



Murdoch
UNIVERSITY

MURDOCH RESEARCH REPOSITORY

This is the author's final version of the work, as accepted for publication following peer review but without the publisher's layout or pagination.

The definitive version is available at :

<http://dx.doi.org/10.1016/j.hydromet.2016.05.020>

Akilan, C., Königsberger, E., Solis, J.S., May, P.M., Kyle, J.H. and Hefter, G. (2016) Investigation of complexation and solubility equilibria in the copper(I)/cyanide system at 25°C. *Hydrometallurgy*, 164 . pp. 202-207.

<http://researchrepository.murdoch.edu.au/32214/>

Copyright: © 2016 Elsevier B.V.
It is posted here for your personal use. No further distribution is permitted.

Investigation of complexation and solubility equilibria in the copper(I)/cyanide system at 25 °C

Chandrika Akilan,¹ Erich Königsberger,² Jose S. Solis,³ Peter M. May,^{1,2} James H. Kyle*² and Glenn Hefter*³

¹ Parker Cooperative Research Centre for Integrated Hydrometallurgy Solutions, Murdoch University, Murdoch, WA 6150, Australia

² Chemical and Metallurgical Engineering, Murdoch University, Murdoch, WA 6150, Australia

³ Chemistry Department, Murdoch University, Murdoch, WA 6150, Australia.

ABSTRACT

The complexation of copper(I) by cyanide ions (CN^-) in aqueous solution has been studied by glass electrode potentiometry at 25 °C and ionic strengths (I) of 1, 3 and 5 M in NaCl media. Overall formation constants, β_n , for the equilibria: $\text{Cu}^+(\text{aq}) + n\text{CN}^-(\text{aq}) \rightleftharpoons \text{Cu}(\text{CN})_n^{(n-1)-}(\text{aq})$ with $n = 2, 3$ and 4, were quantified, along with the ionization constant (K_w) of water and the acid dissociation constant (K_a) of $\text{HCN}(\text{aq})$. The solubility constants $*K_{sn}$ for the equilibria: $\text{CuCN}(\text{s}) + (n-1)\text{HCN}^0(\text{aq}) \rightleftharpoons \text{Cu}(\text{CN})_n^{(n-1)-}(\text{aq}) + (n-1)\text{H}^+(\text{aq})$ were also determined from a re-analysis of published solubility data for $\text{CuCN}(\text{s})$ in acidic cyanide solutions at $I = 1 \text{ M}(\text{NaCl})$ and 25 °C. Because of the instability of uncomplexed $\text{Cu}^+(\text{aq})$ and parameter correlations in the data, neither β_1 nor the solubility product K_{s0} ($\text{CuCN}(\text{s}) \rightleftharpoons \text{Cu}^+(\text{aq}) + \text{CN}^-(\text{aq})$) could be reliably determined from the present data although estimates are presented.

Key words: copper(I), cyanide, stability constants, solubility, thermodynamics, potentiometry

* Corresponding authors. Tel: +61 8 93358253; cell: +61 4 22310217; email addresses: J.Kyle@murdoch.edu.au; G.Hefter@murdoch.edu.au

1. INTRODUCTION

The aqueous solution chemistry of copper is usually dominated by the Cu(II) oxidation state (Greenwood and Earnshaw, 1997) but in the presence of cyanide ions Cu(I) is stabilized through the formation of reasonably strong Cu(I)/CN⁻ complexes (Sharpe, 1976). These complexes are particularly important in the hydrometallurgical extraction of gold from its ores by cyanidation processes (Habashi, 1987; Lu et al., 2002; Marsden and House, 2006; Botz et al., 2011). This is because, even though the gold(I)-cyanide complex, Au(CN)₂⁻, is considerably more stable than the Cu(I)/CN⁻ complexes, gold ores often contain much higher concentrations (up to 1000 times) of copper. Such excesses of copper can bind significant amounts of cyanide lixiviant thereby increasing costs and lowering gold recovery. Furthermore, since the copper in gold ores is often present as Cu(I), in minerals such as chalcocite and covellite, it does not require oxygen to be leached (Kyle et al., 2011; Breuer et al., 2008; Hewitt et al., 2009). Such minerals react much faster with cyanide than does metallic gold, consequently lowering the available cyanide in solution. In addition, under anoxic leaching conditions the sulfur in covellite and chalcocite will form thiocyanate ions (Kyle et al., 2011), which also increases cyanide consumption. Due to their much higher concentrations in leach solutions, the Cu(I)/CN⁻ complexes also compete with Au(CN)₂⁻ for the adsorption sites on the activated carbon used to concentrate gold from dilute cyanide solutions, particularly at lower free cyanide concentrations (Botz et al., 2011; Dai et al., 2012). This competition lowers gold recovery rates and contaminates the final gold product in the subsequent electrowinning step.

Optimization of gold extraction in the presence of high levels of copper necessitates an understanding of the interaction of Cu(I) with the cyanide ion. Such an understanding is typically

expressed in the form of speciation models or graphically as Pourbaix (Eh-pH) or species distribution (% Cu species-pH) diagrams, both of which rely on quantitative knowledge of the formation constants of all relevant species. A typical Pourbaix diagram for the copper-cyanide system at 25 °C, for simplicity focusing on Cu(II) (aq) and the Cu(I)/CN⁻ solution species, is shown in Figure 1. A species distribution diagram for the Cu(I)/CN⁻ solution species is given later (Figure 3).

