810. *The Stability of the* $Ni(CN)_6^{4-}$ *Ion.*

By M. S. Blackie and V. Gold.

The equilibrium constants for the reactions

$$Ni(CN)_6^{4-} + Cd^{2+} \rightleftharpoons Ni(CN)_4^{2-} + Cd(CN)_2\downarrow$$
$$Ni(CN)_6^{4-} + 2Zn^{2+} \rightleftharpoons Ni(CN)_2\downarrow + 2Zn(CN)_2\downarrow$$

have been determined by measurements of proton relaxation times in the supernatant solutions. A combination of the results with Latimer's values of standard Gibbs free energies of formation of the species involved leads to somewhat discrepant values for the free energy of formation of $Ni(CN)_6^{4-}$. The discrepancy is thought to arise from inconsistencies in Latimer's tables, since the tabulated values are incompatible with the chemical identities of the precipitates formed on adding cadmium ions to hexacyanonickelate(II) solution.

Nickel(II) ions in ammoniacal solutions are quantitatively converted into hexacyanonickelate(II) ions on addition of potassium cyanide so that the stoicheiometric ratio CN/Ni in solution is 6 or greater.[1] The reaction

$$Ni(CN)_4^{2-} + 2CN^- \longrightarrow Ni(CN)_6^{4-} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

---

[1] Blackie and Gold, preceding paper.

was found to be complete within the limits of detection by the nuclear magnetic resonance technique employed, so that it was impossible to estimate its equilibrium constant from the measurements. There was no evidence for the formation of $Ni(CN)_5^{3-}$ at any stage.

In the present work, information on the stability of the $Ni(CN)_6^{4-}$ ion has been obtained by adding to its solution metal ions with an affinity for cyanide comparable with that of nickel, in order to detach some of the cyanide groups from $Ni(CN)_6^{4-}$. Since the added metal ions, their cyanide complexes, and the nickel species formed in the reaction were all ineffective in catalysing proton relaxation, the proton relaxation times in the solutions were determined by the concentration of $Ni(CN)_6^{4-}$ which was therefore the only relaxing species present. In this way it was possible to deduce the concentration of $Ni(CN)_6^{4-}$ from proton relaxation times and hence to calculate equilibrium constants for the cyanide transfer reactions. The procedure is believed to be of wider applicability in inorganic co-ordination chemistry.

Experiments were carried out with four different diamagnetic (and non-relaxing) ions, *viz.*, Ag^+, Hg^{2+}, Zn^{2+}, and Cd^{2+}. With two of these (Ag^+ and Hg^{2+}) it was found that the addition of four equivalents per hexacyanonickelate(II) ion reduced the level of relaxing species below the limit of detection, so that the equilibrium constant could not be calculated. With zinc and cadmium ions, on the other hand, the reduced concentration of $Ni(CN)_6^{4-}$ ions could be determined and equilibrium constants were evaluated. The products of these reactions were identified by chemical tests. The measurements were performed on solutions of different ionic strengths and the conclusions are subject to the uncertainties arising from this cause.

Experimental.—The apparatus and general technique of measurement have been described in previous papers.[1, 2]

Aqueous solutions of $K_4Ni(CN)_6$ were prepared by dissolution of $Ni(CN)_2$ in an aqueous solution containing the stoicheiometrically required amount of potassium cyanide. Measurements were carried out on the supernatant solutions obtained on mixing this solution with the requisite amounts of aqueous solutions of the sulphates of zinc, cadmium, silver, or mercury(II), and water. The stoicheiometric molar concentrations of nickel(II) and the added metal sulphate contained in the suspensions obtained on mixing are denoted by a and b, respectively. The concentration of the ion $Ni(CN)_6^{4-}$ remaining in solution, $(a - x)$, was deduced from the measured proton relaxation time on the assumption that no other species contribute to the relaxation. The results are summarised in Tables 1 and 2.

TABLE 1. *Proton relaxation times for the system* $Ni(CN)_6^{4-} + Cd^{2+}$.

