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CRITICAL SURVEY OF STABILITY CONSTANTS OF CYANO COMPLEXES†

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Critical survey of stability constants of cyano complexes

Abstract. All the published stability constants of cyanocomplexes of metal ions, and the acidic dissociation constants of hydrogen cyanide, and those of the protonated metal complexes are critically surveyed. Unfortunately, a great fraction of data is unreliable and only a few thermodynamic data could be classified to the category of recommended values. The reasons of this situation are thorougly treated, and promising research areas are indicated.

1. INTRODUCTION

Cyanide ion forms complexes under different conditions with almost all of the metal ions. An enormous number of complexes have been prepared and investigated by the whole armoury of structural chemistry, but thermodynamic studies concerning the stability of complex ions in solution are rather scarce. The corresponding tables in the volumes of Stability Constants of Metal Complexes show that most of the information is of a qualitative nature, and a considerable proportion of the data both on the existence and on the stability of the complex species is controversial. The main reason for this disappointing situation is that in only a relatively few investigations were all the requirements necessary to obtain reliable stability constants fulfilled (77 B). In addition, the thermodynamic study of cyano complexes involves some further difficulties:

   i/   the volatility of hydrogen cyanide;
   ii/ redox reactions of cyanide leading to the formation of cyanogen and cyanate;
   iii/ photochemical reactions of some of the cyano complexes;
   iv/ redox reactions of some cyano complexes.

In the following, the only systems treated are those for which quantitative data are available. In accordance with the general policy of this series, only published values are considered, and data quoted occasionally as "unpublished results" or as "personal communications" have been deliberately omitted. Problems requiring elucidation will sometimes be mentioned.

Cyanide is an ambidentate ligand, but in the mononuclear complexes metal-carbon bond is almost always involved. Although there is convincing evidence that under certain conditions N-bonded cyano complexes are formed, no rigorous equilibrium study is available for such species. However, the nitrogen atom is directly involved in the formation of polynuclear complexes. It is almost certain that in the protonated species the MCNH bond sequence should be considered.

Concerning the details of the general chemistry of cyano complexes, the reader should consult the excellent monograph by Sharpe (76 S).

2. ACIDIC DISSOCIATION CONSTANTS OF HYDROGEN CYANIDE

As is clear from the data summarized in Table 1 , there is a substantial agreement among the published dissociation constants considering the differences in experimental conditions apart from two early values. This is rather surprising since the methods applied were sometimes awkward, indeed; for example, the hydrolysis of sodium and potassium cyanide was followed by measuring the amount of HCN removed from the solution by bubbling air "very slowly" for 30 minutes. M stands for mol dm^{-3} hereafter.

Table 1. Acidic dissociation constant of hydrogen cyanide.

Method	t/°C	Medium	-log(K/M)	Ref.
Ag	17–19	var	7.58	00 M
con	18	dil	8.89	00 W
col	r.t.	dil	9.14	20 K
p(HCN)	5–35	KCN var	$K_b(CN)^-=K \cdot K_w$.	25 H
	5		-4.75	
	18		-4.64	
	25		-4.60	
	35		-4.52	
pH	14 (?)	var	9.60	31 B
col	14 (?)	var	9.35	31 B
p(HCN)	25	var	9.31	31 Ba
gl	18	var	9.32	32 B
gl	20	0.1 NaNO$_3$	9.14	57 A
sp	25	0 corr	9.22± 0.02	59 A
gl	10	0	9.63	62 I
	15	0 corr	9.49	
	20		9.36	
	25		9.21	
	30		9.11	
	35		8.99	
	40		8.88	
	45		8.78	
pol	30	2 NaNO$_3$	8.52	56 N
gl	20–33	0 corr	9.36	
	26		9.19	
	33		9.05	66 B
gl	25	3 NaClO$_4$	9.48	71 P
gl, CN$^-$	25	0,1–5	9.05(I=0.1)	82 G
			8.88(I=1.0)	
			8.81(I=3.0)	
			8.78(I=5.0)	

Since the experimental conditions are well defined only in case of the experiments performed after 1957 (57A, 59A, 62I, 56N, 66B, 71P, 82G), only the data from these papers are treated in detail.

There is a perfect agreement between three independent studies (59A, 62I, 66B) referring to I = 0 obtained either by extrapolation or by calculation using the extended Debye-Hückel equation.

The recommended value at 25°C is

$$pK = 9.21 \pm 0.02$$

Unfortunately neither of the results referring to higher ionic strength were obtained under the same conditions, but there is a good agreement when differences in the conditions (temperature and medium) are taken into consideration. Therefore the surveyor thinks that although the following values are *tentative* they deserve significant credit.

t/°C	Medium	- log (K/M)	Ref.
20	0.1 NaNO$_3$	9.14 ± 0.02	57 A
30	2.0 NaNO$_3$	8.52 ± 0.03	56 N
25	0.1 NaClO$_4$	9.06 ± 0.03	82 G
25	1.0 NaClO$_4$	8.88 ± 0.03	82 G
25	3.0 NaClO$_4$	8.81 ± 0.03	82 G
25	5.0 NaClO$_4$	8.78 ± 0.03	82 G

There are some data referring to the dissociation enthalpy and entropy of hydrogen cyanide. In fact the first thermodynamic result concerning HCN was obtained by direct calorimetry by Thomsen in his classical studies in 1882. The available data are summarized in Table 2. The results reported Izatt et al. (62I) were obtained under well defined conditions, and are the most exact and reliable presently available.

Table 2. Dissociation enthalpy and entropy of hydrogen cyanide.

Method	$t/^oC$	Medium	ΔH kJ mol^{-1}	ΔS JK^{-1} mol^{-1}	Ref.
cal	18	dil	-45.86	$-$	00T
cal	8	0	-47.3 ± 1	16 ± 1	62T
		0 corr			
cal	25	0	-43.5 ± 1	31 ± 1	62I
		0 corr			
temp. coef.	10–45	0	-47.1 ± 5	23 ± 5	62I [★]
temp. coef.	20–33	0 corr	-41.42 (26 ^oC)	36.5 (26 ^oC)	66B
cal	10	0 corr	-47.4 ± 0.2	17 ± 0.8	70C
cal	25	0 corr	-43.6 ± 0.2	30 ± 0.6	70C
cal	40	0 corr	-40.0 ± 0.2	43 ± 0.5	70C

[★] Calculated by the surveyor

Although surprisingly good dissociation entalphy and entropy values were calculated by Boughton and Keller from the temperature dependence of the dissociation constant, the too narrow temperature range makes the calculation unreliable

3. THERMODYNAMIC DATA FOR CYANO COMPLEXES OF METAL IONS IN SOLUTION

Gadolinium. Gd^{3+} is the only rare earth metal ion for which the stability of the cyano complex has been studied (71D). The effect of cyanide on the distribution of Gd^{3+} between an aqueous 0.5 M Li (ClO_4, CN) and a benzene phase applying dibenzoylmethane as chelating agent was studied in the 7<pH<11 range at an unspecified temperature. Using pK = 9.3 for HCN the following equilibrium constants have been calculated:

$$Gd(OH)_2^+ + CN^- \rightleftharpoons Gd(OH)_2 \, CN \qquad\qquad \log(K/M^{-1}) = 3.0$$
$$GdOH^{2+} + CN^- \rightleftharpoons Gd(OH)(CN)^+ \qquad\qquad \log(K/M^{-1}) = 3.8$$
$$Gd^{3+} \quad\; + CN^- \rightleftharpoons GdCN^{2+} \qquad\qquad\quad \log(K/M^{-1}) = 3.6$$

The relative values of the three stability constants are unexpected, and any discussion is premature until the experiments are repeated. The rather weak cyano complexes of rare earth metal ions obviously deserve more attention.

