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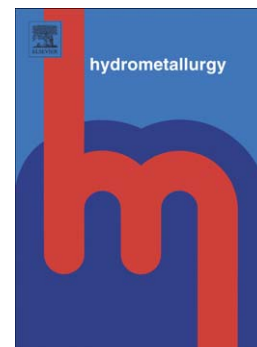
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**A Critical Review of the Thermodynamics of Hydrogen Cyanide and Copper(I)-Cyanide
Complexes in Aqueous Solution**

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Abstract

Despite the importance of cyanide and of metal-cyanide complexes in gold hydrometallurgy, and the need for reliable thermodynamic data for modelling gold solution chemistry, no comprehensive critical overview of the thermodynamics of hydrogen/cyanide and metal/cyanide complex formation has appeared in the literature since that of Beck in 1987. In particular there has been little consideration of the values of the equilibrium constants (and related thermodynamic parameters) at the higher ionic strengths and non-standard temperatures more typical of hydrometallurgical processing. The copper(I)/cyanide system is of particular importance in gold hydrometallurgy as gold is often associated with copper sulfide minerals such as chalcopyrite, chalcocite, covellite and bornite, all of which except chalcopyrite are reasonably soluble in cyanide solutions due to the formation of copper(I)/cyanide complexes. This paper reviews the available thermodynamic data for the hydrogen/cyanide and copper(I)/cyanide systems in aqueous solution with special emphasis on measurements made at elevated ionic strengths and as a function of temperature. It has been found that, while reliable data are available at 25 °C and very low ionic strengths, the data for higher ionic strengths and temperatures are limited. An attempt has been made to rationalize the available data, and to point out areas where further careful measurements are desirable.

Keywords

Cyanide, copper(I), protonation, enthalpy, equilibrium constant, gold, hydrometallurgy, thermodynamics

1. Introduction

Gold associated with sulfidic copper occurs in many ore bodies. When such ores are processed by flotation the gold generally reports to the flotation concentrate, with only minor amounts of copper and gold remaining in the flotation tailings. The gold in the latter, however, is often sufficient to warrant treatment with cyanide to recover the precious metal value that would otherwise be lost. This poses a problem because residual copper minerals in the flotation tailings, generally at concentrations well in excess of the remnant gold, can also be dissolved by the cyanide. Such copper species compete with gold for the cyanide ions in solution and also for adsorption sites on the activated carbon used to recover the gold from solution. In addition, there is usually an environmental requirement for copper to be removed from tailings water prior to disposal or recycling (Marsden and House, 2006). This leads to significant additional processing costs because of increased cyanide consumption and the subsequent need to destroy cyanide in the tailings water (Johnson, 2014).

Copper is in the same Group (1B) of the periodic table as silver and gold and, although less noble, has a similar chemistry. Early work (Leaver and Woolf, 1931; Hedley and Tabachnick, 1958; Shantz and Fisher, 1977) established that most commercially-important copper minerals, except chalcopyrite, are reasonably soluble in cyanide solutions. A range of copper(I)-cyanide complexes, chiefly: $\text{Cu}(\text{CN})_2^-$, $\text{Cu}(\text{CN})_3^{2-}$ and $\text{Cu}(\text{CN})_4^{3-}$, are formed, with the higher-order complexes dominating in alkaline solutions, especially at higher cyanide concentrations (Botz et al., 2011, Dai et al., 2012). A typical speciation diagram is shown in Figure 1. As well as consuming significant amounts of cyanide through the formation of these complexes, the oxidative dissolution of copper sulfide minerals in cyanide solutions also results in losses due to the irreversible conversion of cyanide to thiocyanate (SCN^-) and cyanate (OCN^-). Furthermore, a decrease in the concentration of dissolved oxygen in solution occurs due to the oxidation of sulfide ions to sulfite and thiosulfate resulting in lower rates of gold dissolution (Breuer et al., 2007).