$[Ni^{II}]_{total} = [Cd^{2+}]_{total}$ (a) (mole l.$^{-1}$)	T_1 (sec.)	$T_1^{-1} - T_0^{-1}$ (sec.$^{-1}$)	$[Ni(CN)_6^{4-}]$ * $(a - x)$	x	K_c'
0·25	0·041	24·1	0·0324	0·2176	207
0·50	0·027	36·7	0·0495	0·4505	184
1·00	$0·019_5$	51·0	0·0686	0·9314	198
				Mean	196

* $[Ni(CN)_6^{4-}] = \Delta T^{-1}/742$.

TABLE 2. *Proton relaxation times for the system* $Ni(CN)_6^{4-} + 2Zn^{2+}$.

$[Ni^{II}]_{total} = \frac{1}{2}[Zn^{2+}]_{total}$ (a) (mole l.$^{-1}$)	T_1 (sec.)	$T_1^{-1} - T_0^{-1}$ (sec.$^{-1}$)	$[Ni(CN)_6^{4-}]$ $(a - x)$	$10^{-7}K_z'$
0·010	0·71	1·12	0·00151	7·3
0·050	0·72	1·10	0·00148	7·7
0·100	0·72	1·10	0·00148	7·7
0·500	0·71	1·12	0·00151	7·3
				Mean 7·5

DISCUSSION

The addition of two moles of zinc sulphate per mole of hexacyanonickelate(II) in solution produced a precipitate. The colourless supernatant solution proved to be

---

[2] Blackie, *Trans. Faraday Soc.*, in the press.

exceedingly dilute (in any solute) and it was therefore concluded that both zinc and nickel had been precipitated as cyanides according to the equation

$$\begin{array}{lllll} \mathrm{Ni(CN)_6^{4-}} & + \ \mathrm{2Zn^{2+}} \longrightarrow & \mathrm{Ni(CN)_2\downarrow} & + \ \mathrm{2Zn(CN)_2\downarrow} & \quad (2) \\ a - x & \ \ 2(a - x) & \ \ x & \ \ 2x & \end{array}$$

This deduction is supported by the constancy of K'_z, defined as $K'_z = 1/[4(a - x)^3]$. Of the various possible reactions between $\mathrm{Zn^{2+}}$ and $\mathrm{Ni(CN)_6^{4-}}$, (2) is the only one which has an equilibrium constant of this form.

The addition of one mole of cadmium sulphate per mole of hexacyanonickelate(II) in solution gave a white precipitate and a pale yellow supernatant solution. The precipitate was chemically identified as cadmium cyanide, free from nickel, and the supernatant solution contained nickel and a small amount of cadmium. The reaction is therefore

$$\begin{array}{lllll} \mathrm{Ni(CN)_6^{4-}} & + \ \mathrm{Cd^{2+}} \longrightarrow & \mathrm{Ni(CN)_4^{2-}} & + \ \mathrm{Cd(CN)_2\downarrow} & \quad (3) \\ a - x & \ \ a - x & \ \ x & \ \ x & \end{array}$$

in agreement with the observed constancy of K_c', defined as $K_c' = x/(a - x)^2$. Of the various conceivable reactions between $\mathrm{Cd^{2+}}$ and $\mathrm{Ni(CN)_6^{4-}}$ the only other reaction which has an equilibrium constant of this form is

$$\mathrm{Ni(CN)_6^{4-} + Cd^{2+} \longrightarrow Ni(CN)_2\downarrow + Cd(CN)_4^{2-}} \qquad (4)$$

and this alternative can be dismissed on the basis of the chemical tests. From the value of K_z', ΔG° for reaction (2) is $-10{\cdot}7$ kcal./mole. Similarly, K_c' leads to ΔG° for reaction (3) as $-3{\cdot}1$ kcal./mole.