Vanadium. The only quantitative information available is the formation enthalpy of $V(CN)_6^{4-}$ from V^{2+} and CN^- obtained by direct calorimetry (64G).[★] The following critical remarks are equally valid to other enthalpy values determined by the authors. The ratio of KCN to VSO_4 was 160, and the total concentration of KCN 1.0 M, which ensured that the coordination sphere was saturated with cyanide ions. Nevertheless, the value cannot be unambiguously assigned to this species because of the possibility of aerial oxidation which could occur, particularly with $V(CN)_6^{4-}$, $Cr(CN)_6^{4-}$ and $Co(CN)_5^{3-}$. Furthermore, ion-pair formation between the cyano complex and potassium ion was not considered at all, and a correction was only suggested for ion-pair formation between the matal ions (V^{2+}, Cr^{2+}, CO^{2+}) and sulphate ion. In case of the vanadium complex the effect of hydrolysis was experimentally corrected. The error given is always less that 1 %, but this is evidently over-optimistic, and is in fact only a measure of the reproducibility. Therefore the values given should be regarded only as an approximate one

$$V(CN)_6^{4-} ; \Delta H = -197 \text{ kJ mol}^{-1}, I = 1.0 \text{ M (KCN)}, t = 25.4 \, ^oC.$$
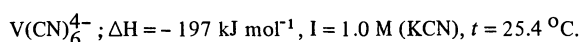
Chromium. There are many equilibrium data referring to different types of reaction involving Cr(II) and Cr(III) cyano complexes but very few, if any, can be rigorously regarded as reliable. This is mainly due to the extreme difficulties in the experiments, resulting in conflicting values on the one hand and lack of reproduction of the work on the other hand.

[★] For the sake of simplicity of expressions [ ] is used to indicate molarities of the reacting species only.

Cr(II). The equilibrium constant of the reaction

$$Cr(CN)_5H_2O^{3-} + CN^- \rightleftharpoons Cr(CN)_6^{4-} + H_2O$$
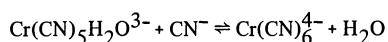
has been determined (70 D) from kinetic data on the effect of cyanide ions on the rate of the oxidation of chromium (II) to chromium (III) with hydrogen peroxide. Results obtained spectrophotometrically (227, 264, 327 nm, $4.10^{-5} < [Cr(II)]/M < 10^{-3}$, $0.01 < [NaCN] < 1.0$, $[NaCN] + [NaClO_4] = 1.0M$, $t = 25\ ^{\circ}C$ have been evaluated to give

$$K = (9.95 \pm 0.03)\ M^{-1}$$

According to the authors the error of the kinetic experiments is about 5 %, so that the uncertainty of the equilibrium constant seems to be about twenty times that of the quoted datum.

The formation enthalpy of $Cr(CN)_6^{4-}$ from $Cr^{2+} + CN^-$ has been determined by direct calorimetry (64G):

$$\Delta H = -264\ kJ\ mol^{-1},\ I = 1.0\ M\ (KCN),\ t = 25.4\ ^{\circ}C.$$

The criticisms made earlier are valid here.

Cr(III). The inertness of chromium(III) complexes made possible an estimate of a value for the isomerization of the monocyanochromium(III) complex. Birk and Espenson (68 B) have thoroughly studied the kinetics and mechanism of the oxidation of $Cr(H_2O)_6^{2+}$ by different cyano complexes of Cr(III) and Co(III). To explain the results, not only was an isomerization step assumed, but a lower limit of the quotient.

$$K = \frac{[Cr\ CN^{2+}]}{[CrNC^{2+}]}$$

could be estimated. At $I = 1\ M\ (HClO_4 + NaClO_4)$, $t = 25\ ^{\circ}C$, $K \leq 21$.

Frank and Anson have made a voltammetric study of the complexes and determined the value (72 F) at $I = 1.0\ M\ (NaClO_4)$, $22\ ^{\circ}C$,

$$K = 208 \pm 5.$$

The hydrogen ion dependence of the rate lead to a rough value for the protonation constant of the N-bonded species (68 Ba):

$$K = \frac{[CrNCH^{3+}]}{[CrNC^{2+}]\ [H^+]}$$

At $I = 1.0\ M\ (HClO_4 + LiClO_4)$ $t = 25\ ^{\circ}C$, $K = (0.94 \pm 0.13)\ M^{-1}$. A much bigger protonation constant has been obtained from the pH dependence of the voltammetric peak potential of $CrNC^{2+}$ (72F):

$$K = 18.7\ M^{-1}\ (t = 25\ ^{\circ}C,\ I = 1.0\ M\ (NaClO_4 + HClO_4)\ )$$

At $2\ ^{\circ}C$, the value has found to be 28.6 No error is given by the authors, but it follows from the data that it is less than 10 %. Evidently this situation does not permit a critical evaluation.

The protonation constants of some C-bonded species have been determined by kinetic and spectrophotometric studies (69 W, 69 Wa, 71 W). The kinetics of the aquation reaction of species prepared by partial aquation of $Cr(CN)_6^{3-}$ and the ion exchange chromatographic fractionation of the reaction mixture have been followed spectrophotometrically. The values listed below appear reliable, although the uncertainities given by the authors seem to be too optimistic.

Reaction:
$$Cr(H_2O)_5CN^{2+} + H^+ \rightleftharpoons Cr(H_2O)_5CNH^{3+}$$
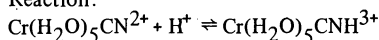
Method: dependence of the rate of the aquation reaction on hydrogen ion concentration by spectrophotometric measurements, at 525 and 240 nm, $I = 2.0\ M(HClO_4 + NaClO_4)$ (69W).

$t/^{\circ}C$	25	35	40
K/M^{-1}	0.185 ± 0.006	0.25 ± 0.02	0.25 ± 0.05

Because the change of the observed absorbancy in a kinetic run was as small as 0.2, and because of the absolute value of the stability constants determined, the real errors are probably much bigger than those quoted.

Reaction:

$$cis- Cr(H_2O)_4(CN)_2^+ + H^+ \rightleftharpoons cis-Cr(H_2O)_4(CN)(CNH)^{2+}$$
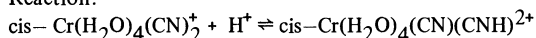
Method: dependence of the rate of aquation on the hydrogen ion concentration, and the measurement of the spectral changes on protonation. ($\lambda = 447$ nm, I = 2.0 M ($HClO_4$+$NaClO_4$))

		$t/^\circ C$		
Method		15	25	35
kin	K/M^{-1}	0.19 ± 0.02	0.21 ± 0.03	0.26 ± 0.3
sp	K/M^{-1}	0.55 ± 0.20	0.55 ± 0.20	0.7 ± 0.3

A comparison of the constants obtained by the two different methods permits a more meaningful estimate of the uncertainty. The comparison of the protonation constants of the mono and dicyanospecies suggests that for the latter the larger values are more likely. (On a statistical basis, the latter should be about twice as large as the former.) Accordingly, the protonation constant of the tricyano-complex is still larger.
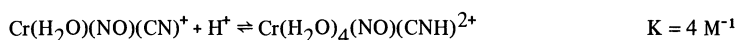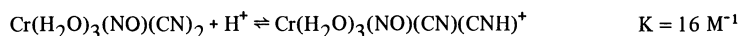
Reaction:

$$1, 2, 3-Cr(H_2O)_3(CN)_3 + H^+ \rightleftharpoons 1,2,3-Cr(H_2O)_3(CN)_2(CNH)^+$$
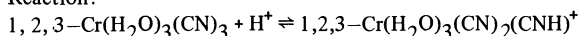
The equilibrium constant was obtained by spectrophotometric experiments under the same conditions (71W). The value obtained at $25^\circ C$ was

$$K = (1.1 \pm 0.4) M^{-1}$$

The protonation constants of two mixed ligand complexes have also been determined. Burgess et al. (68Bc) followed the kinetics of the aquation of cyanonitrosylchromium(III) complexes by *esr* measurements and at $(27.3 \pm 0.3)^\circ C$ and I = 1.7 M ($NaClO_4$ + $HClO_4$) evaluated the equilibrium constants of the following two reactions:

$$Cr(H_2O)_3(NO)(CN)_2 + H^+ \rightleftharpoons Cr(H_2O)_3(NO)(CN)(CNH)^+ \qquad K = 16 \ M^{-1}$$

$$Cr(H_2O)(NO)(CN)^+ + H^+ \rightleftharpoons Cr(H_2O)_4(NO)(CNH)^{2+} \qquad K = 4 \ M^{-1}$$

The authors did not make any remarks on the uncertainity and regard their values as approximate ones. Unfortunately the experimental data are only given graphically, but the spread of the experimental points suggests an error of 20 % in the latter constant.

