) \quad t = 25^\circ\text{C}, \quad I = 1(\text{KCl})$$

Re^V

Murmman and Foerster (63M): spectrophotometric evidence of the species

$$|\text{Re}(\text{en})_2\text{O}_2|^+, |\text{Re}(\text{en})_2(\text{OH})\text{O}|^{2+} \quad \text{and} \quad |\text{Re}(\text{en})_2(\text{OH})_2|^+ \quad \text{are reported}$$

Evaluation of selected values

Further investigation are needed

Fe²⁺Stability constants

Bjerrum (41B): hydrogen electrode at 30 °C in 1 KCl

$$\log \beta_1 = 4.28 \quad \log \beta_2 = 7.53 \quad \log \beta_3 = 9.52$$

These values corrected to 25 °C using enthalpies in (60C) gave the following values

$$\log \beta_1 = 4.34 \quad \log \beta_2 = 7.66 \quad \log \beta_3 = 9.71$$

Pecsok and Bjerrum (57P): glass electrode at 25 °C in I = 1.4

$$\log \beta_1 = 4.34 \quad \log \beta_2 = 7.65 \quad \log \beta_3 = 9.70$$

Evaluation of selected values

$$\begin{aligned} \text{(R)} \log \beta_1 &= 4.34 \pm 0.04 & \text{(41B, 57P)} & \quad t = 25^\circ\text{C}, \quad I = 1 - 1.4 \\ \text{(R)} \log \beta_2 &= 7.65 \pm 0.04 & \text{(41B, 57P)} & \quad t = 25^\circ\text{C}, \quad I = 1 - 1.4 \\ \text{(R)} \log \beta_3 &= 9.70 \pm 0.03 & \text{(41B, 57P)} & \quad t = 25^\circ\text{C}, \quad I = 1 - 1.4 \end{aligned}$$

Enthalpy and entropy values

Ciampolini et al. (60C): calorimetry at 25°C in I = 1 (KCl)

$$\begin{aligned} -\Delta H_1^\circ &= 21.1 \pm 0.8 & -\Delta H_{1-2}^\circ &= 43.5 \pm 0.8 & -\Delta H_{1-3}^\circ &= 66.3 \pm 0.6 \\ \Delta S_1^\circ &= 12 & \Delta S_{1-2}^\circ &= 1 & \Delta S_{1-3}^\circ &= -36 \end{aligned}$$

Calculated from enthalpies and stability constants (57P)

Evaluation of selected values

$$\begin{aligned} \text{(T)} -\Delta H_1^\circ &= 21.1 \pm 0.8 & \text{(60C)} & \quad t = 25^\circ\text{C}, \quad I = 1(\text{KCl}) \\ \text{(T)} -\Delta H_{1-2}^\circ &= 43.5 \pm 0.8 & \text{(60C)} & \quad t = 25^\circ\text{C}, \quad I = 1(\text{KCl}) \\ \text{(T)} -\Delta H_{1-3}^\circ &= 66.3 \pm 0.6 & \text{(60C)} & \quad t = 25^\circ\text{C}, \quad I = 1(\text{KCl}) \end{aligned}$$

Co²⁺

Stability constants

Bjerrum (41B): hydrogen electrode at 30°C in 1 (KCl)

$$\log \beta_1 = 5.89 \quad \log \beta_2 = 10.72 \quad \log \beta_3 = 13.82$$

Edwards (50E): glass electrode at 25°C in 1 KCl

$$\log \beta_1 = 5.93 \quad \log \beta_2 = 10.66 \quad \log \beta_3 = 13.96$$

Konrad (63K): polarographic half wave shift at 20°C in I = 2.72 NaClO₄

$$\log \beta_1 = 6.26 \quad \log \beta_2 = 11.33 \quad \log \beta_3 = 14.90$$

Perrin and Sharma (69P): glass electrode at 37°C in 0.15 (KNO₃)

$$\log \beta_1 = 5.30 \quad \log \beta_2 = 9.57 \quad \log \beta_3 = 11.99$$

All values ± 0.01 log units.

Griesser and Sigel (71G): glass electrode at 25°C in 0.1 (NaClO₄)

$$\log \beta_1 = 5.38 \pm 0.04 \quad \log \beta_2 = 10.24 \quad \log \beta_3 = 13.79$$

Nakon and Martell (72N): glass electrode at 25°C in 0.1 KNO₃

$$\log \beta_1 = 5.89 \pm 0.05 \quad \log \beta_2 = 10.76 \pm 0.05$$

$$K = |\text{Co(en)}_2(\text{O}_2)(\text{OH})\text{Co(en)}_2| |\text{H}^+| / |\text{Co}^{2+}|^2 |\text{en}|^4 \cdot p\text{O}_2$$

pO₂ (in pascal units)

$$\log K = 29.9$$

Evaluation of selectrode values

$$(T) \log K_1 = 5.30 \pm 0.01 \text{ (69P)} \quad t = 37^\circ\text{C}, \quad I = 0.15 \text{ KNO}_3$$

$$(T) \log K_2 = 4.27 \pm 0.01 \text{ (69P)} \quad t = 37^\circ\text{C}, \quad I = 0.15 \text{ KNO}_3$$

$$(T) \log K_3 = 2.42 \pm 0.01 \text{ (69P)} \quad t = 37^\circ\text{C}, \quad I = 0.15 \text{ KNO}_3$$

Enthalpy and entropy values

Ciampolini *et al.* (60C): calorimetry at 25 °C in 1 (KCl)

$$-\Delta H_1^\circ = 28.9 \quad -\Delta H_{1-2}^\circ = 58.4 \quad -\Delta H_{1-3}^\circ = 92.7$$

$$\Delta S_1^\circ = 17 \quad \Delta S_{1-2}^\circ = 8 \quad \Delta S_{1-3}^\circ = -50$$

Values obtained from enthalpies and stability constants (41B)

Evaluation of selected values

Further investigation are needed

Co³⁺

Stability constants

Bjerrum (41B): hydrogen electrode at 30 °C in 1 KCl

$$\log \beta_3 = 48.69$$

Bjerrum *et al.* (52Ba): glass electrode and spectrophotometry in 1 NaNO₃ at 25 °C with active carbon and catalyzt.

$$\log K_3 = 13.99$$

$$K = \frac{|\text{CoL}_3|}{|\text{cis-CoL}_2(\text{H}_2\text{O})_2| |\text{L}|} \quad \log K = 13.28$$

$$K = \frac{|\text{CoL}_3|}{|\text{trans-CoL}_2(\text{H}_2\text{O})| |\text{L}|} \quad \log K = 15.24$$

Bjerrum *et al.* (52Ba): glass electrode and spectrophotometry in 1 NaNO₃ at 30 °C with active carbon catalyzt.

$$\log K_1 = 18.7 \quad \log K_2 = 16.2 \quad \log K_3 = 13.8$$

These values are estimated

Evaluation of selected values

Further investigations are needed.