It was hoped that a combination of K_z' and K_c' with the standard free energies of formation ($\Delta G^\circ{}_f$) of the other species involved in the reactions would lead to consistent values for $\Delta G^\circ{}_f$ of $\mathrm{Ni(CN)_6^{4-}}$, and hence to an approximate value for the stability constant of this ion. The following $\Delta G^\circ{}_f$ values (relating to the usual standard states) are taken from Latimer's tables:[3] $\mathrm{Zn^{2+}}$, $-35{\cdot}2$; $\mathrm{Zn(CN)_2}$ (s), 29; $\mathrm{Zn(CN)_4^{2-}}$, 100·4; $\mathrm{Cd^{2+}}$, $-18{\cdot}6$; $\mathrm{Cd(CN)_2}$ (s), 49·7; $\mathrm{Cd(CN)_4^{2-}}$, 111; $\mathrm{Ni^{2+}}$, $-11{\cdot}5$; $\mathrm{Ni(CN)_2}$ (s), 37?; $\mathrm{Ni(CN_4)^{2-}}$, 117·1 kcal./mole. From the zinc equilibrium, $\Delta G^\circ{}_f$ for $\mathrm{Ni(CN)_6^{4-}}$ is then given by $37(?) + 58 + 70{\cdot}4 + 10{\cdot}7 = 176{\cdot}1$ kcal./mole, a value which is subject to the reservation as to the value for $\mathrm{Ni(CN)_2}$ (s), as indicated by a question mark in Latimer's book. The analogous calculation from the cadmium data is

$$\Delta G^\circ{}_f = 49{\cdot}7 + 117{\cdot}1 + 18{\cdot}6 + 3{\cdot}1 = 188{\cdot}5 \text{ kcal./mole}$$

The values obtained are unsatisfactory in two respects:

(i) The discrepancy of $\sim$12 kcal. between the two results if exceedingly high, implying an uncertainty in the stability constant of $\mathrm{Ni(CN)_6^{4-}}$ of about 10^{10}. The values for the equilibrium constant of the reaction

$$\mathrm{Ni(CN)_6^{4-} \rightleftharpoons Ni^{2+} + 6CN^-}$$

are (from data for zinc) $10^{-37{\cdot}6}$ and (from data for cadmium) $10^{-27{\cdot}5}$. (A recent spectrophotometric determination[4] of this constant in the presence of 5M-potassium acetate or 10M-potassium nitrite gives a value of $\sim 10^{-26}$, but we are unable to follow the procedure by which this figure was obtained.)

(ii) Both of the values imply that the disproportionation reaction

$$\mathrm{2Ni(CN)_4^{2-} \longrightarrow Ni(CN)_2\downarrow + Ni(CN)_6^{4-}}$$

should occur spontaneously in tetracyanonickelate(II) solutions of unit activity, and this conflicts with experience.

---

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

[4] Kišová and Čuprová, *Chem. Listy*, 1958, **52**, 1422; *Coll. Czech. Chem. Comm.*, 1959, **24**, 862.

These contradictions led us to examine Latimer's values in relation to those of our observations which were entirely independent of the relaxation time measurements. This course seemed desirable in view of the novelty of the present application of the technique. So we used Latimer's free energies of formation to calculate the free energies of formation of all possible sets of products obtained from ($2Zn^{2+} + Ni^{2+} + 6CN^-$) and from ($Cd^{2+} + Ni^{2+} + 6CN^-$) to see whether the products with the supposedly lowest free energy of formation were in fact those observed in the two precipitation reactions. For the experiments with zinc the prediction from the free-energy values accords with experiment. For the cadmium experiments, the standard free energies of formation for three possible sets of products are:

$Ni(CN)_4^{2-} + Cd(CN)_2(s)$, 166·8 kcal./mole
$Ni(CN)_4^{2-} + \frac{1}{2} Cd^{2+} + \frac{1}{2} Cd(CN)_4^{2-}$, 154·0 kcal./mole.
$Ni(CN)_2(s) + Cd(CN)_4^{2-}$, 148(?) kcal./mole

The first line represents the products actually observed, but corresponds to the substance with the supposedly highest free energy of formation. The difficulty cannot simply be resolved by revision of the doubtful value for $Ni(CN)_2(s)$, which affects the third line only, but seems to indicate more far-reaching inconsistencies.

We thank Professor D. W. G. Style for his interest in this work.

KING'S COLLEGE, STRAND, LONDON, W.C.2. [*Received, April* 17*th*, 1959.]