Riccieri and Zinato (80R) determined the protonation of $Cr(NH_3)_5CN^{2+}$ by studying the pH dependence of the rate of aquation. At $25^\circ C$ and I = 2 M ($NaClO_4$)

$$K = \frac{[Cr(NH_3)CNH^{2+}]}{[Cr(NH^3)_5CN^{2+}][H^+]} = 0.28 \ M^{-1}$$

The value increases with decrease of temperature and decreases with decreasing ionic strength. This value is tentative until corroborated by an independent study.

No reliable information is available on the overall stability of $Cr(CN)_6^{3-}$. The equilibrium constant of the reaction

$$Cr(CN)_6^{3-} + 3 H^+ + 3H_2O \rightleftharpoons Cr(OH)_3 + 6HCN$$
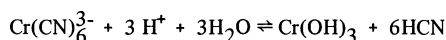
was estimated based from analytical data to be greater than $10^8 M^3$ (I = ? t = ?). Taking into consideration the solubility products of $Cr(OH)_3$, the acidic dissociation constant of HCN, and K_w, it was estimated that $\beta_6 < 10^{35} \ M^{-6}$ (69Q).

The redox potential of the reaction

$$Cr(CH)_6^{4-} \longrightarrow Cr(CN)_6^{3-} + e^-$$

has been determined polarographically by Hume and Kolthoff (43H). The value in 1.0 M KCN at $(25 \pm 0.04)^\circ C$, at a total concentration of chromium 0.001 M has been found to be -1.44 V, which indicates that the overall stability constant of the hexacyanochromate (III) is larger than that of the hexacyanochromate(II) by 12 orders of magnitude.

Polynuclear cyano complexes of chromium (III). Kinetic and spectral effects of Hg^{2+} on $CrCH^{2+}$ unambiguously indicate an interaction leading to new species.
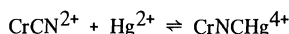
The equilibrium constant of the reaction

$$CrCN^{2+} + Hg^{2+} \rightleftharpoons CrCNHg^{4+}$$
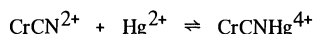
has been determined spectrophotometrically at $25^{\circ}C$, $I = 2.0$ M $(ClO_4) = 1.61$ M, sum of $(H^+, Li^+) = 1.00$ M, sum of concentrations of divalent ions $(CrCN^{2+}, Ba^{2+}, Hg^{2+}) = 0.333$ M (71E)

$$K = 26 \pm 3 \text{ M}^{-1}.$$

The isomeric species, in which the bonding is CrNCHg, is much more stable. The equilibrium constant of the reaction

$$CrCN^{2+} + Hg^{2+} \rightleftharpoons CrNCHg^{4+}$$

could not be measured spectrophotometrically. At $I = 1$ M, $t = 25^{\circ}C$ there is no deviation from the Beer's law when $[CrCN^{2+}] = [Hg^{2+}] = 0.0033$ M, indicating that $K \geq 10^5$ M^{-1} (68B). Potentiometric experiments (Hg electrode (72F), resulted in the following value at $I = 1$ M $(HClO_4 + NaClO_4)$, $t = 22\ ^{\circ}C$

$$K = (3 \pm 0.7) \times 10^7 \text{ M}^{-1}.$$

The stability of a trinuclear species
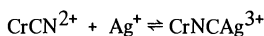
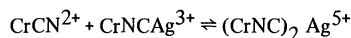$$CrCN^{2+} + CrNCHg^{4+} \rightleftharpoons (CrNC)_2Hg^{6+}$$
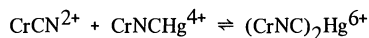
could also be determined. The value, under the same conditions, is

$$K = (4 \pm 2) \times 10^7 \text{ M}^{-1}.$$

Frank and Anson (72F) have used potentiometric titration (Ag electrode) under the same conditions to determine the stability constants of the analogous silver complexes and obtained the following values:

$$CrCN^{2+} + Ag^+ \rightleftharpoons CrNCAg^{3+}$$
$$K = (5 \pm 2) \times 10^5 \text{ M}^{-1}$$
$$CrCN^{2+} + CrNCAg^{3+} \rightleftharpoons (CrNC)_2 Ag^{5+}$$
$$K = (11 \pm 10) \times 10^4 \text{ M}^{-1}.$$

Molybdenum. Until recently no information was available on the stability constant of cyano complexes of molybdenum in any oxidation states. However, the study of the kinetics of the photoaquation of $Mo(CN)_8^{4-}$ by spectrophotometry and potentiometry (using CN^- selective electrode) made possible to estimate K_8 (87G). At 25 $^{\circ}C$, $I = 1$ M $(NaClO_4)$

$$K_8 = \frac{[Mo(CN)_8^{-4}]}{[Mo(CN)_7^{3-}] [CN^-]} = (1.2 \pm 0.1) \times 10^7 \text{ M}.$$

This value is tentative until corroborated by an independent study.

The overall stability constants of the octacyanomolybdate (IV) and (V) probably exceed those of the hexacyanoferrate (II) and (III). Although it is certain that these anionic species form ion-pairs or binuclear complexes with a number of cations, the available data do not permit any critical evaluation. Some of the data appear rather unexpected, and there is no explanation at present, for some of the results reported.

It seems certain that $Mo(CN)_8^{4-}$ has a very small tendency to take up hydrogen ions (73K).

According to the conductivity measurements of Ferranti and Indelli (74F) the stability constant of the ion-pair $KMo(CN)_8^{3-}$ at $25^{\circ}C$, in the concentration range $8 \times 10^{-5} - 1.5 \times 10^{-3}$ M $K_4Mo(CN)_8$ varies between 122 and 57 M^{-1}. The stability constant of the analogous $(Me_4M)Mo(CN)_8^{3-}$ and $(Et_4N)Mo(CN)_8^{3-}$ under the same conditions is a little higher (313 ± 5 and 200 ± 5 M^{-1}, resp.) These values appear reliable, but can be regarded at present only as tentative.

Numerical data for the stability constants of the species $FeMo(CN)_8^-$ (61M, 73M), $CrMo(CN)_8^-$ (61Ma), $UO_2Mo(CN)_8^{2-}$ (71J) and $UO_2Mo(CN)_4(OH)_3H_2O^+$ (69K) have been published. It is worth mentioning that Cr(III) reacts with $Mo(CN)_8^{4-}$ slowly, indicating the formation of a binuclear complex. However, even this result is not unambiguous since Cr(III) was used as its chloride, and it is possible that the results are to be explained by the slow dissociation of the chloro complexes and not by the slow formation of the $CrMo(CN)_8^-$ species.

Tungsten. Even less information is available on the stability of cyano complexes of tungsten. It seems likely, but needs confirmation, that $W(CN)_8^{3-}$ has a greater tendency for protonation than $W(CN)_8^{4-}$. The following dissociation constants have been determined (71S) by pH-metric titration, at $20^\circ C$, with slightly varying ionic strengths (0.1 M):

$$K_{a4} = \frac{[W(CN)_8^{4-}]\,[H^+]}{[HW(CN)_8^{3-}]} = (2.5 \pm 0.8) \times 10^{-2}\ M$$

$$K_{a3} = \frac{[HW(CN)_8^{3-}]\,[H^+]}{[H_2W(CN)_8^{2-}]} = (2 \pm 2) \times 10^{-2}\ M$$

$$K_{a2} = \frac{[H_2W(CN)_8^{2-}]\,[H^+]}{[H_3W(CN)_8^-]} = (4.5 \pm 1.5) \times 10^{-3}\ M$$

Iron. There are no data for the constants of the stepwise formation equilibria of iron(II) and iron(III) complexes, except for the coordination of the sixth cyanide to iron(II). The behaviour of all transition metal cyano complexes seems to indicate that each of the successive formation constants $(K_1,...K_{N-1})$ are much less than $\sqrt[N]{\beta_N}$.

$$K_6 = \frac{[Fe(CN)_6^{4-}]}{[Fe(CN)_5H_2O^{3-}]\,[CN^-]}$$

has been obtained by kinetic experiments (by measuring the rate of the forward and the reverse reaction) and by spectrophotometric determination of the equilibrium concentration of the aquapentacyanoferrate(II) complex. Emschwiller and Legros (55E) found that at $20^\circ C$, I = 0.2, pH 7.73 there is an excellent agreement between the values obtained from kinetic and equilibrium measurements:

$$K_6 = (2 \pm 0.03) \times 10^8\ M^{-1}.$$

A more detailed study by Legros (64L) resulted in much worse agreement, and indicated a strong dependence of the value on the concentration of the complexes and pH of the solution. James and Murray (75J) obtained the following value by kinetic measurements at $25^\circ C$, I = 1.0 $NaClO_4$ and much smaller complex concentration (10^{-4} M):

$$K_6 = 1.2 \times 10^{10}\ M^{-1}$$

The authors did not give any uncertainty and the procedure by which they obtained this value is not entirely clear.