Ni²⁺

Stability constants

Bjerrum (41B): hydrogen electrode at 30 °C in 1 KCl

$$\log K_1 = 7.66 \quad \log K_2 = 6.40 \quad \log K_3 = 4.55$$

Carlson *et al.* (45C): glass electrode in 1 (KCl) at 30 °C

$$\log K_1 = 7.52 \quad \log K_2 = 6.28 \quad \log K_3 = 4.26$$

Edwards (50E): glass electrode in 1 (KCl) at 25 °C

$$\log K_1 = 7.72 \quad \log K_2 = 6.36 \quad \log K_3 = 4.33$$

Basolo and Murmann (52B): glass electrode at 0 and 25 °C in 0.5 KNO₃

$$\log K_1 = 7.92 \quad \log K_2 = 6.77 \quad \log K_3 = 5.36 \quad \text{at } 0^\circ\text{C}$$

$$\log K_1 = 7.60 \quad \log K_2 = 6.48 \quad \log K_3 = 5.03 \quad \text{at } 25^\circ\text{C}$$

Hares (52H): glass electrode in 1 KCl at 30 °C

$$\log K_1 = 7.45 \quad \log K_2 = 6.23 \quad \log K_3 = 4.34$$

McIntyre (53M): glass electrode at 0 and 30 °C in I = 0.3

$$t = 0 \text{ } ^\circ\text{C}$$

$$\log K_1 = 7.83$$

$$\log K_2 = 6.61$$

$$\log K_3 = 4.84$$

$$t = 30 \text{ } ^\circ\text{C}$$

$$\log K_1 = 7.28$$

$$\log K_2 = 6.09$$

$$\log K_3 = 4.20$$

Cotton and Harris (55C): glass electrode at 0 and 49.1 °C and I = 0.15

$$t = 0 \text{ } ^\circ\text{C}$$

$$\log K_1 = 7.88$$

$$\log K_2 = 6.70$$

$$\log K_3 = 4.78$$

$$t = 49.1 \text{ } ^\circ\text{C}$$

$$\log K_1 = 6.92$$

$$\log K_2 = 5.75$$

$$\log K_3 = 3.90$$

Poulsen and Bjerrum (55P): glass electrode in 1 KNO₃ at 25 °C

$$\log K_1 = 7.51$$

$$\log K_2 = 6.35$$

$$\log K_3 = 4.42$$

Morinaga (56M): polarography at 25 °C in I = 0.1

$$\log K_1 = 7.52$$

$$\log K_2 = 6.28$$

$$\log K_3 = 4.26$$

Pecsok and Bjerrum (57P): glass electrode at 25 °C and I = 1.4

$$\log K_1 = 7.51$$

$$\log K_2 = 6.35$$

$$\log K_3 = 4.42$$

McIntyre et al. (59M): glass electrode at 10 - 40 °C and I → 0.

t/°C

log K₁

log K₂

log K₃

10 7.74 ± 0.05 6.44 ± 0.04 4.67 ± 0.02

20 7.52 ± 0.06 6.32 ± 0.06 4.49 ± 0.05

30 7.27 ± 0.02 6.11 ± 0.03 4.20 ± 0.03

40 7.04 ± 0.03 5.89 ± 0.03 4.05 ± 0.51

Caullet (63C): spectrophotometry at 25 °C and I = 1.2

$$\log K_1 = 7.55$$

$$\log K_2 = 6.20$$

$$\log K_3 = 4.77$$

Näsänen et al. (65N): glass electrode at 25 °C in NaClO₄ solutions with I = 0 - 2.5

$$\log K_1 = 7.32 + 0.290 I$$

$$\log K_2 = 6.18 + 0.343 I$$

$$\log K_3 = 4.11 + 0.409 I$$

Näsänen et al. (65N): glass electrode at 25 °C in 1 KNO₃

$$\log K_1 = 7.54$$

$$\log K_2 = 6.39$$

$$\log K_3 = 4.39$$

Holmes and Williams (67H): glass electrode at 25 °C in 0.30 (ClO₄⁻)

$$\log K_1 = 7.49$$

$$\log K_2 = 6.45$$

$$\log K_3 = 4.11$$

Perrin and Sharma (68P): glass electrode at 37 °C in 0.15 (KNO₃)

$$\log K_1 = 6.982$$

$$\log K_2 = 5.807$$

$$\log K_3 = 3.662$$

Faraglia *et al.* (70Pa): glass electrode at 25 °C and 0.5 (Li)ClO₄

$$\log K_1 = 7.36 \pm 0.01 \quad \log K_2 = 6.26 \pm 0.02 \quad \log K_3 = 4.40 \pm 0.03$$

Griesser and Sigel (71G): glass electrode at 25 °C and 0.1 (NaClO₄)

$$\log K_1 = 6.97 \pm 0.05 \quad \log K_2 = 6.18 \quad \log K_3 = 4.38$$

Newman *et al.* (72Na): glass electrode at 25 °C I → 0

$$\log K_1 = 7.30 \quad \log K_2 = 5.95 \quad \log K_3 = 4.08$$

Evaluation of selected values

$$(R) \log K_1 = 7.52 \pm 0.06 \text{ (59M)} \quad t = 20 \text{ °C, } I \rightarrow 0$$

$$(R) \log K_2 = 6.32 \pm 0.06 \text{ (59M)} \quad t = 20 \text{ °C, } I \rightarrow 0$$

$$(R) \log K_3 = 4.49 \pm 0.05 \text{ (59M)} \quad t = 20 \text{ °C, } I \rightarrow 0$$

$$(R) \log K_1 = 7.54 \pm 0.04 \text{ (55P, 57P, 65N)} \quad t = 25 \text{ °C, } I = 1$$

$$(R) \log K_2 = 6.40 \pm 0.05 \text{ (55P, 57P, 65N)} \quad t = 25 \text{ °C, } I = 1$$

$$(R) \log K_3 = 4.45 \pm 0.05 \text{ (55P, 57P, 65N)} \quad t = 25 \text{ °C, } I = 1$$

$$(R) \log K_1 = 7.27 \pm 0.02 \text{ (59M)} \quad t = 30 \text{ °C, } I \rightarrow 0$$

$$(R) \log K_2 = 6.11 \pm 0.03 \text{ (59M)} \quad t = 30 \text{ °C, } I \rightarrow 0$$

$$(R) \log K_3 = 4.20 \pm 0.03 \text{ (59M)} \quad t = 30 \text{ °C, } I \rightarrow 0$$