Moreover, as noted above, Cu(CN)_2^- and Cu(CN)_3^{2-} compete with gold for adsorption sites on activated carbon resulting in lower gold recoveries (Ibrado and Fuerstenau, 1989; Dai et al., 2012). Dai et al. (2010) have developed a mechanistic model to better understand the competitive adsorption of gold(I)- and copper(I)-cyanide complexes onto activated carbon. They found that reported standard state (infinite dilution) equilibrium constants were unable to account satisfactorily for their observations whereas constants determined at higher ionic strength (I) could. In addition, Lukey et al. (1999) have shown qualitatively, using Raman spectroscopy, that the speciation among the Cu(I)-CN^- complexes in solution can vary significantly with changes in ionic strength. However, current knowledge of the equilibrium constants for the Cu(I)-CN^- complexes at high ionic strengths is limited and inadequate for modelling this behaviour.

Another significant concern in processing copper-containing gold ores is the discharge of Cu(I)-CN^- complexes to tailings storage facilities. This is because such complexes, like most metal cyanide species, are highly toxic to most forms of animal life. Deaths of birds, fish and other animals, occurring as a result of cyanide discharges from gold mines are well-documented (Donato et al., 2007). High profile examples include the cyanide spills due to the collapse of tailings dams at Omai in Guyana and Baia Mare in Romania. The Romanian disaster serves to highlight this problem as Cu(I)-CN^- complexes were traced for some 2000 km through many countries to the mouth of the Danube River (Korte et al., 2000; Kovács et al., 2014).

The increasing restrictions on the discharge of Cu(I)-CN^- complexes to tailings dams has led to the development of various processes to economically treat copper-containing gold ores by recovering the copper and recycling the cyanide. Two procedures that have been in commercial use are the acidification-volatilisation-regeneration (AVR) process (Riveros et al. 1993; Stevenson et al., 1998) and the sulfidation-acidification-recycle-thickening (SART) process (Barter et al., 2001; Fleming, 2005). Neither of these processes is straightforward due to the need for solid-liquid separation so as to obtain a clear solution prior to treatment, and the difficulty in effectively lowering cyanide to acceptable levels by acidification. An alternative method for the recovery of Cu(I)-CN^- complexes from waste solutions using ion exchange resins

has also received considerable attention due to the strong affinity of certain resins for metal-cyanide complexes (van Deventer et al., 2014; Silva et al., 2003; Leao and Ciminelli, 2002; Fernando et al., 2002; Leao et al., 2001; Lukey et al., 1999; 2000). However, economically-viable elution and recovery of both the copper and the cyanide has proven to be problematic. Direct electrowinning of copper from waste streams has also been investigated (Lemos et al., 2006, Dutra et al., 2008; Lu et al., 2002a) but generally has a low current efficiency, due to the low copper concentrations, with a resultant high energy consumption. Moreover, the cyanide can be partially destroyed by oxidation at the anode.

The importance of Cu(I)-CN^- complexes in the treatment of copper-gold ores, and the increasing need for reliable modelling of such processes so as to better optimize them, means that reliable knowledge of the thermodynamics of the Cu(I)-CN^- system under hydrometallurgically-relevant conditions has become crucial. In particular, there is a need for reliable equilibrium constants measured (or calculated using appropriate thermodynamic relationships) at different temperatures, ionic strengths and solution (background electrolyte) composition. A recent review of the thermodynamics of the aqueous Cu(I)-CN^- system compiled by Lu et al. (2002b) from the plethora of often conflicting information in the literature presents only a list of recommended equilibrium constants at zero ionic strength (infinite dilution) and mostly at 25 °C. As already noted, such constants do not accurately describe observed behaviour under working conditions.

Given these issues, it is clear that accurate knowledge of the equilibrium constants for the Cu(I)-CN^- complexes under cyanide-leaching, carbon-adsorption (low temperature and high or low ionic strength) and carbon-desorption (high temperature and high ionic strength) conditions is of great importance in modelling and understanding these processes. Accordingly, this paper presents a critical review of the available thermodynamic data for the Cu(I)-CN^- system with special emphasis on measurements made under more practical conditions of temperature and ionic strength, as is required for the modelling of actual gold extraction procedures.