Recently a much smaller value $(5.2 \pm 1.5) \times 10^7\ M^{-1}$ was determined by the study of kinetics of the photochemical aquation of $Fe(CN)_6^{4-}$ at $25\ ^\circ C$, I = 1 M (83G). This value is regarded as *tentative* until it is confirmed by an independent study.

Approximate values of the cumulative stability constants of $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$ can be estimated from the calorimetrically determined enthalpy and entropy values. For the enthalpies of the formation of these complexes the following values are available:

$t/^\circ C$	I/M	$\Delta H(Fe(CN)_6^{4-})$	$\Delta H(Fe(CN)_6^{3-})$	Ref.
		(kJ mol^{-1})		
25.4	1.0(KCN)	-308.4	-294.5	65G
25.0	($\longrightarrow$ 0)	-358.9	-293.5	65W

Guzzetta and Hadley obtained both values directly, while Watt et al. determined the enthalpy of oxidation of Fe^{3+} and $Fe(CN)_6^{4-}$ by permanganate and evaluated ΔH for the iron(III) complex using the directly obtained ΔH value for the iron(II) complex. The values obtained by Watt et al. appear reliable indeed. It is not clear, however, that the extrapolation to zero ionic strength can completely eliminate the effect of the ion-pair formation between K^+ and the hexacyanoferrate(II) and (III) complexes. It is interesting that the difference between the values obtained in the two studies is larger in case of the hexacyanoferrate(II) complex. This ion

forms a much more stable ion pair with potassium ion than does the iron(III) complex. Guzzetta and Hadley determined the values in 1 M KCN solution and the effect of ion-pair formation is evidently larger in these circumstances.

The entropies were determined by several calorimetric studies, or by using the standard redox potential of the $Fe(CN)_6^{4-}$ / $Fe(CN)_6^{3-}$ couple (see later). Apparently the best values have been evaluated by Busey (65B) and the thermodynamic data are as follows:

	$\Delta H^{\ominus}$	$\Delta H^{\ominus}$	$\Delta G^{\ominus}$	$\log (\dfrac{\beta_6}{M^{-6}})$
	kJ mol^{-1}	J mol^{-1}K^{-1}	kJ mol^{-1}	
$Fe^{3+}{}_{(aq)}+6CN^-{}_{(aq)} = Fe(CN)_6^{3-}{}_{(aq)}$	-293.5	-143.5	-250.6	43.9
$Fe^{2+}{}_{(aq)}+6CN^-{}_{(aq)} = Ft(CN)_6^{4-}{}_{(aq)}$	-358.4	-526.8	-210.5	36.9

Taking all the uncertainties into consideration, the probable error of the absolute values of both overall stability constants is less than one logarithmic unit, but the ratio of the two products is much more exact. This follows from the fact that the standard redox potential of the hexacyanoferrate(III)-hexacyanoferrate(II) couple is fairly precisely known.

According to the most careful measurements of Kolthoff and Tomsicek (35K) the values of the standard redox potential at zero ionic strength is (-0.356 ± 0.001) V. Although the more recent value given by Rock (66R) is slightly different (-0.3704 ± 0.0005) V, and he minimized the effect of the liquid junction potential by using the $Pb(Hg)$ / $Pb_2Fe(CN)_{6(s)}$ $Fe(CN)_6^{4-}$ electrode, the fact that Rock did not take into account the formation of the $KFe(CN)_6^{3-}$ and $KFe(CN)_6^{2-}$, ion-pairs places greater reliance on the value found by Kolthoff and Tomsicek. The measurements of Jordan and Ewing (62J) are in complete agreement with the determinations by Kolthoff and Tomsicek.

There are many studies referring to the formation of ion pairs between the hexacyanoferrate(II)–(III) complexes and cations. Most of the data were obtained by careful conductivity measurements and there are no great deviations among the data obtained by different authors. More recently a number of contants were obtained by using ion selective electrodes.

The protonation of hexacyanoferrate(II) and hexacyanoferrate(II) complexes was carefully studied by pH metric titration by Jordan and Ewing (62J). The acidity constants of the protonated hexacyanoferrate(III) species are larger than 0.1 M, but the uptake of one and two protons by the hexacyanoferrate(II) ion could be quantitatively followed

$$K_{a3} = \frac{[HFe(CN)_6^{3-}]\,[H^+]}{[H_2Fe(CN)_6^{2-}]} = (6 \pm 2) \times 10^{-3} \text{ M}$$

$$K_{a4} = \frac{[Fe(CN)_6^{4-}]\,[H^+]}{[HFe(CN)_6^{3-}]} = (6.7 \pm 0.3) \times 10^{-5} \text{ M}.$$

These values were obtained by extrapolating to infinite dilution. Both dissociation enthalpies were found to be zero. Therefore

$$- RT \ln K_{a4} = \Delta G_4^{\ominus} = - T \Delta S_4^{\ominus} = (23.85 \pm 0.09) \text{ kJ mol}^{-1}$$

$$- RT \ln K_{a3} = \Delta G_3^{\ominus} = - T \Delta S_3^{\ominus} = (13.0 \pm 0.9) \text{ kJ mol}^{-1}$$

The thermodynamic data for the protonation of hexacyanoferrate(III) determined by Hanania et al. (67H) show substantial agreement with the values determined by Jordan and Ewing, who used potentiometric titrations and calorimetric measurements. The interaction between hexacyanoferrate(II) and potassium ions was taken into consideration and the data appear reliable:

$$t = 25^{\circ}C, \text{ I} = 0 \text{ (extrapolated)}$$

$K_{a3} = (5 \pm 1.3) \times 10^{-3}$ M	$K_4 = (5.25 \pm 0.24) \times 10^{-5}$ M
$\Delta H_3^{\ominus} = - 4.2$ kJ mol^{-1}	$\Delta H_4^{\ominus} = (2.1 \pm 2.1)$ kJ mol^{-1}
$\Delta S_3^{\ominus} = - 88$ J K^{-1} mol^{-1}	$\Delta S_4^{\ominus} = 59$ J K^{-1} mol^{-1}

Lazarev et al. (70L) determined the same two acidic dissociation constants in 3 M LiClO$_4$, by three different methods (pH-metric titration, redox potentiometry, spectrophotometry). The values show an internal consistency but the absolute values cannot be regarded reliable since ion-pair formation with Li$^+$ was not taken into consideration.

Table 3. Termodynamic data for the ion-pairs of hexacyanoferrate(II).

Metal ion	$t/^oC$	I/M	Method	$\log(K/M^{-1})$	$\Delta H^{\ominus}/kJ\ mol^{-1}$	$\Delta S^{\ominus}/J\ K^{-1}\ mol^{-1}$	Ref
K^+	25	0	K^+ el,cal	2.35 ± 0.02	4.2 ± 1.26	54 ± 8.4	67E
Tl^+	25	0	sp	2.99 ± 0.05	–	–	58P
Tl^+	35	0	sp	3.05 ± 0.03	–	–	58P
Tl^+	50	0	sp	3.06 ± 0.04	–	–	58P
Ca^{2+}	25	0	cond	3.77 ± 0.04	–	–	59J
La^{3+}	25	0	sp	5.06 ± 0.08	–	–	58P

Table 4. Thermodynamic data for the ion-pairs of hexacyanoferrate(III).