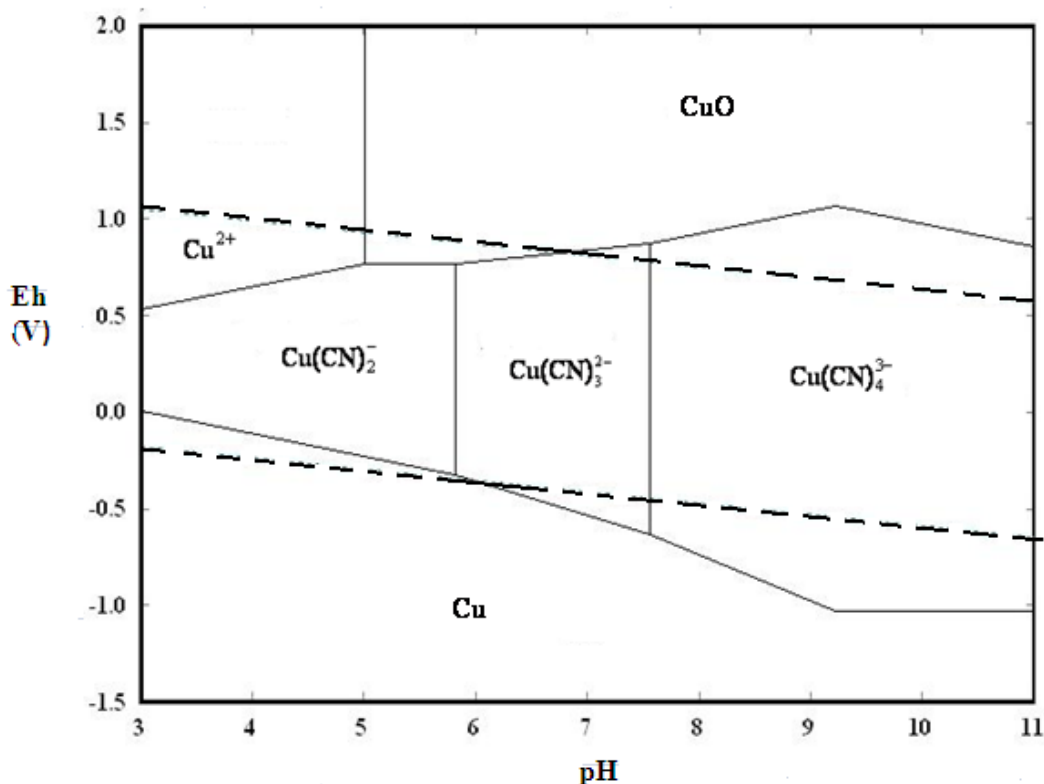


Figure 1. Pourbaix diagram for the Cu(I)-CN system in 3 M (NaCl) at 25 °C; $[\text{CN}^-]_{\text{T}}/[\text{Cu}^+]_{\text{T}} = 7$; $[\text{Cu}^+]_{\text{T}} = 0.005 \text{ M}$; $[\text{CN}^-]_{\text{T}} = 0.035 \text{ M}$.

Given the importance of Cu(I)/CN⁻ complexes it is not surprising that the Cu(I)/CN⁻ system has been investigated on numerous occasions. However, almost all of those studies were

made on dilute solutions (Beck, 1987; Lu et al., 2002; Kyle and Hefter, 2015). This is unfortunate because the formation constants obtained under such conditions do not adequately account for observed behaviour under hydrometallurgical conditions (Dai et al. 2010).

The limitations of the existing stability constant database for the Cu(I)/CN^- system have been detailed recently by Kyle and Hefter (2015). These authors noted that little information was available on the ionic strength dependence of the formation constants and related thermodynamic parameters for Cu(I)/CN^- complexes, under conditions relevant to hydrometallurgical processing. It was also pointed out that there was virtually no experimental information for the 1:1 complex, $\text{CuCN}^0(\text{aq})$. This is problematic because most of the programs used to model complex hydrometallurgical systems require definition of a full suite of β_n values (ie, $n \geq 1$), even though in principle this is not necessary. With the increasing use of modelling for process design for the extraction of metals from their ores, the reliability of the relevant data is becoming ever more important: such programs are only as good as the data on which the calculations are based.

This paper reports results obtained from two independent experimental studies made in our laboratories of the Cu(I)/CN^- system in concentrated NaCl media: by Solis (1995) at $I = 1$ M and more recently by Akilan at $I = 1, 3$ and 5 M. Both studies used glass electrode potentiometric titrations and similar methodology. A preliminary mention of Solis' work has been made (Hefter et al., 1993) but his final results (Solis, 1995) have not been published. Akilan's data were cited, without experimental detail, as "unpublished" in our earlier review (Kyle and Hefter, 2015). These details are provided here for the first time. In addition, a re-analysis, using modern

computational methods, of solubility data also measured in our laboratories (Königsberger et al., 1994) is presented.

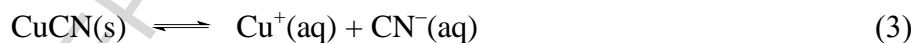
Assuming only ‘mononuclear’ species are formed, the complexation of copper(I) by cyanide ions in aqueous solution can be written as:



for which the corresponding overall equilibrium constants can be expressed (ignoring activity coefficients):

$$\beta_n = \frac{[\text{Cu}(\text{CN})_n^{(n-1)-}]}{[\text{Cu}^+][\text{CN}^-]^n} \quad (2)$$

The solubility product of $\text{CuCN}(\text{s})$, corresponding to the equilibrium:



can be expressed as

$$K_{s0} = [\text{Cu}^+][\text{CN}^-] \quad (4)$$

However, the solubility equilibria most easily determined, at reasonably low pH and total cyanide levels, are:



for which the corresponding solubility constants can be written

$$*K_{sn} = \frac{[\text{Cu}(\text{CN})_n^{(n-1)-}][\text{H}^+]^{(n-1)}}{[\text{HCN}^0]^{(n-1)}} = K_{s0} \beta_n K_a^{(n-1)} \quad (6)$$

where K_a is the dissociation constant of $\text{HCN}^0(\text{aq})$ (see eqs. (9) and (10) below).