Enthalpy and entropy values

Basolo and Murmann (52B): calculated from stability constants in 0.5 KNO₃

$$-\Delta H_1^\circ = 20 \quad -\Delta H_2^\circ = 18 \quad -\Delta H_3^\circ = 21$$

$$\Delta S_1^\circ = 80 \quad \Delta S_2^\circ = 63 \quad \Delta S_3^\circ = 30$$

Basolo and Murmann (54B): calorimetry at 0 °C in 0.5 KNO₃

$$-\Delta H_{1-3}^\circ = 105 \quad \Delta S_{1-3}^\circ = 4$$

Davies *et al.* (54D): calorimetry at 25 °C in 0.1 KCl

$$-\Delta H_{1-2}^\circ = 72 \quad \Delta H_{1-3}^\circ = 117$$

$$\Delta S_{1-2}^\circ = 14 \quad \Delta S_{1-3}^\circ = -59$$

Cotton and Harris (55C): calculated from stability constants in I = 0.15

$$-\Delta H_1^\circ = 33 \pm 1 \quad -\Delta H_2^\circ = 32 \pm 2 \quad -\Delta H_3^\circ = 29 \pm 4$$

$$\Delta S_1^\circ = 42 \pm 4 \quad \Delta S_2^\circ = 8 \pm 8 \quad \Delta S_3^\circ = -21 \pm 20$$

Poulsen and Bjerrum (55P): calorimetry at 25 °C in 1 KNO₃

$$-\Delta H_1^\circ = 37.7 \pm 0.4 \quad -\Delta H_{1-2}^\circ = 76.2 \pm 0.4 \quad -\Delta H_{1-3}^\circ = 116.7 \pm 0.4$$

$$\Delta S_1^\circ = 17 \quad \Delta S_{1-2}^\circ = 10 \quad \Delta S_{1-3}^\circ = -42$$

McIntyre *et al.* (59M): calculated from stability constants in I = 0

$$-\Delta H_1^\circ = 39.7 \quad -\Delta H_2^\circ = 31.4 \quad -\Delta H_3^\circ = 36.4$$

$$\Delta S_1^\circ = 8 \quad \Delta S_2^\circ = 13 \quad \Delta S_3^\circ = -38$$

Ciampolini *et al.* (60C): calorimetry at 25 °C in 1 (KCl)

$$-\Delta H_1^\circ = 37.2 \quad -\Delta H_{1-2}^\circ = 76.4 \quad -\Delta H_{1-3}^\circ = 118.6$$

Ciampolini *et al.* (60C): calorimetry at 25 °C in 1KNO₃.

$$-\Delta H_1^{\circ} = 37.9 \quad -\Delta H_{1-2}^{\circ} = 74.9 \quad -\Delta H_{1-3}^{\circ} = 114.6$$

Holmes and Williams (67H): calorimetry at 25 °C in 0.3 NaClO₄.

$$-\Delta H_1^{\circ} = 38.7 \pm 0.6 \quad -\Delta H_2^{\circ} = 38.5 \pm 0.6 \quad -\Delta H_3^{\circ} = 39.6 \pm 0.6$$

$$\Delta S_1^{\circ} = 14 \pm 2 \quad \Delta S_2^{\circ} = 5 \pm 2 \quad \Delta S_3^{\circ} = -54 \pm 3$$

Peltonen and Kivalo (68Pa) calorimetry at 25 °C in I = 1 KNO₃.

$$-\Delta H_1^{\circ} = 37.9 \pm 0.7 \quad -\Delta H_2^{\circ} = 38.7 \pm 1.1 \quad -\Delta H_3^{\circ} = 40.4 \pm 0.7$$

Evaluation of Selected Values

$$(R) - \Delta H_1^{\circ} = 37.7 \pm 0.4 \quad (55P, 68Pa) \quad t = 25 \text{ }^{\circ}\text{C}, \quad I = 1$$

$$(R) - \Delta H_2^{\circ} = 38.5 \pm 0.4 \quad (55P, 68Pa) \quad t = 25 \text{ }^{\circ}\text{C}, \quad I = 1$$

$$(R) - \Delta H_3^{\circ} = 40.5 \pm 0.4 \quad (55P, 68Pa) \quad t = 25 \text{ }^{\circ}\text{C}, \quad I = 1$$

Pd²⁺

Stability Constants:

Job (28J): conditions are not reported.

$$\log \beta_2 = 26.9.$$

Pilyte *et al.* (65P): electrodeposition of Pd on a Pt surface from a solution of $[\text{Pd}(\text{en})_2]^{2+}$ (0.1 M) at pH 8 and $t = 20 \text{ }^{\circ}\text{C}$.

$$\log \beta_2 = 27.3$$

Rasmussen and Jørgensen (68R): potentiometry in 1 NaClO₄ at 25 °C.

$$\log K_1 > 20 \quad \log K_2 = 18.4$$

Evaluation of Selected Values

Further investigations are needed.

Pt²⁺

Stability Constants:

Grinberg and Gelfman (61G): potentiometry with Pt electrode at 18 °C in 1 KNO₃. Platinum was in the form of chloride of the bis(ethylenediamine)platinum(II) complex and potential was determined as a function of concentration of ethylene diamine. The obtained pK values are in the range of 36.1–37.2.

Evaluation of Selected Values

Further investigations are needed.