Metal ion	$t/^oC$	I/M	Method	$\log(K/M^{-1})$	$\Delta H^{\ominus}/kJ\ mol^{-1}$	$\Delta S^{\ominus}/J\ K^{-1}mol^{-1}$	Ref
K^+	25	0	K^+ el, cal	1.46 ± 0.02	0.21 ± 0.21	34 ± 8.4	67E
Mg^{2+}	25	0	cond	2.79 ± 0.03	–	–	52G
Ca^{2+}	25	0	cond	2.83 ± 0.03	–	–	52G
Sn^{2+}	25	0	cond	2.85 ± 0.03	–	–	52G
Ba^{2+}	25	0	cond	2.88 ± 0.03	–	–	52G
La^{3+}	25	0	cal	3.61 ± 0.04	3.6 ± 0.10	83.2 ± 1.0	72S
Pa^{3+}	25	0	cal	3.64 ± 0.03	3.7 ± 0.05	81.9 ± 0.50	72S
Nd^{3+}	25	0	cal	3.77 ± 0.04	3.4 ± 0.05	83.6 ± 1.0	72S
Sm^{3+}	25	0	cal	3.73 ± 0.04	3.8 ± 0.05	84.4 ± 1.0	72S
Eu^{3+}	25	0	cal	3.65 ± 0.04	4.1 ± 0.10	84.0 ± 1.0	72S
Gd^{3+}	25	0	cal	3.59 ± 0.04	4.4 ± 0.10	83.6 ± 1.0	72S
Tb^{3+}	25	0	cal	3.76 ± 0.07	4.0 ± 0.15	85.7 ± 1.5	72S
Dy^{3+}	25	0	cal	3.68 ± 0.06	4.3 ± 0.15	85.3 ± 1.5	72S
Ho^{3+}	25	0	cal	3.66 ± 0.04	4.5 ± 0.10	85.3 ± 1.5	72S
Er^{3+}	25	0	cal	3.68 ± 0.05	4.4 ± 0.15	85.3 ± 1.5	72S
Tm^{3+}	25	0	cal	3.67 ± 0.04	4.4 ± 0.10	85.3 ± 1.5	72S
Yb^{3+}	25	0	cal	3.66 ± 0.04	4.4 ± 0.10	84.8 ± 1.0	72S
Lu^{3+}	25	0	cal	3.70 ± 0.06	4.2 ± 0.15	85.3 ± 1.5	72S

The most reliable thermodynamic data for ion-pairs involving $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$ are summarized in Tables 3 and 4.

The association of potassium ion with cyano complexes of iron(II) and iron(III) has been thoroughly studied. The results obtained by a potentiometric study using a potassium selective glass electrode and calorimetry are evidently the most reliable. The values obtained by Chlebek and Lister (66C) by the same potentiometric method are in substantial agreement with these results, the slight difference being due to the fact that Chlebek and Lister used tetramethylammonium salt to adjust the ionic strength and did not consider the interaction of the quaternary ion with the cyano complexes. There is ample evidence for such an interaction (67C, 65L), and numerical values were in fact determined by reaction kinetic (67C) and NMR studies (65L), but the stability constants are only approximate and are therefore not included in Table 3.

The stability of ion-pairs of $Fe(CN)_6^{4-}$ has also been studied by measuring the effect of different ions on the redox potential of the $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ couple, and on the mobility on $Fe(CN)_6^{4-}$. The results are in substantial agreement with the data in Table 3, and indicate that in addition to the ions listed, all the alkali and alkali earth ions form rather stable ion-pair (66S, 66Sa, 69N), but forther studies are necessary for a critical evaluation.

Ion pair formation is responsible for the increase of the solubility of $[Co(NH_3)_6Fe(CN)_6]$ with increasing concentration of chlorides and nitrates of alkali alkali earth and rare earth metal ions (66M, 67R). The calculated stability constants are much smaller than the values in Table 4. The probable explanation of the discrepancy is that in the calculations no other interactions were considered. For the stability of $ErFe(CN)_6$ log $(K/M^{-1}) = 3.96$ W was obtained by solubility measurements (63L). The results obtained by Stampfli and Choppin (72S) for the almost complete series of lanthanide ions suggest that this value is too high. The thermodynamic data obtained by calorimetric measurements agree fairly well with the earlier values found by conductometric studies. The values tabulated in Table 3 and 4 are considered as tentative ones.

Some interesting observations suggest that in the solutions of $Fe(CN)_5H_2O^{3-}$ (54E) and $(Fe(CN)_5H_2O^{2-}$ (70E) binuclear species are formed. However, no equilibrium data have been determined so far, and even the exact compositions of the species in solution are unknown, so that much further work is needed.

Cobalt. No reliable stability constant involving cyano complexes of cobalt is at hand. The value given for β_6 of the $Co(CN)_6^{4-}$ species is obviously meaningless, since this species does not exist in significant concentration. The value was determined in potentiometric experiments using a so called cobalt amalgam electrode (68K), but cobalt does not form an amalgam.

The formation enthalpy of the pentacyanocobaltate(II) ion was calorimetrically determined by Izatt et al (68I) for the reaction

$$Co^{2+} + 5\ CN^- \rightleftharpoons Co(CN)_5^{3-}$$

$$\Delta H^{\ominus} = -258 \pm 2.1\ kJ\ mol^{-1}$$
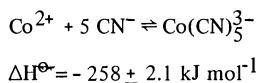
at $t = 0\ ^oC$. This value is much smaller than the previously determined one and is regarded as being more reliable. In case of the earlier study (64G) other reactions probably took place in the calorimeter.

The protonation constant of the $Co(CN)_5^{3-}$ ion was determined from the dependence of the rate of the decomposition of this complex on the hydrogen ion concentration (68E).

The value of the equilibrium constant

$$K = \frac{[Co(CN)_5^{3-}][H^+]}{[CO(CN)_4(CNH^{2-}]} = (1.43 \pm 0.19)\ M.$$

at $25\ ^oC$, $I = 0$.

Spectrophotometric evidence was obtained (67P) for the interaction of the pentacyanocobalte(II) complex with alkali metal ions. The stability constant of the $RbCo(CN)_5^{2-}$ ion pair at $20\ ^oC$ in 3 M (Rb, Na)Cl medium is $(3.7 \pm 0.3)\ M^{-1}$.

Nickel. The behaviour of the $Ni^{2+} - CN^-$ system shows that each of the stepwise formation constants K_1, K_2 and K_3 are much less than $\sqrt[4]{\beta_4}$. Therefore only the stability constant of the tetracyanonickelate(II) complex can be determined. The values evaluated from potentiometric determination of free Ni^{2+} concentration cannot be reliable since the electrode reactions involving Ni^{2+} are not strictly reversible. In recent studies, the stability constant was determined by following pH-potentiometrically and spectrophotometrically the effect of acid on the decomposition of tetracyanonickelate(II). These independent studies have led to the same result. Freund and Schneider (59F) studied the decomposition of the compex spectrophotometrically and did not find evidence for the existence of intermediate complexes.

Using 4×10^{-10} M as the value of the dissociation constant of HCN, they obtained log $(\beta_4/M^{-4}) = 31 \pm 0.06$ ($t = 24.92\ ^oC$) by extrapolation to zero ionic strength. However, these authors have calculated the dissociation constant of HCN as the average of several reported values determined under different conditions. This is clearly not correct, and Christensen et al. (63C) recalculated the result of Freund and Schneider using 9.216 for the pK of HCN, and obtained 30.3 ± 0.1 for log (β_4/M^{-4}). The values obtained by Cristensen et al. from a pH metric study agrees excellently with this corrected constant: log $(\beta_4/M^{-4}) = 30.1 \pm 0.2$ ($t = 25^o$, $I = 0$). These authors have determined calorimetrically the $\Delta H^{\ominus}$ value: $(-180.2 \pm 1)\ kJ\ mol^{-1}$, and calculated $\Delta S^{\ominus} = -29\ JK^{-1}\ mol^{-1}$. Rate studies revealed the existence of protonated species of tetracyanonickelate(II). The values of protonation constants were measured (68Ka) by spectrophotometric determination of the effect of acid on the decomposition of the complex at rather low pH. The following values were obtained ($t = 25\ ^oC$, $I = 0.1$ (NaClO_4)):

$$\log\ (\beta_4/M^{-4} = 30.5 \pm 0.3$$

$$K_1 = \frac{[HNi(CN)_4^-]}{[Ni(CN)_4^{2-}][H^+]} = 10^{5.4 \pm 0.2}\ M^{-1}\ ;\qquad K_2 = \frac{[H_2Ni(CN)_4]}{[HNi(CN)_4^-][H^+]} = 10^{4.5 \pm 0.2}\ M^{-1}.$$

A detailed potentiometric study by Persson(74P), however, did not indicate the existence of so stable protonated species, although their kinetic role was later corroborated (76P). Persson could calculate besides the value of β_4, approximate values of the other three stability constants:

$$\beta_1 = (1.08 \pm 0.4) \times 10^7\ M^{-1};\qquad\qquad \beta_3 \sim 10^{22}\ M^{-3};$$
$$\beta_2 \simeq 9 \times 10^{13}\ M^{-2};\qquad\qquad \beta_4 = (1.16 \pm 0.08) \times 10^{31}\ M^{-4}$$

at $t = 25\ ^oC$ and $I = 3$ M (NaClO_4). It is likely that the little bit higher value of β_4 is due to that $pK_{HCN} = 9.484$ was used in the calculations while under the condition $pK_{HCN} = 8.81$ seems to be more reliable.