It should be noted that, because of the instability of uncomplexed $\text{Cu}^+(\text{aq})$, the equilibria represented in eqs. (1) and (3) can be measured only in a medium that stabilizes Cu(I). In the present study this was achieved by the use of high concentrations of NaCl as the ‘swamping’ electrolyte (Hefter et al., 1993). In this situation, any Cu(I)/Cl^- or $\text{Cu(I)/Cl}^-/\text{CN}^-$ complexes formed are considered to be part of the medium. This is analogous to the treatment of aquo complexes in conventional (non-complexing) media.

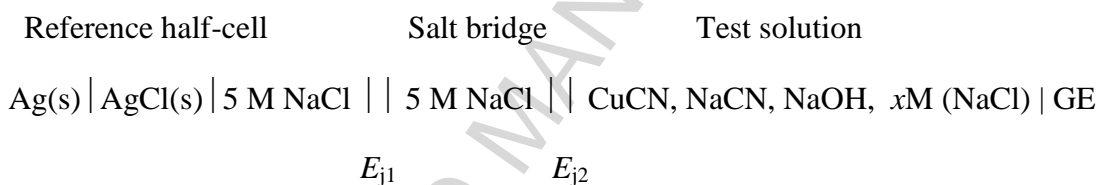
2. EXPERIMENTAL

2.1 Materials

Analytical grade reagents and calibrated A-grade glassware were used throughout. All solutions were prepared using high purity water (Millipore Milli-Q system) that had been boiled for ~30 minutes under high purity nitrogen to minimize dissolved oxygen and carbon dioxide. The stoichiometric ionic strength, I ($= 0.5\sum c_i z_i^2$) of all solutions was adjusted by addition of appropriate amounts of NaCl (Chem-Supply, Australia, 99.5 % purity). Standard HCl and NaOH solutions were prepared using commercial concentrated ampoules (Merck, Germany). Copper(I) cyanide solutions were prepared fresh daily by adding solid CuCN (Sigma Aldrich, USA, 99%) to a solution containing appropriate amounts of NaCl and NaCN (Sigma Aldrich, 99%) and adjusting the pH to the desired value by addition of NaOH(aq). Total copper concentrations were determined by aerial oxidation to Cu(II) followed by complexometric titration against a commercial volumetric standard EDTA solution (Convol, BDH, UK) using fast sulphon black F indicator (Vogel, 1961).

2.2 Titrations

Commercial glass electrodes (Metrohm, Switzerland, Model 6.0101.000) were used throughout. The electrodes were stored in 10 mM HCl + 150 mM NaCl in between titrations. All potentials were measured relative to Ag/AgCl reference electrodes consisting of a silver wire in contact with solid AgCl. The reference electrode filling solution was 5.0 M NaCl(aq), used in conjunction with a salt bridge also containing 5.0 M NaCl(aq). Electrochemical cells used in this work can therefore be represented as:



where E_{j1} and E_{j2} are liquid junction potentials, $x = 1, 3$ or 5 , and GE represents a glass electrode.

Potentiometric titrations were performed in air-tight pyrex-glass cells that were either tall-form (Solis) or squat 20 mL Metrohm cells (Akilan) using piston burettes (Metrohm Dosimat 665). Cell potentials were monitored to ± 0.1 mV by high impedance digital voltmeters of in-house construction. The cell temperature was maintained at (25 ± 0.01) °C. The electrode combination was calibrated in terms of $p[\text{H}] (= -\log [\text{H}^+])$, which for brevity will be denoted pH throughout this paper) either *in situ* (Solis) or *ex situ* (Akilan) using 10.00 mM HCl in the target medium prior to each titration. The *in situ* calibration involved equilibration of the electrodes in the target medium, followed by the addition of appropriate amounts of Cu(I) and CN^- , followed by the titration. The *ex situ* calibration employed equilibration of the electrodes in a solution of the target medium in a separate cell, transfer to the titrand in a second cell, followed by the titration. All other aspects of the two sets of titrations at $I = 1$ M (NaCl) were essentially the same. In both sets of measurements the cell contents were gently stirred throughout the titrations.

To minimise cyanide losses by volatilisation of HCN(aq), sparging with nitrogen was discontinued at $\text{pH} \approx 10$ but the cell solutions were maintained under a nitrogen blanket.

For cyanide protonation titrations, the initial cell solutions consisted of (5 to 20) mM NaCN in 10 mM NaOH and the appropriate amount of NaCl. For the Cu^+/CN^- complexation studies, the initial cell concentration of Cu^+ was either (5 or 10) mM and the mole ratio of Cu:CN ranged from 1:3 to 1:10 (Solis) or 1:4 to 1:7 (Akilan). The titrant was typically 100.0 mM HCl at the target ionic strength. Titrations were terminated when a visible white precipitate, presumably CuCN(s) , started to form; a few of the measurements preceding precipitation were discarded before processing. Titration data were analysed using the ESTA (Equilibrium Simulation for Titration Analysis) suite of programs (May *et al.*, 1985, 1988).

2.3 Solubility measurements

The solubility of CuCN(s) was measured at $(25 \pm 0.05)^\circ\text{C}$ in solutions containing appropriate concentrations of NaCN, HCN and NaCl in a thermostated pyrex-glass percolation apparatus (Gamsjäger and Königsberger, 2003). The approach to equilibrium was followed using a GE and a low-leakage commercial Ag/AgCl reference electrode (Orion, USA, Model 90-02). A slow stream of high purity nitrogen, which was pre-saturated with respect to both water vapour and HCN(g) using in-line solutions of identical composition, was maintained throughout. Saturated solutions were considered to be at equilibrium when the potential drift was <0.1 mV/h. Equilibration times were typically (24 to 48) h. Filtered samples of the saturated solutions were allowed to oxidize in air and the Cu(II) determined by electrogravimetry (Owen *et al.*, 1983).