Cu²⁺

Stability Constants:

Carlson *et al.* (45C): glass electrode at 30 °C in 0.5 KNO₃.

$$\log K_1 = 10.55 \quad \log K_2 = 9.05$$

Bjerrum and Nielsen (48B): glass electrode at 25 °C in 1 KNO₃.

$$\log K_1 = 10.72 \quad \log K_2 = 9.31$$

$$\log K_3 = -0.90 \text{ (spectrophotometric)}$$

Laitinen et al. (49L): polarography at 25 °C in 0.1 KNO₃.

$$\log \beta_2 = 19.72$$

Basolo and Murmann (52B): glass electrode at 0 and 25 °C in 0.5 KNO₃.

$$\begin{array}{ll} t = 0 \text{ } ^\circ\text{C} & t = 25 \text{ } ^\circ\text{C} \\ \log K_1 = 11.34 & \log K_1 = 10.76 \\ \log K_2 = 9.95 & \log K_2 = 9.37 \end{array}$$

Spike and Parry (53S): glass electrode at 25 °C in 2.15 (KNO₃).

$$\log K_1 = 11.02 \quad \log K_2 = 9.59$$

McIntyre (53M): glass electrode at 0 and 30 °C in I → 0.

$$\begin{array}{lll} t = 0 \text{ } ^\circ\text{C} & t = 30 \text{ } ^\circ\text{C} & t = 0 \text{ } ^\circ\text{C} \log K_1 = 11.26 \log K_2 = 9.78 \\ \log K_1 = 11.26 & \log K_2 = 10.36 & t = 30 \text{ } ^\circ\text{C} \log K_1 = 10.36 \log K_2 = 8.93 \end{array}$$

Cotton and Harris (55C): glass electrode at 0 and 49.1 °C in I = 0.15.

$$\begin{array}{ll} t = 0 \text{ } ^\circ\text{C} & t = 49.1 \\ \log K_1 = 11.45 & \log K_1 = 10.01 \\ \log K_2 = 9.83 & \log K_2 = 8.46 \end{array}$$

Jonassen et al. (55J): spectrophotometry at 25 °C in 0.5 KNO₃

$$K = \frac{|\text{CuL}_2\text{OH}^+|}{|\text{CuL}_2^{2+}| |\text{OH}^-|} \log K = 0.73$$

Poulsen and Bjerrum (55P): glass electrode at 25 °C in I = 1.4.

$$\log K_1 = 10.72 \quad \log K_2 = 9.31 \quad \log K_3 = 1.0$$

Martell et al. (57M): glass electrode at 25 °C in 0.1 KNO₃

$$\log K_1 = 10.5$$

Bennett (57B): glass electrode at 30 °C in I = 0.1

$$\log K_1 = 11.12 \quad \log K_2 = 9.61$$

Vink (57V): spectrophotometry at 25 °C in variable ionic media

$$K = \frac{|\text{CuL}_2\text{OH}^+|}{|\text{CuL}_2^{2+}| |\text{OH}^-|}, \log K = 0.477$$

Beshkova and Bachkova (58Ba): Cu amalgam electrode at 25 °C in 1 KNO₃

$$\log K_1 = 10.75 \quad \log K_2 = 9.28$$

McIntyre et al. (59M): glass electrode at 10 - 40 °C an I = 0.

t/ °C	log K ₁	log K ₂
10	11.01 ± 0.03	9.57 ± 0.02
20	10.67 ± 0.04	9.23 ± 0.05
30	10.36 ± 0.03	8.93 ± 0.01
40	10.06 ± 0.02	8.66 ± 0.04

Näsänen and Meriläinen (63N): glass electrode at 25 °C in NaClO₄ solutions

$$\begin{array}{l} \log K_1 = 10.48 + 0.646 I - 0.254 I^{1.5} + 0.052 I^2 \\ \log K_2 = 9.07 + 0.626 I - 0.122 I^{1.5} + 0.202 I^2 \end{array}$$

Perrin and Sharma (66Pa): glass electrode at 20 °C in I = 0

$$\log K_1 = 10.66 \quad \log K_2 = 9.33$$

Perrin et al. (67P): glass electrode at 37 °C in 0.15 KNO₃

$$\log K_1 = 10.175 \quad \log K_2 = 8.765$$

Faraglia et al. (70Fa): glass electrode at 25 °C and 0.5 (Li)ClO₄

$$\log K_1 = 10.61 \pm 0.01 \quad \log K_2 = 9.29 \pm 0.01$$

Griesser and Sigel (71G): glass electrode at 25 °C and 0.1 (NaClO₄)

$$\log K_1 = 10.44 \pm 0.06 \quad \log K_2 = 9.16$$

Hauer et al. (71H): glass electrode at 25 °C and 0.1 (NaClO₄)

$$\log K_1 = 10.40 \pm 0.01 \quad \log \beta_2 = 19.36 \pm 0.01 \quad \log \beta_{1-11} = 2.7 \pm 0.1$$

Srinivasan and Subrahmanya (71S): polarography in 2 KNO₃

$$\log \beta_2 = 20.33$$

Barbucci et al. (72B) glass electrode at 25 °C in 0.5 KNO₃

$$\log \beta_1 = 10.60 \pm 0.01 \quad \log K_2 = 9.15 \pm 0.01$$

$$\log \beta_{1-21} = -9.19 \quad \log \beta_{2-22} = 8.48$$

Newman et al. (72Na): glass electrode at 25 °C and I → 0

$$\log K_1 = 10.50 \quad \log K_2 = 9.02$$

Nakagawa et al. (75N): Cu amalgam at 25 °C in I = 0.1

$$\log \beta_2 = 19.40$$

Evaluation of selected values

$$(R) \log K_1 = 11.01 \pm 0.03 \quad (59M) \quad t = 10 \text{ °C}, \quad I = 0$$

$$(R) \log K_2 = 9.57 \pm 0.02 \quad (59M) \quad t = 10 \text{ °C}, \quad I = 0$$

$$(R) \log K_1 = 10.60 \pm 0.01 \quad (72B) \quad t = 25 \text{ °C}, \quad I = 0.5 \text{ KNO}_3$$

$$(R) \log K_2 = 9.15 \pm 0.01 \quad (72B) \quad t = 25 \text{ °C}, \quad I = 0.5 \text{ KNO}_3$$

Enthalpy and entropy values

Basolo and Murmann (52B): calculated from equilibrium constants at 0-25 °C in 0.5 KNO₃ with glass electrode

$$-\Delta H_1^\circ = 36 \quad -\Delta H_2^\circ = 36$$

$$\Delta S_1^\circ = 88 \quad \Delta S_2^\circ = 59$$

Basolo and Murmann (54B): calorimetry at 0 °C in 0.5 KNO₃

$$-\Delta H_{1-2}^\circ = 103 \quad \Delta S_{1-2}^\circ = 30$$

Davies (54D): calorimetry at 25 °C in 0.1 KCl

$$-\Delta H_{1-2}^\circ = 106 \quad \Delta S_{1-2}^\circ = 30$$

Cotton and Harris (55C): calculated from equilibrium constants at 0-49 °C in I = 0.15

