790. *The Stability of the* $Zn(CN)_4^{2-}$ *Ion.*

By M. S. BLACKIE and V. GOLD.

The equilibrium constant for the reaction $Zn(CN)_4^{2-} \rightleftharpoons Zn^{2+} + 4CN^-$ at 25° has been re-determined by an e.m.f. method. The value found is $1{\cdot}9_1 \times 10^{-17}$ mole^4 l.$^{-4}$.

THE equilibrium constant for the reaction

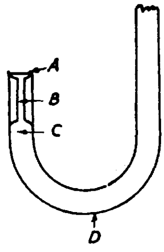
$$Zn(CN)_4^{2-} \rightleftharpoons Zn^{2+} + 4CN^- \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

was first determined electrometrically by Euler,[1] who obtained the value $1{\cdot}3 \times 10^{-17}$ mole^4 l.$^{-4}$. More recent determinations [2] have given values ranging from $2{\cdot}5 \times 10^{-13}$ to *ca.* 10^{-20}, the former extreme being a recent Russian result [3] and the latter the limit of a range of values obtained by Britton and Dodd [4] in 1932. Latimer's free-energy values [5] are consistent with a value of 1×10^{-17}. In view of the discrepancies, the determination has been repeated by the use of e.m.f. measurements, as in Euler's original work. One half-cell contained a zinc electrode in contact with a 0·01M-solution of zinc sulphate, and the other half-cell an identical electrode with a solution of zinc sulphate containing an excess of added potassium cyanide. For reasons of experimental convenience, the two half-cells were connected through a salt bridge specially designed to afford both easy assembly and the desirable [6] cylindrical symmetry of the junctions. The presence of liquid junctions in the cell nevertheless imposes certain limitations on the significance of the procedure.

Experimental.—The cell

$$\begin{array}{lcccc} Zn \mid ZnSO_4\ aq. & \vdots & KCl\ aq. & \vdots\ ZnSO_4 + & KCN\ aq. \mid Zn \\ c_1 = 0{\cdot}01\text{M} & & 3{\cdot}5\text{M} & c_2 = z\text{M} & 8z\text{M} \end{array}$$

was set up, electrodes of spectroscopically pure zinc being used. Other chemicals were analytical reagents. E.m.f.s were measured at 25·00° ± 0·05° on a Cambridge Vernier potentiometer.



A detail of the construction of the salt bridge and method of forming liquid junctions are shown in the Figure. The open end *A* of the salt bridge was below the level of liquid in the half-cell. The main part of the tube (*D*) was filled with 3·5M-potassium chloride set in 3% aqueous agar-agar. The portion *B*–*C* was filled with aqueous 3·5M-potassium chloride, and zinc solution (of the same composition as that in the half-cell) was then carefully added to fill the portion *A*–*B*. The liquid junction was thus formed as a kind of free-diffusion junction in the narrow part of the tube at *B*. The portion *A*–*C* was emptied and washed out on changing solutions in the half-cell.

DISCUSSION

The e.m.f. of the cell considered is given by

$$E = (\boldsymbol{RT}/2\boldsymbol{F}) \ln (a_2/a_1) + \Delta\pi_j$$

where a_1 and a_2 are the activities of zinc ions in the two half-cells and $\Delta\pi_j$ is the residual liquid-junction potential. In view of the low ionic concentrations in the half-cells, compared with that in the salt bridge, we shall assume that $\Delta\pi_j$ may be set equal to zero in the following calculation. We shall also assume that the single-ion activities a_1 and a_2 may be

---

[1] Euler, *Ber.*, 1903, **36**, 3400.

[2] " Stability Constants. Part II: Inorganic Ligands," Chem. Soc. Special Publ. No. 7 (1958).

[3] Stabrovskii, *Zhur. obshchei Khim.*, 1951, **21**, 1223.

[4] Britton and Dodd, *J.*, 1932, 1940.

[5] Latimer, " The Oxidation States of the Elements and their Potentials in Aqueous Solution," 2nd edn., Prentice-Hall Inc., New York, 1952.