3. RESULTS AND DISCUSSION

3.1 Water ionization and protonation constants

Because HCN is a very weak acid ($pK_a^0 = 9.21$ at $25\text{ }^\circ\text{C}$), to evaluate the $\text{Cu(I)}/\text{CN}^-$ complexes (eq. 1) it is necessary to make measurements at high pH. Consequently, quantification of the ionization constant of water:



$$K_w = [\text{H}^+][\text{OH}^-] \quad (8)$$

and the protonation (dissociation) constant of HCN:



$$K_a = \frac{[\text{H}^+][\text{CN}^-]}{[\text{HCN}^0]} \quad (10)$$

is also required. The former were determined by strong acid/strong base titrations in 1, 3 or 5 M (NaCl) as appropriate. The results obtained are summarized as pK_w values in Table 1 and are in excellent agreement ($\leq \pm 0.01$) with previous determinations in the same media (Verhoeven et al., 1990; Kron et al., 1995). The cyanide protonation constants, as $pK_a(\text{HCN})$, are also listed in Table 1 and agree to within about ± 0.01 with earlier measurements from our laboratory (Verhoeven et al., 1990) even at the highest ionic strength. Note that the standard deviations given in the footnotes to Table 1 for the present work are ‘internal’ values, determined from the statistical analysis of the titration data. True uncertainties will be greater than those listed in Table 1 because many of the experimental errors in potentiometric titrations are systematic (May and Murray, 1988).

Table 1. Comparison of present and literature values for the ionization constant of water, pK_w , and protonation constant for cyanide, $pK_a(\text{HCN})$, at varying ionic strengths in NaCl media at 25 °C.

<i>I/M</i>	pK_w^a	Data ^b	Literature ^c	$pK_a(\text{HCN})^d$	Data ^b	Literature ^c
1.0 ^e	13.717	304/10	13.714	8.967	NA ^f	8.946
1.0	13.710	295/5	13.714	8.941	205/6	8.946
3.0	13.977	326/6	13.989	9.208	136/6	9.220
5.0	14.448	235/5	14.465	9.649	128/5	9.660

^a Present results; standard deviation 0.001. ^b Number of data points/number of titrations. ^c Verhoeven et al. (1990). ^d Present results; standard deviation 0.003. ^e Data from Solis (1995). ^f Details not available.

3.2 Copper(I)/cyanide complexes by potentiometric titrations

Formation constants for the Cu(I)/CN⁻ complexes (eqs. 1 & 2) were obtained by titrating differing total concentrations of Cu(I) at various Cu(I):CN⁻ ratios in alkaline solution with HCl at constant *I*. The results are summarized in Table 2.

Table 2. Present values of the formation constants for Cu(I)/CN⁻ complexes in NaCl media at 25 °C obtained using potentiometric data alone.^a

<i>I/M</i>	OBJT/10 ⁻⁸	$\log \beta_1^b$	$\log \beta_2$	$\log \beta_3$	$\log \beta_4$	$\log K_2^c$	$\log K_3^c$	$\log K_4^c$	Data
1.0 ^d	6.6	16.34	23.94	29.38	31.77	7.60	5.43	2.39	NA ^e
1.0	8.9	16.34	23.76	29.38	31.89	6.82	5.63	2.51	545/13
3.0	3.3	16.41	23.93	29.33	32.25	7.52	5.40	2.92	288/10
5.0	6.3	16.68	24.01	29.26	32.52	7.33	5.25	3.26	219/6

^a Standard deviations for $\log \beta_n$ values ($n \geq 2$) ranged from 0.01 to 0.04 under all conditions. OBJT is an objective function based on optimization of total concentrations (May et al., 1988). ^b Estimated values (see text). ^c Stepwise formation constants: $\log K_n = \log \beta_n - \log \beta_{n-1}$ corresponding to the equilibria: $\text{Cu}(\text{CN})_{n-1}^{(n-2)-}(\text{aq}) + \text{CN}^-(\text{aq}) \rightleftharpoons \text{Cu}(\text{CN})_n^{(n-1)-}(\text{aq})$ ^d Data from Solis (1995). ^e Details not available.

The reproducibility of the experimental data is illustrated in a plot (Figure 2) of the observed metal-ligand formation function, \bar{Z}_M , against the free ligand concentration (as p[L]), where:

$$\bar{Z}_M = \frac{T_L - A \left(1 + \sum_n \beta_{LH_n} [H^+]^n \right)}{T_M} \quad (11)$$

with

$$A = \frac{T_H - [H^+] + [OH^-]}{\sum_n n \beta_{LH_n} [H^+]^n} \quad (12)$$

where T_i denotes the total or analytical concentration of the species i .