$$-\Delta H_1^\circ = 50 \pm 2 \quad \Delta S_1^\circ = 38 \pm 12$$

$$-\Delta H_2^\circ = 47 \pm 1 \quad \Delta S_2^\circ = 17 \pm 4$$

Poulsen and Bjerrum (55P): calorimetry at $t = 25^{\circ}\text{C}$ in 1 KNO_3

$$-\Delta H_1^{\circ} = 54.4 \quad \Delta S_1^{\circ} = 23$$

$$-\Delta H_2^{\circ} = 51.9 \quad \Delta S_2^{\circ} = 10$$

Holmes and Williams (67H): calorimetry at 25°C in $0.3 (\text{ClO}_4^-)$

$$-\Delta H_1^{\circ} = 52.1 \pm 0.7 \quad \Delta S_1^{\circ} = 25 \pm 2$$

$$-\Delta H_2^{\circ} = 51.4 \pm 0.7 \quad \Delta S_2^{\circ} = -0.4 \pm 3$$

Peltonen and Kivalo (68Pa): calorimetry at 25°C in 1 KNO_3

$$-\Delta H_1^{\circ} = 55.6 \pm 1.3$$

$$-\Delta H_2^{\circ} = 51.8 \pm 1.6$$

Barbucci *et al.* (72B): calorimetry at $t = 25^{\circ}\text{C}$ in 0.5 KNO_3

$$-\Delta H_1^{\circ} = 52.5 \pm 0.2 \quad \Delta S_1^{\circ} = 26 \pm 1$$

$$-\Delta H_2^{\circ} = 52.9 \pm 0.4 \quad \Delta S_2^{\circ} = -2 \pm 2$$

Evaluation of selected values

$$(R) \quad -\Delta H_1^{\circ} = 52.1 \pm 0.7 \text{ (67H)} \quad t = 25^{\circ}\text{C}, \quad I = 0.3 (\text{ClO}_4^-)$$

$$(R) \quad -\Delta H_2^{\circ} = 51.4 \pm 0.7 \text{ (67H)} \quad t = 25^{\circ}\text{C}, \quad I = 0.3 (\text{ClO}_4^-)$$

$$(R) \quad -\Delta H_1^{\circ} = 52.5 \pm 0.2 \text{ (72B)} \quad t = 25^{\circ}\text{C}, \quad I = 0.5 \text{ KNO}_3$$

$$(R) \quad -\Delta H_2^{\circ} = 52.9 \pm 0.4 \text{ (72B)} \quad t = 25^{\circ}\text{C}, \quad I = 0.5 \text{ KNO}_3$$

Cu^+

Stability constants

Bjerrum and Nielsen (48B): Cu amalgam electrode at 25°C and $I \approx 0.7$

$$\log \beta_2 = 10.8 \text{ (estimated)}$$

James and Williams (61J): platinum electrode at 25°C and $I = 0.11 (\text{K}_2\text{SO}_4)$

$$\log \beta_2 = 11.4$$

Srinivasan and Subrahmanya (71S), polarography in 2 KNO_3

$$\log \beta_2 = 10.63$$

Evaluation of selected values

Further investigations are needed

Ag^+

Stability constants

Job (28J): potentiometry with Ag electrode at 16°C

$$\log \beta_1 = 5 \quad \log \beta_2 = 7.84$$

Britton and Williams (36B): glass and Ag electrodes at 18°C in $I = 0.02$

$$\log \beta_2 = 7.70$$

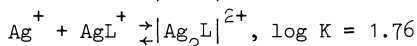
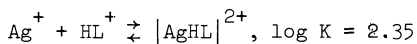
Bjerrum (50B): glass and Ag electrodes at 25°C in 1 KNO_3

$$\log K_1 = 6 \quad \log K_2 = 1.4$$

Schwarzenbach (52S): glass electrode at 20°C in 0.1 NaNO_3

$$\log K_1 = 4.70 \quad \log K_2 = 3.00$$

$$\log \beta_{202} = 13.23$$



Armeanu and Luca (61A): Ag electrode and solubility at 25 °C in I < 0.01

$$\log \beta_2 = 7.73 \quad \log \beta_3 = 9.75$$

Pool and Sandberg (69Pa): Ag electrode against a $\text{Zn}/\text{Zn}(\text{ClO}_4)_2$ saturated solution in DMSO at 25 °C and I = 0.1

$$\log \beta_1 = 6.27 \pm 0.10 \quad \log \beta_2 = 9.54 \pm 0.04 \quad \log \beta_{201} = 5.8$$

Bardin (70B): Ag electrode in nitromethane at 25 °C

$$\log K_1 = 9.8 \quad \log K_2 = 15.6$$

H. Ohtaki and Y. Ito (730): glass electrode at 25 °C in $3(\text{LiClO}_4)$

$$\log \beta_{101} = 6.13 \pm 0.02$$

$$\log \beta_{111} = 13.56 \pm 0.02$$

$$\log \beta_{122} = 27.37 \pm 0.02$$

$$\log \beta_{201} = 7.67 \pm 0.05$$

$$\log \beta_{202} = 14.53 \pm 0.07$$

$$\log \beta_{1-11} = -4.59 \pm 0.05$$

Van Pouche (75V): glass and Ag electrode at 25 °C in 0.5 KNO_3

$$\log \beta_{102} = 7.64$$

$$\log \beta_{111} = 12.38$$

$$\log \beta_{122} = 24.98$$

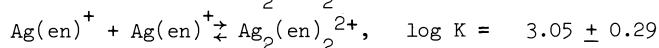
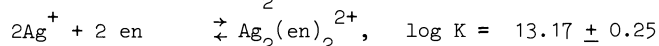
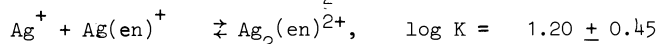
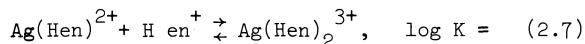
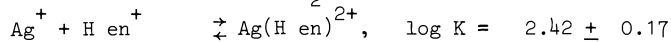
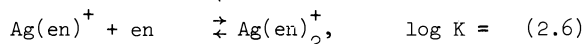
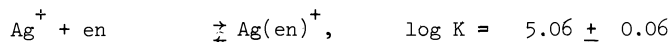
$$\log \beta_{112} = 16.51$$

$$\log \beta_{202} = 13.15$$

These values are obtained using the protonation constant $\log K_1 = 10.04$.

No evidence is found about the species $|\text{Ag}_2\text{L}|^{2+}$ and $|\text{AgL}|^+$ in the range investigated.

B. Magyar and G. Schwarzenbach (78Ma): glass electrode, solubility and three phases vapour tensiometry at 25 °C in 1M (KNO_3)



Evaluation of selected values

The system Ag-en contains a great number of species but the results obtained by different authors are often in considerable disagreement. A species that surely forms is AgHL. Using the values of $pK_1 = 10.04$ and the value given by Schwarzenbach (52S) of 2.35, we obtain the value $\log \beta_{111} = 12.39$, in excellent agreement with the value of Van Poucke (75V) of 12.38 in $I = 0.1$ and $t = 20^\circ\text{C}$. This result was confirmed by Magyar and Schwarzenbach (78Ma), $\log \beta_{111} = 12.66$ in $I = 1 \text{ KNO}_3$ at 25°C .