Table 5. The stability constant of the pentacyanonickelate(II) complex.

$t/^{\circ}C$	Medium	K_5/M^{-1}	Remark	Ref.
25.2	$NaCN+NaClO_4 = 1.34$ M	0.19 ± 0.01	—	60M
23	$NaCN+NaClO_4 = 2.5$ M	0.201 ± 0.009	vis sp	64V
25	$KCN+KF = 4$ kg.mol^{-1}	1.07 ± 0.02	vis sp K_5/mol.kg^{-1}	65Ca
20	$NaCN+NaClO_4 = 2$ M	0.168 ± 0.003	vis sp	71Pa
25.2	$NaCN = 6$ M	0.4	ir sp approx. value	

Table 6. Stability constants of some mixed ligand complexes of nickel(II)

Y	K_1/M^{-1}	K_2/M^{-1}	K_1K_2/M^{-2}	Ref.
IDA	—	—	1.6×10^{11}	70C
MIDA	—	—	2.1×10^{10}	70C
EDDA	1.2×10^5	1.3×10^3	1.5×10^8	70Ca
NTA	5.2×10^4	1.0×10^3	5.3×10^7	70Ca
EGTA	—	—	1.1×10^9	70Ca
HPDTA	5.1×10^3	3.0×10^2	1.5×10^6	70Ca
HEEDTA	6.1×10^3	—	—	70Ca
EDTA	$(3.8 \pm 0.2) \times 10^3$	—	—	61Mb
DCTA	2.57×10^2	—	—	83K
PDTA	1.36×10^2	1.69×10^{-1}	2.3×10^1	78K
DTPA	1.16×10^4	3.1×10^0	3.6×10^4	78K
TMDTA	1.85×10^4	6.51×10^1	1.2×10^6	79K
trien	1.6×10^4	—	—	69Kb

$$K_1 = \frac{[Ni\,Y\,CN]}{[Ni\,Y]\,[CN^-]} \; ; \qquad K_2 = \frac{[Ni\,Y\,(CN)_2]}{[NiY\,CN]\,[CN^-]} \; ; \qquad K_1K_2 = \frac{[Ni\,Y\,(CN)_2]}{[Ni\,Y]\,[CN^-]^2}$$

Recently the formation of pentacyanonickelate(II) complex was quantitatively studied by different methods. In contrast with earlier claims (59K, 59Ba, 63P) the non-existence of the hexacyanonickelate(II) complex is definitely proven (64V, 62B). The stability constant of pentacyanonickelate(II) was always determined at high ionic strength since this complex is a rather weak one. In all cases the stability constant was spectrophotometrically determined. The error of the values evaluated from measurements in the visible or near u.v. region is much less than those obtained from infrared absorption studies. The available values are summarized in Table 5.

The tetracyanonickelate(II) complex forms weak mixed ligand complexes with halides and pseudohalides, but no reliable constant is available (62B). In the reaction of polyamine and aminopolycarboxylato complexes of nickel(II) with cyanide ion, mixed cyano complexes are formed and a number of stability constants were derived from rate studies. (61 Mb, 69J, 69Ka, 70C, 70Ca, 78K, 79K, 83K).

The values summarized in Table 6 are regarded as tentative ones and they suggest that the more stable the 1:1 chelate, the less stable the mixed cyano complex (70B, 83K).

Palladium. As in the case of nickel(II), the tetracyano complex of palladium is much more stable than the others, and therefore only the overall stability constant of $Pd(CN)_4^{2-}$ could be determined. Unfortunately there are very big differences between the values determined by two independent teams and at present a reliable constant is not available. In both studies the electrometric method was applied, using a palladium electrode. Fasman et al. (65F) determined the value at different temperatures and different cyanide ion concentrations and at $t = 25^{\circ}C$, I = 1 M (KCN) found $log(\beta_4/M^{-4}) = 51.7$. Izatt et al. (67I) however determined the value $log(\beta_4/M^{-4}) = 42.4$ ($t = 25^{\circ}C$, I = 0). The principal reason for the difference is that two widely different values of the half cell potential for the Pd/Pd^{2+} couple were used in the evaluation of the experimental results. Fasman et al. took the value (- 0.987 V) determined by Templeton, Watt and Garner (43T), while Izatt et al. employed the value (- 0.915 V) which they determined themselves. It must be added that Izatt et al. (70I) redetermined the half cell potential under similar experimental conditions (3.94 mol.kg^{-1} HClO$_4$) and obtained fairly good agreement with the value found by Templeton, Watt and Garner.

A further point which prevents the recommendation of a stability constant is the curious fact that according to Izatt et al. (67I) the pentacyanopalladata(II) complex is rather stable (log $(K_5/M^{-1}) = 2.9$, at $t = 25\ °C$, $I = 0$) while independent ir spectroscopic studies by Jorgensen (73J) and by the author of this survey did not indicate the formation of this species.

Ruthenium. Obviously, the equilibrium chemistry of cyano complexes of ruthenium is potentially as rich as that of the analogous iron complexes, but these equilibria have not been studied so far. The only equilibrium constant available is the dissociation constant of the ion-pair $KRu(CN)_6^{3-}$ (70F) determined by conductivity measurements at 25 °C, log $(K/M^{-1}) = 2.48$ and the value is remarkably near the log K of $KFe(CN)_6^{3-}$.

Copper. Most of the studies have been directed toward the cyano complexes of copper(I). This is a simpler system than the $Cu^{2+} - CN^-$, because in the latter case an additional redox reaction has to be considered.

According to Vladimirova and Kakovskii (50V) the values of $\log(\beta_2/M^{-2})$ at 25 °C, is 23.72. The authors did not give the uncertainty of their value. On the basis of the experimental data and the uncertainties of pH and the acidic dissociation constant of HCN, the overall uncertainity is at least 0.3 logarithmic unit. However, the value for β_2 seems to be too large. Rothbaum (57R) have determined the value at 20°C in a medium of varying CuCn + KCN concentrations and calculated log $(\beta_2/M^{-2}) = 21.7 \pm 1$. Recently a careful electrochemical study (72H) provided the following values ($t = 22\ °C$; Medium: 0.01 M Cu^+ with KCN varying between 2.5 and 10×10^{-2} M):

$$\log (\beta_2/M^{-2}) = 21.7 \pm 0.2$$
$$\log (\beta_3/M^{-3}) = 26.8 \pm 0.2$$
$$\log (\beta_4/M^{-4}) = 27.9 \pm 0.2$$

For the stability constants of the tricyano and tetracyano complexes the most reliable values are obtained from pH-metric and calorimetric measurements (67I). The following values refer to $t = 25°$ and $I = 0$:

Complex	$\log(K/M^{-1})$	$\dfrac{\Delta G^{\ominus}}{\text{kJ mol}^{-1}}$	$\dfrac{\Delta H^{\ominus}}{\text{kJ mol}^{-1}}$	$\dfrac{\Delta S^{\ominus}}{\text{J K}^{-1}\text{ mol}^{-1}}$
$Cu(CN)_3^{2-}$	5.30 ± 0.01	-30.3 ± 0.1	-46.6 ± 0.4	-54.6 ± 1
$Cu(CN)_4^{3-}$	1.5 ± 0.2	-8.4 ± 0.1	-47.0 ± 0.4	-1.30 ± 2

Although the error given seems to be too small, more reliance should be placed on these contants than on those obtained by infrared spectroscopic studies (56P) $\log(K_3/M^{-1}) = 4.48 \pm 0.06$, $\log(K_4/M^{-1}) = 1.58 \pm 0.03$). There is a very good agreement between the contants obtained by pH-metric titrations and spetrophotometric experiments in the u.v. region (59B). Some calorimetrically determined constants show considerable deviation from the values regarded as reliable. However, the experimental conditions were not given in the paper (65B) which deals mainly with the theory of the calorimetric method.