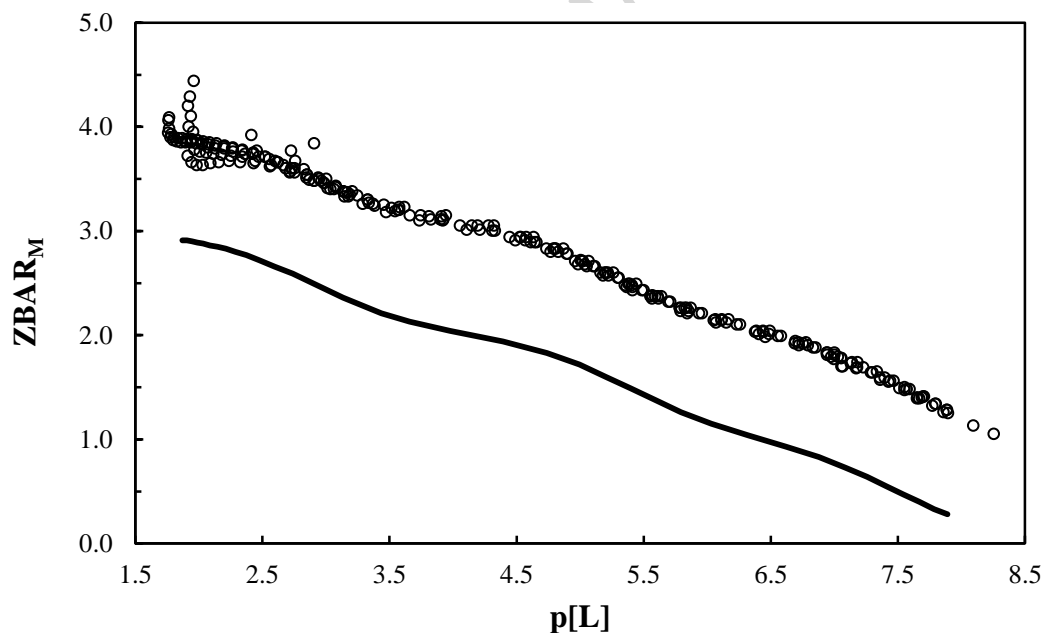


Figure 2. Representative plots of the metal formation function \bar{Z}_M ($ZBAR_M$) against $p[L]$ for the $Cu(I)/CN^-$ system in 3 M (NaCl) at 25 °C: observed data points (symbols); calculated (line; with $ZBAR_M$ offset by -1.0 for visual clarity).

All the data points lie close to a single line, indicating their excellent reproducibility. The slight differences and ‘curl-backs’ at $p[L] \leq 3$ (corresponding to relatively high pH) are thought

be due to the minor accumulation of errors in the data or possibly the formation of trace amounts of ternary $\text{Cu(I)/CN}^-/\text{OH}^-$ complexes. Attempts to include the latter in the speciation model were unsuccessful. Note that the observed \bar{Z}_M values (Figure 2) were independent of $[\text{Cu(I)}]_T$, indicating that ‘polynuclear’ species did not form to any significant extent under the present conditions. The (somewhat poorly defined) plateaus in the \bar{Z}_M plot correspond to the step-wise formation of $\text{Cu(CN)}_2^-(\text{aq})$, $\text{Cu(CN)}_3^{2-}(\text{aq})$ and $\text{Cu(CN)}_4^{3-}(\text{aq})$. Attempts to extend the measurements to $\text{p[L]} > 8$, corresponding to lower pH values, so as to obtain information on the formation of the 1:1 complex, $\text{CuCN}^0(\text{aq})$, were thwarted by the precipitation of $\text{CuCN}(\text{s})$. The agreement between the observed data and the proposed model (the heavy line in Figure 2) is excellent and the values of the objective function OBJT (May et al., 1988) are satisfactory.

Although $\text{CuCN}^0(\text{aq})$ could not be quantified from the potentiometric titration data (see above), its inclusion in the speciation model was required for the calculations to converge and also to fix the numerical values of the overall formation constants of the higher order ($n > 1$) species. A value of $\log\beta_1 = 16.34$ at $I = 1 \text{ M}(\text{NaCl})$ and $t = 25 \text{ }^\circ\text{C}$ was estimated using the JESS software and used to process the independently-measured potentiometric data sets of Akilan and Solis. Values of $\log\beta_1 = 16.41$ and 16.68 were estimated in the same manner for $I = 3$ and $5 \text{ M}(\text{NaCl})$ respectively. However, it should be noted that the ESTA optimizations showed that the $\log\beta_n$ values were linearly correlated. Accordingly, only differences between them, i.e., the stepwise formation constants $\log K_n$ ($n = 2, 3$ and 4), could be determined. Test optimizations confirmed that changing any of the β_n values by several orders of magnitude resulted in identical (to the 4th decimal place) stepwise formation constants. In other words, while the β_n values ($n \geq 2$) depend on the numerical value chosen for β_1 ($\equiv K_1$), the values of K_n ($n \geq 2$) do not.

The formation constants derived from the two independently-measured sets of data at $I = 1$ M (NaCl) are listed in Table 2. The level of agreement is gratifying; the small differences are a reflection of the real difficulties of quantifying the chemical speciation in this ‘difficult’ system. As the present formation constants of the Cu(I)/CN⁻ complexes are the only values available at high I in any medium (Kyle and Hefter, 2015) no direct comparison with literature data is possible.

A typical species distribution calculated for the Cu(I)/CN⁻ system at $I = 1$ M (NaCl) and $t = 25$ °C using the present β_n values (Table 2) is shown as a function of pH in Figure 3 over the range $3 \leq \text{pH} \leq 10$. As would be expected, at a given pH an increase in the CN⁻/Cu(I) ratio results in increased formation of the higher order complexes. Under the conditions of Figure 3 there are negligible amounts of free Cu(I) over the entire pH range and the higher order complexes dominate the speciation over most of the pH range.