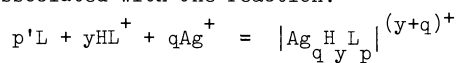
Ohtaki and Ito (730) found $\log \beta_{111} = 13.56$, which was higher than the values obtained by Schwarzenbach and his coworkers (52S, 78Ma), and by Van Poucke (75V). Ohtaki and Cho (770) reexamined the Ag-en system in the same ionic medium ($I = 3 \text{ LiClO}_4$) and confirmed the value $\log \beta_{111} = 13.53$. This value may be less certain compared with the previous one found by Ohtaki and Ito, because they allowed the formation constants of the complexes species to vary in the solution as well as the dissociation constants of ethylenediamine itself in the course of the least-squares refinement in their work (770). Although the value obtained by Ohtaki et al. (730, 770) is higher than that by the previous workers (52S, 75V, 78Ma), the larger ionic strength in the former work than in the latter must be taken into account. In the 3 LiClO_4 medium the values of pK_1 and pK_2 are 8.04_4 and 10.65_0 , respectively (730). On the other hand, the values are $pK_1 = 7.22$ and $pK_2 = 10.03$ in 0.1 NaNO_3 (52S). The AgL_2 species is also found by many authors and the value obtained by Schwarzenbach (52S) for $\log \beta_{102}$, again confirmed by Magyar and Schwarzenbach (78Ma), is in agreement with that found by Van Poucke (75V). This species is not found by Ohtaki and Ito (730), but Ohtaki and Cho (770) suggested the formation of the AgL_2 species in their work, which has been examined in a higher pH region compared with the work by Ohtaki and Ito (730). The $\log \beta_{102}$ value reported by them is 9.45, which is again larger than that found by Van Poucke (75V) and Magyar and Schwarzenbach (78Ma). The dimeric species Ag_2L_2 is found by the authors (730, 75V, 770 and 78Ma). The value found in 3 LiClO_4 is larger than that obtained in 0.1 M NaNO_3 . Bjerrum and Bang (79B), however, reported that Ag-en polymerizes beyond the dimeric stage assumed by many authors, on the basis of solubility measurements in $1 (\text{ClO}_4^-, \text{NO}_3^-)$ at 20 and 25°C . For other species like AgH_2L_2 and AgL , we cannot draw definitive conclusions.

Enthalpy and entropy values

Van Poucke (75V): calorimetry at 25°C in 0.5 KNO_3

	$-\Delta H^\circ$	ΔS°
$ \text{AgHL} ^{2+}$	25.4	-41.0
$ \text{AgH}_2\text{L}_2 ^{3+}$	50.8	-77.0
$ \text{AgHL}_2 ^{2+}$	56.9	-65.7
$ \text{AgL}_2 ^+$	52.5	-30.1
$ \text{Ag}_2\text{L}_2 ^{2+}$	97.2	-74.1

Values associated with the reaction:



where $p = p' + y$.

	$-\Delta H^\circ$	ΔS°
$ \text{AgL} ^+$	48.5 ± 1.4	-66 ± 5
$ \text{AgL}_2 $	55.2 ± 1.3	-39 ± 5
$ \text{Ag}_2\text{L}_2 $	107.8 ± 2.7	-109 ± 9

Evaluation of selected values

The reliability of these values is tied up to the values of the constants. See Stability Constants section for comments. For the $|\text{Ag}_2\text{L}_2|^{2+}$ and $|\text{AgL}_2|^+$ the agreement between the values is such to confirm the existence of these species.

Zn²⁺Stability constantsBjerrum (45B): glass electrode at 25 °C in 1 KNO₃

$$\log K_1 = 5.92 \quad \log K_2 = 5.15 \quad \log K_3 = 1.86$$

Carlson et al. (45C): glass electrode at 30 °C in 1 KCl

$$\log K_1 = 5.71 \quad \log K_2 = 4.66 \quad \log K_3 = 1.72$$

Spike and Parry (53S): glass electrode at 25 °C in 2.15 KNO₃.

$$\log K_1 = 6.15 \quad \log K_2 = 5.34$$

McIntyre et al. (53M): glass electrode at 30 °C in I = 0

$$\log K_1 = 5.56 \quad \log K_2 = 4.87$$

Nyman et al. (55Na):polarography at 25 °C in 0.1 KNO₃ $\log \beta_2 = 13.65 \log K_3 = 0.83$ glass electrode at 25 °C in 0.5 KNO₃ $\log K_1 = 6.00 \log K_2 = 5.08 \log K_3 = 2.07$ Zn amalgam electrode at 25 °C in 0.5 KNO₃: $\log K_1 = 6.00 \log K_2 = 4.81 \log K_3 = 2.17$

Morinaga (56M): polarography at 25 °C in I = 0.1

$$\log K_1 = 5.71 \quad \log K_2 = 4.66 \quad \log K_3 = 1.72$$

Pecsok and Bjerrum (57P): glass electrode at 25 °C in I = 1.4

$$\log K_1 = 5.92 \quad \log K_2 = 5.15 \quad \log K_3 = 1.86$$

McIntyre et al. (59M): glass electrode at 10-40 °C in I → 0

t/°C	log K ₁	log K ₂	log K ₃
10	5.85 ± 0.01	5.13 ± 0.03	3.26 ± 0.02
20	5.77 ± 0.06	5.06 ± 0.02	3.28 ± 0.05
30	5.55 ± 0.09	4.89 ± 0.05	3.22 ± 0.03
40	5.51 ± 0.14	4.76 ± 0.06	3.18 ± 0.51

Kanemura and Watters (67K): glass electrode at 25 °C in 1 KNO₃

$$\log K_1 = 5.71 \quad \log K_2 = 5.14 \quad \log K_3 = 1.83$$

Sundaresan et al. (67Sa): polarography at 30 °C in 0.5 KCl

$$\log \beta_2 = 11.2 \quad \log \beta_3 = 12.3$$

Perrin and Sharma (69P): glass electrode at 37 °C and 0.15 (KNO₃)

$$\log K_1 = 5.53 \quad \log \beta_2 = 10.28 \quad \log \beta_3 = 12.70$$

Pool and Sandberg (67Pa): potentiometry in DMSO at 25 °C and I = 0

$$\log \beta_1 = 7.18 \pm 0.10 \quad \log \beta_2 = 13.85 \pm 0.06 \quad \log \beta_3 = 18.70 \pm 0.04$$