The values of the overall stability constant for the tetracyano complex was determined by Kunschert (04K) at 18°C: $\log(\beta_4/M^{-4}) = 27.3$. Penneman and Jones (56P) recalculated Kunschert's data, considering the activity coefficients and using a better value for the potential of the Cu/Cu^+ couple. Their value is $\log(\beta_4/M^{-4}) = 28.93$. The aforementioned value obtained by Hancock, Finkelstein and Evers (72H) appears more reliable, but a careful potentiometric reinvestigation of the system using well defined and different ionic media is desirable.

According to NMR studies using copper-63 and 65, polynuclear complexes are formed when the concentration of copper(I) is high (70Y). Infrared (66C, 66Ca) and NMR (70Y) studies indicated the formation of mixed ligand complexes, but no reliable stability constants are available. The dicyanocopper(I) complex can react with dicyanogen and a monomeric species is formed which readily polymerizes (68T, 79B). The formation of this unusual species must be considered in the study of the $Cu^{2+} - CN^-$ system where dicyanogen is formed.

There have been only two attempts to determine the overall stability constant of the tetracyanocuprate(II) complex. Paterson and Bjerrum (65P) determined the value by potentiometric experiments in a water-methanol solvent (mole fraction of methanol = 0.45) at $t = -45°C$, with I varying between 0.05 and 0.1 M (NaCN). The value found is log $(\beta_4/M^{-4}) = 26.7$. The uncertainity is not given, but is probably less then 0.5 logarithmic unit.

Katagiri et al. (81K) calculated β_4^{II} based on an electrochemical study using the following formula:

$$\beta_4^{II} = \beta_4^{I} \cdot \exp \left\{ \frac{F}{RT} [E^° (Cu^{2+}/Cu^+) - E^° (Cu(CN)_4^{2-} \cdot Cu(CN)_4^{3-})] \right\}$$

(β_4^{I} and β_4^{II} are the overall stability constant of the tetracyanocuprate(I) and (II) complexes, resp.) Applying $\beta_4^{I} = 10^{30.53}$ M^{-4}, they obtained $\beta_4^{II} = 10^{22}$ M^{-4} at 25°C.

Considering that for β_4^I a much smaller value seems reliable, this value is probably too high. (Very recently Katagiri (86K) corrected this value and the new value is even bigger: $\beta_4 = 10^{24}$ M^{-4}.) As a matter of course, this value cannot be directly compared to a constant referring to another medium and -45°C.

The stability constants of the mixed ligand species Cu(EDTA)CN$^-$ and Cu(DCTA)CN have been calculated from spectrophotometric measurements (83K). These constants are analogous to those of summarized in Table 6. The logarithm of the constants are as follows: for the Cu(EDTA)CN complex at I = 0.15 M at room temperature $\log(K_1/M^{-1})$ = 3.76: for the Cu(DCTA)CN complex at I = 0.12 M and 27° C $\log(K_1/M^{-1})$ = 2.64. Obviously, these data should be regarded as tentative ones.

Silver. Although many papers have been published on the stability constants of different cyano complexes of silver(I), only a few studies meet the requirements for obtaining reliable constants. The following potentiometrically obtained values are regarded as the most reliable (Table 7).

The overall stability constant of the AgOHCN$^-$ mixed ligand complex was determined amperometrically (56K) and pH metrically (70Z). The two values ($\log(\beta_{11}/M^{-2})$ = 13.22 and 13.23, resp.) agree excellently although the ionic strength was zero in the former and 4.25 M in the latter case. The comparison of the cyano complexes of silver(I) are surprisingly independent of the ionic strength.

Table 7. Stability products of cyanocomplexes of silver(I).

$t/^\circ$C	Medium	β_2/M^{-2}	β_3/M^{-3}	Ref
20.5	I = 0, ☆	20.85	21.8	65Z
21	I = 3.25 M (NaClO$_4$)	20.23 $\pm$ 0.06		70Z
25	0.024 M KCN	20.9 $\pm$ 0.1	21.8 $\pm$ 0.1	71H

☆ corrected using the Debye-Hückel equation.

Table 8. Thermodynamic data of cyanocomplexes of zinc(II)

n	$\log(\beta_n/M^{-n}$	$\dfrac{\Delta G^\ominus}{\text{k J mol}^{-1}}$	$\dfrac{\Delta H^\ominus}{\text{k J mol}^{-1}}$	$\dfrac{\Delta S^\ominus}{\text{J K}^{-1}\text{ mol}^{-1}}$
2	11.967 $\pm$ 0.017	-63.4	-45.4 ± 2.5	60.5
3	16.050 $\pm$ 0.023	-92.0	-806 ± 2.5	38.2
4	19.62 $\pm$ 0.06	-112.0	-116.8 ± 2.5	-14.3

Gold. It follows from the few stability constants referring to Au(CN)$_2^-$ that it is one of the most stable complexes, but no reliance can be placed on the numerical values. It is almost certain that no higher complexes are formed. An equilibrium study of cyano complexes of Au(I) and Au(III) appears desirable.

Zinc. There are many studies referring to the stability of cyano complexes of zinc (II), but only the most recent ones can be regarded statisfactory. Izatt et al. (65I), have determined by pH-metric and calorimetric titrations the thermodynamic constants, referring to $t = 25^\circ$C and I = 0 (Table 8).

The stability constants were also determined by Persson (71P) using potentiometric (Zn amalgam electrode, glass electrode) measurements at $t = 25^\circ$C, I = 3 M NaClO$_4$:

$$\log(\beta_1/M^{-1}) = 5.34 \pm 0.1 \qquad \log(\beta_3/M^{-3}) = 16.68 \pm 0.05$$
$$\log(\beta_2/M^{-2}) = 11.02 \pm 0.03 \qquad \log(\beta_4/M^{-4}) = 21.57 \pm 0.10$$

The fact that, according to Persson, K_2 is much bigger than K_1 may explain why Izatt et al. did not find the monocyano species. The overall formation enthalpy has been determined by Guzzetta and Hadley (64G). Their value shows an excellent agreement with that obtained by Izatt et al.

Cadmium. Complex equilibria involving Cd^{2+} and CN$^-$ have been studied by different techniques under different conditions, and some careful potentiometric and pH-metric titration studies have provided reliable constants. Fortunately, these experiments were made under the same conditions: $t = 25^\circ$C, I = 3 M (NaClO$_4$), and the agreement seems satisfactory (Table 9).

A comparison of the two sets of the constants suggests, however, that the uncertainties in the constants are larger than those given by the authors.

Infrared spectroscopic studies (61P, 71A) prove that no formation of higher cyano complexes of cadmium(II) occurs, in contrast to the claim of Prytz and Osterud (52P) based on polarographic measurements.