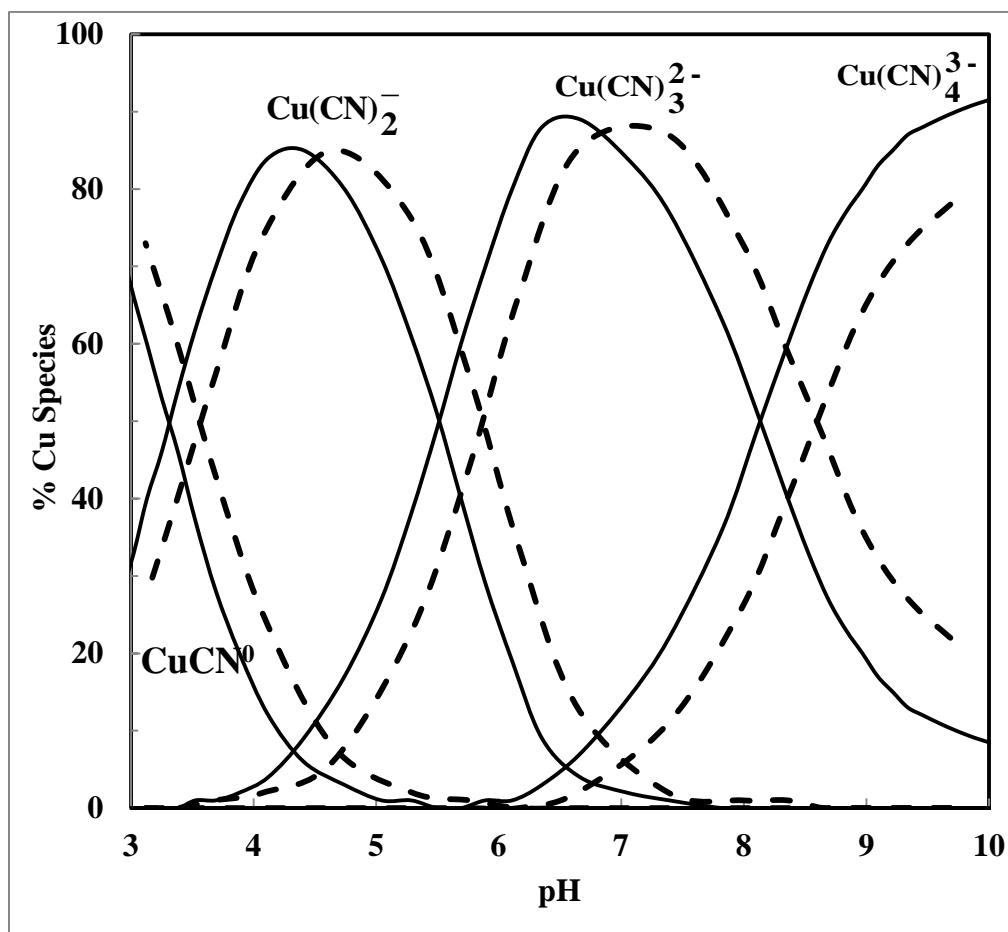


Figure 3. Species distribution for the Cu(I)/CN⁻ complexes as a function of pH in 3 M (NaCl) at 25 °C using the β_n values from Table 2: $[\text{CN}^-]_{\text{T}}/[\text{Cu}^+]_{\text{T}} = 7$ (full line) or 5 (dotted line); $[\text{Cu(I)}]_{\text{T}} = 0.005 \text{ M}$; $[\text{CN}^-]_{\text{T}} = 0.035 \text{ M}$ or 0.025 M . Note that at $\text{pH} < \text{ca. } 4.5$ the solutions are super-saturated with respect to CuCN(s).

3.3 Solubility of copper(I) cyanide

The solubility of CuCN(s) in aqueous solutions has been reviewed in detail by Fritz and Königsberger (1996) and briefly by Kyle and Hefter (2015). In pure water, where agreement among the few existing data is poor, the best estimate of the solubility corresponds (eqs. 3 & 4) to $\text{p}K_{\text{s}0}^{\circ} = 19.74$ at infinite dilution. This solubility product, originally determined by Vladimirova and Kakovskii (1950) but adjusted by Lu et al. (2002) using a more appropriate value of $\text{p}K_{\text{a}}$, implies an extremely low solubility for CuCN(s). However, equilibrium (3) is in essence

hypothetical because uncomplexed $\text{Cu}^+(\text{aq})$ is unstable. In practice the solubility of $\text{CuCN}(\text{s})$ is best measured in the presence of excess CN^- , which increases the solubility to more easily determined levels and stabilizes the dissolved $\text{Cu}(\text{I})$. The numerous data available under such conditions have been evaluated by Fritz and Königsberger (1996) and are in reasonable agreement. Those data included unpublished measurements from our laboratories on the solubility of $\text{CuCN}(\text{s})$ in HCN/NaCN buffers at $I = 0.15, 0.25, 0.50$ and 1.00 M (NaCl) and $t = 25$ °C (Königsberger et al., 1994). Unfortunately, because of the absence of reliable $\log \beta_n$ values at low I (Kyle and Hefter, 2015) only the data at $I = 1.00$ M (NaCl) can be re-examined at present. For convenience the relevant solubility data are reproduced in Table 3. Preliminary results reported by Solis (1995) are not considered reliable because of difficulties experienced in obtaining reproducible solubilities.

Table 3. Solubility of $\text{CuCN}(\text{s})$ in NaCN/HCN solutions at $I = 1$ M (NaCl) and $t = 25$ °C (after Königsberger et al., 1994).^a

$[\text{NaCN}]_{\text{T}}/\text{mM}$	$[\text{HCN}]_{\text{T}}/\text{mM}$	$\text{p}[\text{H}]_{\text{ini}}$	$\text{p}[\text{H}]_{\text{eqm}}$	$[\text{Cu}^+]_{\text{T,eqm}}/\text{mM}$
10.0	20.0	8.690	4.144	9.67
10.0	5.00	9.281	4.748	9.69
50.0	50.0	9.000	4.25	41.2
40.0	40.0	9.005	4.294	34.4
30.0	15.0	8.996	4.332	26.2
15.0	15.0	8.991	4.418	13.4
5.00	5.00	8.990	4.502	5.04

^a Subscript abbreviations: T – total; ini – initial; eqm – equilibrium.

The solubilities in Table 3 were re-analysed using the ChemSage optimizer (Königsberger and Eriksson, 1995). The optimization procedure adopted was to adjust the values of β_1 and K_{s0} with respect to the experimental solubility data, while those of pK_a and $\log \beta_n$ ($n \geq 2$) were fixed at the values listed in Tables 1 and 2. This re-evaluation gave $\log \beta_1 = 15.80 \pm 0.15$ and $pK_{s0} = 19.49 \pm 0.02$ at $I = 1$ M(NaCl) and 25 °C. Both of these values are broadly consistent with previous estimates.

Attempts to optimize pK_{s0} and all $\log \beta_n$ values (ie, including β_1) simultaneously using the solubility data alone were unsatisfactory. Test optimizations again showed that the $\log \beta_n$ values were linearly correlated and the same objective function was obtained when β_n values were changed by orders of magnitude. Thus, as for the homogeneous Cu(I)/CN⁻ system above, only the stepwise K_n values could be derived from the solubility data. Likewise it was established that K_{s0} could not be determined independently but the solubility constants (eqs. 5 & 6) $*K_{sn}$ (= $K_{s0} \beta_n K_a^{(n-1)}$), with $n = 2$ or 3, could be derived unambiguously. Note that the $n = 4$ species, Cu(CN)₄³⁻(aq), was insignificant in the restricted pH range (4.1 < pH < 4.7) of the present solubility measurements (*cf.* Fig. 3).