Faraglia et al. (70Fa): glass electrode at 25 °C and 0.5 LiClO₄

$$\log K_1 = 5.75 \pm 0.01 \quad \log K_2 = 5.09 \pm 0.01$$

Griesser and Sigel (71G): glass electrode at 25 °C and 0.1 (NaClO₄)

$$\log K_1 = 5.59 \pm 0.14 \quad \log K_2 = 5.02 \quad \log K_3 = 3.78$$

Evaluation of selected values

$$(R) \log K_1 = 5.77 \pm 0.06 \quad (59M) \quad t = 20 \text{ }^\circ\text{C}, \quad I = 0$$

$$(R) \log K_2 = 5.06 \pm 0.02 \quad (59M) \quad t = 20 \text{ }^\circ\text{C}, \quad I = 0$$

$$(R) \log K_1 = 5.55 \pm 0.09 \quad (59M) \quad t = 30 \text{ }^\circ\text{C}, \quad I = 0$$

$$(R) \log K_2 = 4.89 \pm 0.05 \quad (59M) \quad t = 30 \text{ }^\circ\text{C}, \quad I = 0$$

Enthalpy and entropy values

Spike and Parry (53S): calculated from stability constants in 2.15 KNO₃, values at 25 °C

$$-\Delta H_1^\circ = 27.6 \quad -\Delta H_2^\circ = 24.7$$

Davies and Singer (54D): calorimetry at 25 °C in 0.1 KCl

$$-\Delta H_{1-2}^\circ = 48.1 \quad -\Delta H_{1-3}^\circ = 77.4$$

$$\Delta S_{1-2}^\circ = 31.8 \quad \Delta S_{1-3}^\circ = -41$$

McIntyre *et al.* (59M): calculated from stability constants in I → 0

$$-\Delta H_1^\circ = 20.9 \quad -\Delta H_2^\circ = 21.8$$

$$\Delta S_1^\circ = 37.7 \quad \Delta S_2^\circ = -21$$

Ciampolini *et al.* (60C): calorimetry at 25 °C in 1 KNO₃

$$-\Delta H_1^\circ = 29.3 \pm 0.8 \quad -\Delta H_{1-2}^\circ = 49.8 \pm 0.8 \quad -\Delta H_{1-3}^\circ = 71.5 \pm 0.6$$

$$\Delta S_1^\circ = 14.5 \quad \Delta S_2^\circ = 4.2 \quad \Delta S_3^\circ = -35.5$$

Evaluation of selected values

$$(T) -\Delta H_1^\circ = 29.3 \pm 0.8 \quad (60C) \quad t = 25 \text{ }^\circ\text{C}, \quad I = 1 \text{ KNO}_3$$

$$(T) -\Delta H_{1-2}^\circ = 49.8 \pm 0.8 \quad (60C) \quad t = 25 \text{ }^\circ\text{C}, \quad I = 1 \text{ KNO}_3$$

$$(T) -\Delta H_{1-3}^\circ = 71.5 \pm 0.6 \quad (60C) \quad t = 25 \text{ }^\circ\text{C}, \quad I = 1 \text{ KNO}_3$$

Cd²⁺

Stability constants

Bjerrum and Andersen (45B): glass electrode at 25 °C in 1 KNO₃

$$\log K_1 = 5.63 \quad \log K_2 = 4.59 \quad \log K_3 = 2.07$$

Carlson *et al.* (45C): glass electrode at 30 °C in 0.5 KNO₃

$$\log K_1 = 5.47 \quad \log K_2 = 4.55 \quad \log K_3 = 2.07$$

Douglas *et al.* (50D): polarography at 25 °C in 0.1 KNO₃

$$\log \beta_3 = 12.18$$

Spike and Parry (53S): glass electrode at 25 °C in 2.15 KNO₃

$$\log K_1 = 5.84 \quad \log K_2 = 4.78 \quad \log K_3 = 2.07$$

Cotton and Harris (55C): glass electrode at 0 - 49.1 °C in I = 0.15

$$t/^\circ\text{C} \quad \log K_1 \quad \log K_2$$

$$0 \quad 5.85 \quad 4.72$$

$$49.1 \quad 5.21 \quad 4.20$$

Keller and Eyke (61K): polarography in 0.1 KNO₃

$$\log \beta_3 = 11.89$$

Milyukov (62M): glass electrode at 27 °C in 1 KNO₃

$$\log K_1 = 5.6 \quad \log K_2 = 4.6 \quad \log K_3 = 2.0$$

Kanemura and Watters (67K): glass electrode at 25 °C in 1 KNO₃

$$\log K_1 = 5.51 \quad \log K_2 = 4.67 \quad \log K_3 = 2.05$$

Sharff and Paris (67S): glass electrode at 25 °C in 0.5 NaNO₃

$$\log K_1 = 5.69 \quad \log K_2 = 4.67 \quad \log K_3 = 2.44$$

Pool and Sandberg (69Pa): potentiometry in DMSO at 25 °C and 0.1 KClO₄

$$\log \beta_1 = 7.0 \pm 0.1 \quad \log \beta_2 = 13.0 \pm 0.1 \quad \log \beta_3 = 17.63 \pm 0.08$$

Falqui (70F): polarography at 25 °C

$$\log K_1 = 5.84 \quad \log K_2 = 4.79 \quad \log K_3 = 2.09$$

Fridman and Danilova (71F): amalgam electrode at 25 °C and 2.0 (NaNO₃)

$$\log K_1 = 5.65 \quad \log \beta_2 = 10.0$$

Cryf and Van Poucke (73C): ion-selective at 25 °C and 1.0 KNO₃

$$\log K_1 = 5.68 \pm 0.2 \quad \log \beta_2 = 10.25 \pm 0.02 \quad \log \beta_3 = 12.26 \pm 0.06$$

Hall (76H): polarography at 25 °C in 0.5 KNO₃

$$\log \beta_2 = 10.3 \quad \log \beta_3 = 12.3 \quad \log \beta_{1-2} = 12.2$$

Evaluation of Selected Values

$$(R) \log K_1 = 5.57 + 0.06 \quad (45B, 67K) \quad t = 25 \text{ °C} \quad I = 1 \text{ KNO}_3$$

$$(R) \log K_2 = 4.63 \pm 0.04 \quad (45B, 67K) \quad t = 25 \text{ °C} \quad I = 1 \text{ KNO}_3$$

$$(R) \log K_3 = 2.05 \pm 0.01 \quad (45B, 67K) \quad t = 25 \text{ °C} \quad I = 1 \text{ KNO}_3$$