[6] Guggenheim, *J. Amer. Chem. Soc.*, 1930, **52**, 1315.

equated to the mean activity of zinc sulphate, an assumption that is more justifiable at low than at high ionic strengths. The reference half-cell always contained 0·01M-zinc sulphate, the mean activity of which [7] is 0·00387M.

The following equilibria have been considered together with (1), in connection with the problem:

$$CN^- + H_2O \rightleftharpoons HCN + OH^- \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (2)$$

$$ZnOH^+ \rightleftharpoons Zn^{2+} + OH^- \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (3)$$

The equilibrium constant of (1), K_1, is the required quantity. The basicity constant of cyanide ion (in terms of activities), $K_2 = (HCN)(OH^-)/(CN^-)$, is identical with the ratio K_w/K_A where K_w is the ionic product of water and K_A the acid dissociation constant of hydrocyanic acid. K_2 was calculated from tables of standard Gibbs free energies of formation [8] to have the value $2{\cdot}434 \times 10^{-5}$. The formation of $ZnOH^+$ and reaction (3) will be neglected in the following two paragraphs. Their rôle is briefly considered thereafter.

The thermodynamic equilibrium constant for (1) is defined in terms of activities by

$$K_1 = (Zn^{2+})(CN^-)^4/(Zn(CN)_4^{2-})$$

It is convenient also to define the auxiliary function K_1''

$$K_1'' = (Zn^{2+})[CN^-]^4/[Zn(CN)_4^{2-}]$$

where square and round brackets signify concentrations and activities respectively. The ratio K_1/K_1'' is identical with the activity coefficient ratio $\gamma^4_{CN^-}/\gamma_{Zn(CN)_4^{2-}}$ which is unity in the range of applicability of the Debye–Hückel limiting law for 1 : 1- and 2 : 1-electrolytes.

Assuming this law for 1 : 1-electrolytes, we may replace the thermodynamic constant K_2 by the corresponding classical constant K_2', where $K_2/K_2' = \gamma_{OH^-}\gamma_{HCN}/\gamma_{CN^-}$. The concentrations of CN^- and $Zn(CN)_4^{2-}$ ions are calculated from the relations

$$[Zn(CN)_4^{2-}] = [Zn^{2+}]_{stoich.} - [Zn^{2+}]; \ [CN^-] = [CN^-]_{stoich.} - 4[Zn(CN_4^{2-}] - [HCN]$$

$$K_2' = [HCN]^2/[CN^-]$$

The activity of zinc ions, a_2, is obtained from the e.m.f. measurements on the basis of the assumptions stated in the first paragraph of the Discussion. Combining this activity with the concentration ratio $[CN^-]^4/[Zn(CN)_4^{2-}]$, we obtain K_1''. A summary of results and calculations is given in the Table.

Table of results.

$[Zn^{2+}]_{stoich.}$	$[CN^-]_{stoich.}$	E (v)	(Zn^{2+}) *	$[Zn(CN)_4]^{2-}$	$[CN^-]$	Ionic strength	$10^{17} K_1''$
10^{-2}	8×10^{-2}	0·3148	$8{\cdot}96 \times 10^{-14}$	10^{-2}	$3{\cdot}903 \times 10^{-2}$	10^{-1}	2·08
5×10^{-3}	4×10^{-2}	0·2882	$6{\cdot}98 \times 10^{-13}$	5×10^{-3}	$1{\cdot}932 \times 10^{-2}$	5×10^{-2}	1·94
10^{-3}	8×10^{-3}	0·2242	$1{\cdot}022 \times 10^{-10}$	10^{-3}	$3{\cdot}701 \times 10^{-3}$	10^{-2}	1·92
5×10^{-4}	4×10^{-3}	0·1958	$9{\cdot}49 \times 10^{-10}$	5×10^{-4}	$1{\cdot}792 \times 10^{-3}$	5×10^{-3}	1·91
10^{-4}	8×10^{-4}	0·1270	$1{\cdot}98 \times 10^{-7}$	$9{\cdot}93 \times 10^{-5}$	$3{\cdot}152 \times 10^{-4}$	10^{-3}	1·96 †
5×10^{-5}	4×10^{-4}	0·0951	$2{\cdot}33 \times 10^{-6}$	—	—	5×10^{-4}	—

* $(Zn^{2+}) = \dfrac{0{\cdot}00387}{\text{antilog }(2E/0{\cdot}05916)}$.