3.4 Simultaneous evaluation of solubility and potentiometric data

As is usual when processing results obtained by different techniques, unconstrained optimizations of either the potentiometric or solubility data *alone* led to somewhat inconsistent values (ca. ± 0.5) for $\log K_n$. Using a Bayesian optimization approach (Königsberger and Eriksson, 1995), the best method for processing both types of data was to take into account the likely predominant species in the pH ranges covered. This procedure resulted in a consistent set of constants for both the solubility and potentiometric data, with objective functions that were

only twice those found for the unconstrained optimizations. Assuming $pK_a = 8.941$ (Table 1) the following constants were determined at $I = 1$ M (NaCl) and 25 °C: $\log K_2 = 7.9 \pm 0.2$, $\log K_3 = 5.5 \pm 0.1$ and $\log K_4 = 2.45 \pm 0.05$; and $\log K_{s1} = -3.5 \pm 0.1$, $\log *K_{s2} = -4.50 \pm 0.01$ and $\log *K_{s3} = -7.95 \pm 0.10$. These $\log K_n$ values — with the exception of Akilan's $n = 2$ result — are the same, within the stated uncertainties, as those obtained from the potentiometric data alone (Table 2). This indicates a broad consistency between the present potentiometric and solubility data.

Note that only four of these constants are independent. The stated uncertainties reflect the (small) inconsistencies between the experimental data sets and their limited precision. The small uncertainty in $\log *K_{s2}$ is due to $\text{Cu}(\text{CN})_2^-(\text{aq})$ being the predominant species (ca. 80 % to 90 % of $[\text{Cu}]_T$) under the conditions of the solubility measurements. The present value of $\log *K_{s2}$ is numerically identical to that reported previously (Königsberger et al., 1994) but is much more precisely determined. It may be noted that the situation with respect to the solubility of $\text{CuCN}(\text{s})$ is similar to that of other solid electrolytes containing basic anions such as carbonate, phosphate or sulfide. As discussed by Gamsjäger and Königsberger (2003) the solubility constants for such systems are meaningful only when evaluated within a reliable aqueous speciation model.

3.5 Hydrometallurgical implications

As noted in the Introduction, reliable and relevant thermodynamic data are becoming increasingly important in the modelling of complex hydrometallurgical systems. The software currently used in most simulations almost invariably attempts to convert constants obtained under standard conditions (25 °C and infinitely dilute solutions) into values that can be used to model hydrometallurgical processes working at much higher temperatures and ionic strengths. This can result in the use of inappropriate and/or unreliable constants for the construction of, for

example, Pourbaix or species-distribution diagrams (Figures 1 & 3) relevant to the required process conditions. In the current study, the effects of changes in ionic strength (in NaCl solutions) on the equilibrium constants pK_w , $pK_a(\text{HCN})$, and $\log \beta_n$ for Cu(I)/CN⁻ complexes have been determined. In addition, a more accurate estimation of the solubility constants \log^*K_{sn} for solid copper(I) cyanide at $I = 1 \text{ M}$ (NaCl) has been accomplished.

From these data, it is clear that the changes in ionic strength can alter significantly the species-distribution and Pourbaix diagrams for this system. For example, under the alkaline conditions that apply in gold leaching ($\text{pH} = 10$) and a CN⁻/Cu(I) ratio of ≥ 4 , the relative concentrations of Cu(CN)₄³⁻(aq) and Cu(CN)₃²⁻(aq) change from 2.7:1 in 1 M (NaCl), to about 6:1 in 3 and 5 M (NaCl), which corresponds to an increase in cyanide consumption by the copper present. These calculations are consistent with data from the Eastern Goldfields of Western Australia where, in the presence of hypersaline waters, it has been shown (Lukey et al., 1999) that the predominant copper species in gold leaching solutions is Cu(CN)₄³⁻(aq). Copper(I)-cyanide complexes are thought to adsorb onto activated carbon via an ion pairing mechanism involving cations such as Ca²⁺ (Marsden and House, 2006), with the adsorption affinity following the order: Cu(CN)₂⁻(aq) > Cu(CN)₃²⁻(aq) >> Cu(CN)₄³⁻(aq) (Dai et al., 2010). It follows that an increase in the concentration of the less-well-adsorbed Cu(CN)₄³⁻(aq) relative to Cu(CN)₃²⁻(aq) at higher ionic strengths will decrease total copper adsorption onto carbon, thereby enhancing gold adsorption. Clearly, an increase in Cu(CN)₄³⁻(aq) in solution produces a competition between higher cyanide consumption and improved gold adsorption.

In addition, there are a number of processes for the recovery of cyanide from copper(I) cyanide solutions (e.g., the Sceresini, AVR and SART processes) that rely on acidification to increase the concentrations of the di-cyano complex and even to precipitate the copper as CuCN(s) (Dai et al, 2012, and references therein). These processes are difficult to model at present due to the scarcity of reliable information of the Cu(I)/CN^- equilibria at low pH under process conditions. The present combination of solubility and stability constant measurements should significantly improve the reliability of such calculations.