The formation constants have been determined in dimethylformamide solution (72J) by solubility measurements at $t = 25^\circ$C and I = 0.1 M ((C$_2$H$_5$)$_4$NClO$_4$). The authors do not quote uncertainities for the following constants, which can be regarded as approximate

$$\log (K_1/M^{-1}) = 4.7 \qquad \log (K_3/M^{-1}) = 3.08$$
$$\log (K_2/M^{-1}) = 4.4 \qquad \log (K_4/M^{-1}) < 1$$

Table 9. Two sets of stability products of cyanocomplexes of cadmium(II).

n	log (β_n/M^{-n}) (44L)	log(β_n/M^{-n}) (71P)
1	5.54 ± 0.06	5.62 ± 0.02
2	10.6 ± 0.1	10.84 ± 0.04
3	15.26 ± 0.06	15.72 ± 0.03
4	18.85 ± 0.05	19.20 ± 0.03

Table 10. Thermodynamic data of cyanocomplexes of mercury(II).

n	$t/^{\circ}C$	log(K_n/M^{-1})	$\dfrac{\Delta H^{\ominus}}{kJ\ mol^{-1}}$	$\dfrac{\Delta S^{\ominus}_n}{J\ K^{-1}\ mol^{-1}}$
1	10	17.97 ± 0.05		
	25	17.00 ± 0.08	-96.6 ± 2.5	2.9
	40	16.26 ± 0.07		
2	10	16.74 ± 0.05		
	25	15.75 ± 0.08	-107.0 ± 2.5	-56
	40	15.02 ± 0.07		
3	10	3.81 ± 0.03		
	25	3.56 ± 0.02	-31.9 ± 1.0	-26
	40	3.37 ± 0.02		
4	10	2.81 ± 0.05		
	25	2.66 ± 0.01	-302 ± 1.0	-50
	40	2.42 ± 0.03		

Mixed cyano-iodo complexes were detected by Raman spectroscopy (72Y), and it is likely that mixed chloro-cyano complexes are also formed. However, the report by Penneman and Jones (61P), that the solubility of cadmium cyanide is much larger in sodium chloride solution than in pure water is invalidated by the fact that the solubility value in water used (31 M) is clearly incorrect (64B).

Mercury. Due to considerable work in the last decade, a number of reliable equilibrium constants have been reported for the stepwise formation of cyano complexes of mercury(II). The Hg(II)–CN⁻ system has been studied by polarographic, potentiometric and pH-metric measurements at different temperatures and in different media. For I = 0, the values obtained by Christensen, Izatt and Eatough (65C) by a careful pH-metric and calorimetric study may be considered as accurate and reliable (Table 10.).

At $t = 20^{\circ}C$ and I = 0.1 M (NaNO$_3$) the pH-metrically and potentiometrically determined data by Anderegg (57A) are as follows: $\log(K_1/M^{-1}) = 18.00 \pm 0.06$; $\log(K_2/M^{-1}) = 16.70 \pm 0.06$; $\log(K_3/M^{-1}) = 3.83 \pm 0.02$; log $(K_4/M^{-1}) = 2.98 \pm 0.08$. The constants were determined polarographically at 30°C and in a constant ionic medium 2.0 M (NaNO$_3$) by Newman, Cabral and Hume (58N) who obtained $\log(\beta_2/M^{-2}) = 33.9$; $\log(\beta_3/M^{-3}) = 38.1$ and $\log(\beta_4/M^{-4}) = 40.6$. These authors did not mention the standard deviation of the experimentally determined quantities and the uncertainty of the constants. This latter probably does not exceed 0.1 logarithmic unit.

Tanaka and Murayama (57T) have also studied the Hg(II)–CN⁻ system polarographically at 25°C, I = 0.2 M (KNO$_3$). Their values however, are not included in this compilation because of the application of buffers containing complex forming anions, and also because of the use of erroneous auxiliary data in the evaluation of the constants.

Azzam and Shimi's (64A) potentiometric studies have indicated the formation of pentacyano and hexacyanomercurate(II) species at higher concentrations of cyanide. Because of continuously varying medium (the concentration of KCN was varied between 1-7 M) their results are of doubtful validity. The careful infrared studies by Ashurst, Finkelstein and Goold (71A) point to the absence of such higher complexes.

There are reliable data on the stability of some mixed ligand complexes involving mercury(II) as central ion and CN⁻ as ligand. The formation of the mixed ligand complexes of mercury(II) may occur in reproportionation reactions, or by the uptake of a foreign ligand by the parent complex, which in the present case is Hg(CN)$_2$. The constant

$$K = \frac{[HgCNX]^2}{[HgX_2]\ [Hg(CN)_2]}$$

was determined for X = Cl⁻, Br⁻, I⁻, SCN⁻ and OH⁻. The data are summarised in Table 11.

The formation of Hg(CN)$_n$X(X = Cl⁻, Br⁻ I⁻; n = 1,2) was proven by Raman spectroscopic (66Cc) and infrared (61P) studies. Some equilibrium constants were determined polarographically and spectrophotometrically by Newman and Hume (61N). Their results are shown in Table 12.

Table 11. Equilibrium constants of reproportionation reactions of some mixed ligand complexes of mercury(II).

X	Method	$t/^{\circ}C$	Medium	K	Ref.
Cl^-	sp	25	I = 0	8.4 ± 0.4	64Ba
Cl^-	sp	25	I = 0 dioxane	12 ± 2	64Bb
Br^-	sp	25	I = 0	1.94 ± 0.1	64 Ba
Br^-	sp	25	I = 0 dioxane	1.74 ± 0.2	64Bb
I^-	sp	25	I = 0	0.11 ± 0.01	64Ba
I^-	sp	25	I = 0	0.13	68C
I^-	sol	25	I = 0	0.14	68C
			0.1 M $Hg(CN)_2$		
I^-	sp	25	I = 0 dioxane	0.2 ± 0.03	64Ba
SCN^-	sp	25	I = 0	0.66 ± 0.03	71G
OH^-	sol	23	I = 2 ($NaNO_3$)	260	59N
OH^-	pol	30	I = 2 ($NaNO_3$)	280	59N

Table 12. Stability constants of some mixed ligand complexes of mercury(II).

Reaction	Method	$t/^{\circ}C$	Medium	K/M^{-1}
$Hg(CN)_3^- + Cl^- = Hg(CN)_3Cl^{2-}$	pol	30	I = 2M($NaNO_3$)	0.4
$Hg(CN)_3^- + Br^- = Hg(CN)_3Br^{2-}$	pol	30	I = 2M($NaNO_3$)	2.3
$Hg(CN)_3^- + SCN^- = Hg(CN)_3SCN^{2-}$	pol	30	I = 2M($NaNO_3$)	2.9
$Hg(CN)_2 + Cl^- = Hg(CN)_2Cl^-$	sp	30?	I = 4M($NaClO_4$)	0.56 ± 0.05

Table 13. Stability constants of some binuclear complexes.

| Inert complex	Method	K/M^{-1}
$Fe(CN)^{4-}$	sp	240 ± 25
$Fe(CN)_6^{3-}$	pot	170
$Mo(CN)_8^{4-}$	sp	19.9 ± 2
$Mo(CN)_8^{3-}$	pot	19.8 ± 2

Penneman and Jones (71P) have found evidence for the formation of polynuclear species (Hg_2CN^{3+}, $Hg_3(CN)_2^{4+}$), but no equilibrium constant was determined. $Hg_2(CN)_3^+$ is formed on dissolving mercury cyanide in hydrogen fluoride (71Ca). The equilibrium constant

$$K = \frac{[HgCN^+]^2[HCN][HF_2^-]}{[Hg_2(CN)_3^+]} = 1.2 \times 10^{-6} \text{ mol}^3 \text{ kg}^{-3}$$

was determined by conductivity measurements at $t = 0$ $^{\circ}C$.

Some further constants were determined in the $HgI_2 - I^- - CN^-$ system (68C), but these are rather ill-defined and are therefore not included.

Mercury cyanide reacts with coordinatively saturated inert cyano complexes (71B) and the equilibrium constant of the following reactions have been determined :

$$M(CN)_N^{m-} + Hg(CN)_2 = Hg(CN)_2 \cdot M(CN)_N^{m-}$$
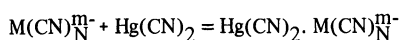
$M(CN)_N^{m-} = Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$, $Mo(CN)_8^{4-}$ and $Mo(CN)_8^{3-}$. The obtained values referring to $t = 25^{\circ}C$, I = 0 are given in Table 13.

The organometallic ion CH_3Hg^+ reacts with a number of ligands, and the stability constant of the monocyano complex has been determined by Schwarzenbach and Schellenberg (65S). The value at $t = 20^{\circ}C$, I = 0.1 M (KNO_3) is $\log(K/M^{-1}) = 14.1$. More recent studies (73G) have confirmed this value.

Cyanogen. The study of the effect of cyanide ion on the distribution of cyanogen between cyclohexane and an aqueous (3M $NaClO_4$, CN) solution at $25^{\circ}C$ yielded

$$K = \frac{[(CN)_3^-]}{[(CN)_2][CN^-]} = (0.31 \pm 0.03) \text{ M}$$

for the stability constant of $(CN)_3^-$ (79Ba).

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