Enthalpy and Entropy Values

Spike and Parry (53S): calculated from stability constant

$$-\Delta H_1^\circ = 29.4 \quad \Delta H_{1-2}^\circ = 56.5$$

Davies et al. (54D): calorimetry at 25 °C in 0.1 KCl

$$-\Delta H_{1-2}^\circ = 55.6 \quad \Delta S_{1-2}^\circ = -7.1$$

$$-\Delta H_{1-3}^\circ = 82.4 \quad \Delta S_{1-3}^\circ = 64$$

Cotton and Harris (55C): calculated from stability constants at I = 0.15 and t = 0 - 49.1 °C

$$-\Delta H_1^\circ = 22.2 \pm 1.7 \quad \Delta S_1^\circ = 29 \pm 4$$

$$-\Delta H_2^\circ = 18.0 \pm 2 \quad \Delta S_2^\circ = 25 \pm 8$$

Bertsch et al. (58B): calculated from stability constants at I = 0 and t = 10-40 °C

$$-\Delta H_1^\circ = 25.9 \quad \Delta S_1^\circ = 12 - 17(10 - 40 \text{ °C})$$

$$-\Delta H_2^\circ = 31.4 \quad \Delta S_2^\circ = -21 - 17(10 - 40 \text{ °C})$$

Milyukov (62M): calorimetry at 27 °C 1 KNO₃

$$-\Delta H_1^\circ = 25.9 \quad -\Delta H_2^\circ = 25.9 \quad -\Delta H_3^\circ = 25.9$$

$$\Delta S_1^\circ = 21 \quad \Delta S_2^\circ = 0.2 \quad \Delta S_3^\circ = -47$$

Evaluation of selected values

Further investigation are needed.

Hg²⁺

Stability constants

Bjerrum (50B) Hg and glass electrodes at 25 °C in 1 KNO₃.

$$\log \beta_2 = 23.42$$

Morinaga (56M): polarography at 25 °C in 0.1 KNO₃.

$$\log \beta_2 = 23.18 \quad \log \beta_3 = 23.06$$

Watters and Mason (56W): polarography at 25 °C in 0.1 KNO₃.

$$\log K_1 = 14.3 \quad \log K_2 = 9.0 \quad \log \beta_{1-11} = 37.4$$

$$\log \beta_{1-12} = 28.6 \quad \log \beta_{1-23} = 42.3 \quad \log \beta_{1-22} = 33.0$$

Roe et al. (61R): polarography in 0.1 KNO₃ at 10 - 40 °C.

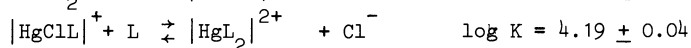
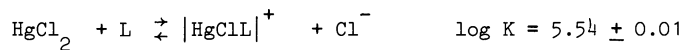
t °C	log β ₂	log β ₃
10	24.36 ± 0.04	24.1 ± 0.1
25	23.18 ± 0.02	23.09 ± 0.01
40	21.94 ± 0.01	21.74 ± 0.01

Bjerrum and Larsen (64B): glass electrode at 25 °C in 1 KNO₃.

$$\log \beta_{101} = 14.34 \quad \log \beta_{111} = 16.6$$

$$\log \beta_{102} = 23.44 \quad \log \beta_{122} = 34.5$$

Partridge et al. (66P): glass electrode at 25 °C and I = 0.

Evaluations of selected values

We conclude from these data that the complex $|\text{HgL}|^{2+}$ is formed with a constant of 14.3 ± 0.1 . All the authors found the complex $|\text{HgL}_2|^{2+}$ with an overall constant of 23.3 ± 0.1 . Other authors found some protonated complexes, e.g., Watters and Mason (56W), and Bjerrum and Larsen (64B), found $\text{HgH}_2\text{L}_2^{4+}$. However, the two values determined do not agree. Watters and Mason (56W) also found the hydroxo-complex that is not confirmed by the subsequent authors.

$$\text{T) } \log K_1 = 14.3 \pm 0.1 \quad (56W, 64B) \quad t = 25 \text{ °C, } I = 0.1 - 1 \text{ (KNO}_3\text{)}$$

$$\text{T) } \log \beta_2 = 23.3 \pm 0.1 \quad (50B, 56M, 61R, 64B) \quad t = 25 \text{ °C, } I = 0.1 - 1 \text{ (KNO}_3\text{)}.$$

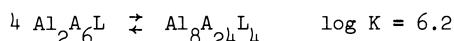
Enthalpy and entropy values

Roe et al. (61R): calculated from stability constants.

$$-\Delta H_{1-2}^{\circ} = 137.6 \pm 2.5 \quad \Delta S_{1-2}^{\circ} = -20.9 \pm 8.3$$

Evaluation of selected values

Further investigations are needed.

Al³⁺Bains and Bradley (62B): freezing point in benzene at $t = 5.4$ °C.

where HA = isopropyl alcohol and L = en

Evaluation of selected values

Further investigation are needed.

Tl⁺Stability constants

Job (28J): solubility at 16 °C in variable media.

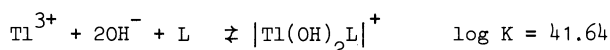
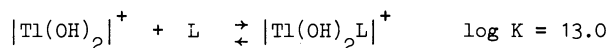
$$\log K_1 = 0.3$$

Job (28J): spectroscopy at 16 °C in variable media.

$$\log K_1 = 0.4$$

Evaluation of selected values

Further investigations are needed

Tl³⁺Stability constantsLobov et al. (67L): glass electrode at 25 °C in 2 (L - 2HNO₃) L = ethylenediamine.Evaluation of selected values

Further investigations are needed

Sn²⁺Stability constantsTsvetanov, et al. (74T): polarography on the system Sn²⁺ - en. Only the complex Sn(en₂)²⁺ was found

$$\log \beta_2 = 8.58 \pm 0.45$$

Evaluation of selected values

Further investigations are needed

Pb²⁺Stability constantsKeller and Eyke (61K): polarography at 25 °C in 0.1 KNO₃.

$$\log \beta_2 = 8.66$$

Komatsu (74K): polarography at 25 °C in 0.2 KCl.

$$\log \beta_2 = 8.44$$

Evaluation of selected values

$$(T) \log \beta_2 = 8.5 \pm 0.1 \quad (61K, 74K) \quad t = 25 \text{ °C}, \quad I = 0.1 - 0.2$$

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