REFERENCES

- Beck, M.T., 1987. Critical survey of stability constants of cyano complexes. *Pure Appl. Chem.* 59, 1703-1720.
- Bek, R.Y., Zhukov, B.D., Borodikhina, L.I., Poddubny, N.P., 1972. Investigation of the electro-deposition of copper from cyanide electrolytes. II. Copper cyanide association constants, *Izv. Sibirsk. Otdel. Acad. Nauk SSSR, Ser. Khim. Nauk* 9, (4) 52-56.
- Botz, M.M., Fleming, C.A., Ford, K.J.R., 2011. Cyanide leaching of gold-copper porphyries: chemistry and challenges. In Deschênes, G., Dimitrakopoulos, R., Bouchard, J., Eds., *World Gold 2011, CIMM, Canada*, 285-301.
- Breuer, P.L., Jeffrey, M.I., Hewitt, D.M., 2008. Mechanisms of sulphide ion oxidation during cyanidation. Part I; The effect of lead(II) ions. *Minerals Engineering* 21, 579-586.
- Dai, X., Jeffrey, M.I., Breuer, P.L., 2010. A mechanistic model of the equilibrium adsorption of copper cyanide species onto activated carbon. *Hydrometallurgy* 101, 99-107.
- Dai, X., Simons, A., Breuer, P., 2012. A review of copper cyanide recovery for the cyanidation of copper containing gold ores. *Minerals Eng.*, 25, 1-13.
- Fritz, J.J., Königsberger, E., 1996. *IUPAC Solubility Data Series, Volume 65, Copper(I) Halides and Pseudohalides.*, Oxford University Press, Oxford, pp. 261-275.
- Gamsjäger, H., Königsberger, E., 2003. Solubility of sparingly soluble ionic solids in liquids. In Hefter, G.T., Tomkins, R.P.T., Eds., *The Experimental Determination of Solubilities*, Wiley, New York.
- Greenwood, N.N., Earnshaw, A., 1997. *Chemistry of the Elements*. Butterworth-Heinemann, Oxford, 2nd Edn.
- Habashi, F., 1987. One hundred years of cyanidation, *CIM Bulletin* 80, (905) 108-114.
- Hefter, G., May, P.M., Sipos, P., 1993. A general method for the determination of copper(I) equilibria in aqueous solution. *J. Chem. Soc. Chem. Commun.*, 1704-1706.
- Hewitt, D.M., Breuer, P.L., Jeffrey, M.I., 2009. Mechanisms of sulphide ion oxidation during cyanide leaching. Part II. Surface catalysis by pyrite. *Minerals Engineering* 22, 1166-1172.
- Königsberger, E., Solis, J.S., May, P.M., Hefter, G.T., 1994. Solubility constants of AgCN and CuCN. 6th International Symposium on Solubility Phenomena, Buenos Aires, Argentina, cited in Fritz and Königsberger (1996), p. 274.

- Königsberger, E., Eriksson, G., 1995. A new optimization routine for ChemSage. *CALPHAD* 19, 207-214.
- Kron, I., Marshall, S.L., May, P.M., Hefter, G.T., Königsberger, E., 1995. The ionic product of water in highly concentrated aqueous electrolyte solutions. *Monatsh. Chem.* 126, 819-837.
- Kyle, J.H., Hefter, G.T., 2015. A critical review of the thermodynamics of hydrogen cyanide and copper(I)-cyanide complexes in aqueous solution. *Hydrometallurgy* 154, 78-87.
- Kyle, J.H., Aye, K.T., Breuer, P.L., Meakin, R.L., 2011. The dissolution of covellite and chalcocite in cyanide solutions. In Deschênes, G., Dimitrakopoulos, R., Bouchard, J., Eds., *World Gold 2011*, CIMM, Canada, 533-544.
- Lu, J., Dreisinger, D.B., Cooper, W.C., 2002. Thermodynamics of the aqueous copper-cyanide system. *Hydrometallurgy* 66, 23-36.
- Lukey, G., Van Deventer, J., Huntington, S., Chowdhury, R., Shallcross, D., 1999. Raman study on the speciation of copper cyanide complexes in highly saline solutions. *Hydrometallurgy* 53, 233-244.
- Marsden, J.O., House, C.I., 2006. *The Chemistry of Gold Extraction*, 2nd ed. Society for Mining, Metallurgy, and Exploration, Littleton, Colorado. Chapter 6.
- May, P.M., Murray, K., Williams, D.R., 1985. The use of glass electrodes for the determination of formation constants. II: Simulation of titration data. *Talanta* 32, 483-489.
- May, P.M., Murray, K., Williams, D.R., 1988. The use of glass electrodes for the determination of formation constants. III: Optimization of titration data: The ESTA library of computer programs. *Talanta* 35, 825-830.
- May, P.M., Murray, K., 1988. The use of glass electrodes for the determination of formation constants. V: Monte Carlo analysis of error propagation. *Talanta* 35, 933-941.
- Owen, J.F., Patterson, C.S., Rice, G.S., 1983. Electrogravimetric determination of cobalt, nickel, and copper in presence of chloride ion. *Anal. Chem.* 55, 990-992.
- Sharpe, A.G., 1976. *The Chemistry of Cyano Complexes of the Transition Metals*, Academic Press, New York.
- Solis, J.S., 1995. *Thermodynamics of Cyanide Complexes*. Ph.D. Thesis, Murdoch University.
- Verhoeven, P., Hefter, G., May, P.M., 1990. Dissociation constant of hydrogen cyanide in saline solutions. *Miner. Metall. Process.* 7, 185-188.

Vladimirova, M.G., Kakovskii, I.A., 1950. The physicochemical constants characteristic of the formation and composition of the lowest cuprous cyanide complex. J. Appl. Chem. USSR, 23, 580-598 and 615-632.

Vogel, A.I., 1961. A Textbook of Quantitative Inorganic Analysis, 3rd edition, Longmans, London.

ACCEPTED MANUSCRIPT

Highlights

- Formation and equilibrium constants for aqueous copper cyanide complexes.
- Includes measured dissociation constants for hydrogen cyanide and water.
- Formation and equilibrium constants measured 1, 3 and 5 M ionic strength.
- Solubility Constant for CuCN(s) also determined from reaction with HCN(aq) .
- Implications for hydrometallurgical processes at high ionic strength discussed.

ACCEPTED MANUSCRIPT