† Calculated by assuming $K_3'' = 4 \times 10^{-5}$. Neglecting association, we find $K_1'' = 1{\cdot}91 \times 10^{-17}$.

The presence of hydroxide ions in solution from the hydrolysis of cyanide raises the possibility of the formation of $ZnOH^+$ by the reverse of reaction (3). The classical equilibrium constant $K'_3 = [Zn^{2+}][OH^-]/[ZnOH^+]$ has been the subject of several investigations but its value is still in considerable doubt. Davies,[9] basing his conclusions on

---

[7] Cowperthwaite and La Mer, *J. Amer. Chem. Soc.*, 1931, **53**, 4333.

[8] " Selected values of Chemical Thermodynamic Properties " (N.B.S. Circular 500, U.S. Dept. of Commerce, Washington, D.C., 1952).

[9] Davies, *J.*, 1951, 1256.

experimental work by Owen and Gurry [10] and by Kolthoff and Kameda,[11] finds a value of 4×10^{-5}. Earlier investigations [2] had given much lower values, whereas one more recent study [12] gives the higher value $1{\cdot}6 \times 10^{-4}$. A much lower result (2×10^{-6}) has also recently been reported.[13]

In principle, the association can be entirely allowed for by solving the five simultaneous equations (which may also be expressed in different forms)

$$\begin{aligned}
[\mathrm{Zn^{2+}}]_{\mathrm{stoich.}} &= [\mathrm{Zn(CN)_4{}^{2-}}] + [\mathrm{Zn^{2+}}] + [\mathrm{ZnOH^-}] \\
[\mathrm{CN^-}]_{\mathrm{stoich.}} &= [\mathrm{CN^-}] + 4\,[\mathrm{Zn(CN)_4{}^{2-}}] + [\mathrm{HCN}] \\
[\mathrm{HCN}] &= [\mathrm{OH^-}] + [\mathrm{ZnOH^+}] \\
K_2' &= [\mathrm{OH^-}][\mathrm{HCN}]/[\mathrm{CN^-}] \\
K_3'' &= (\mathrm{Zn^{2+}})[\mathrm{OH^-}]/[\mathrm{ZnOH^+}]
\end{aligned}$$

for the relevant concentrations. Using this procedure we find that the concentration of $[\mathrm{ZnOH^+}]$ is entirely negligible except for the two most dilute solutions. For the penultimate solution, consideration of the association results in a small correction which is barely outside the limits of experimental accuracy of the value of K_1''. For the most dilute solution the effect of association is large and, in view of the uncertainty in the value of K_3, a reliable value of K_1'' cannot be calculated for this point.

It was pointed out at the beginning of the Discussion that K_1'' should not differ from K_1 in the range of applicability of the Debye–Hückel limiting law. Accordingly, it is expected that K_1'' should approach K_1 and constancy as the ionic strength decreases to zero. This trend towards constancy is found.

The fairly close agreement of our value with Euler's is largely fortuitous, since *inter alia* Euler did not consider hydrolysis of cyanide ion. Our procedure is subject to the uncertainty inherent in the assumption of complete elimination of liquid-junction potentials by the use of a salt bridge. However, it seems that the largest source of error in the calculated results lies in the assumed values for the activity coefficient of 0·01M-zinc sulphate and for the acid dissociation constant of hydrocyanic acid.

King's College, Strand, London, W.C.2. [*Received, April* 17*th*, 1959.]

---

[10] Owen and Gurry, *J. Amer. Chem. Soc.*, 1938, **60**, 3074.
[11] Kolthoff and Kameda, *J. Amer. Chem. Soc.*, 1931, **53**, 832.
[12] Brown and Cranston, *J.*, 1940, 578.
[13] Schwab and Polydoropoulos, *Z. phys. Chem.*, 1953, **274**, 234.