However, before such a review can be undertaken it is necessary to consider two other equilibria that are always present in Cu(I)-CN⁻ solutions: the self-ionization of water and the dissociation of hydrogen cyanide (hydrocyanic acid).

2. Dissociation Constants for Water and Hydrogen Cyanide

In any study of the formation of Cu(I)-CN⁻ complexes under varying conditions of pH, solution composition, temperature and pressure, precise knowledge of the dissociation of water and of hydrogen cyanide (HCN) under the same conditions is also required. This is because both of these equilibria occur to some extent in all metal-cyanide solutions and therefore must be included in any meaningful quantitative treatment of the chemical speciation in such solutions.

A detailed review of the vast body of data for the dissociation of water:



is beyond the scope of this paper. An excellent (if by now a little old) coverage of the data available for this important equilibrium over a wide range of conditions is given in the book of Baes and Mesmer (1976). It is also worth noting some more recent data obtained under conditions of interest to the present study: glass-electrode potentiometric values, at high ionic strengths in various salt solutions (Kron et al., 1995), of the ionic product of water, $\text{p}K_w = -\log(K_w = [\text{H}^+][\text{OH}^-])$, corresponding to eq. (1) where the square brackets denote concentrations; and the calorimetric determination of the corresponding enthalpy of ionization of water in concentrated NaCl(aq) and NaClO₄(aq) by Solis et al. (1996a).

The dissociation of hydrogen cyanide in aqueous solution:



for which the equilibrium constant can be written:

$$K_a = [\text{H}^+][\text{CN}^-]/[\text{HCN}] \quad (3)$$

has been well studied (Table 1). Comprehensive (non-critical) listings of the data available to the end of 1974 are provided in the successive compilations of Sillén and Martell (1964, 1971) and Högfeltdt (1982), while a few additional values are given in the data selected by Smith and Martell (1976, 1982, 1989). Subsequent investigations were collected from the literature and from the Joint Expert Speciation System (JESS) database of May and Murray (2000). As many of the earlier studies are now only of historic interest, Table 1 lists only those values obtained at or close to 25 °C that are thought to be reliable by the present authors.

Of the numerous results reported at infinite dilution (Table 1) the most recent independent estimate of $pK_a^\circ(\text{HCN})$ at 25 °C appears to be that of Finch et al. (1993), who calculated a value of 9.24 (without providing uncertainty limits) from the standard molar Gibbs energies of formation, $\Delta_f G_m^\circ$ (Wagman et al., 1982), for $\text{CN}^-(\text{aq})$, $\text{H}_2\text{O}(\text{l})$, $\text{HCN}(\text{aq})$ and $\text{OH}^-(\text{aq})$. However, it should be noted that such calorimetrically derived data are not generally considered to be the most precise way of determining equilibrium constants (Cabani and Gianni, 1972; Hedwig and Powell, 1973; Powell et al., 2007). The JESS software package (May and Murray, 2000) can also be used to calculate a weighted-average value of $pK_a^\circ(\text{HCN})$ at 25 °C using a specific interaction theory (SIT)-like equation (May, 2000), its own database (which includes most, but not all, of the data in Table 1) and subjective weights assigned by the database compilers. This procedure gives $pK_a^\circ = 9.19$ at 25 °C. Because of their inclusive nature (no data are omitted) and the subjectivity of the assigned weightings, no error limits are assigned to JESS-derived values.

It is noteworthy that these two most recent values of $pK_a^\circ(\text{HCN}) = 9.19$ and 9.24 closely straddle the zero ionic strength value of $pK_a^\circ(\text{HCN}) = 9.21 \pm 0.02$ at 25 °C selected by Beck (1987) in his critical review for IUPAC. Beck's estimate was based on three independent studies (Ang, 1959; Izatt et al., 1962; Boughton and Keller, 1966) that used extrapolations or calculations employing extended Debye-Hückel equations and which are in quantitative agreement with each other, within their stated error limits. It should be noted that this value has been accepted in many subsequent studies (see for example, Banyai et al., 1992; Verhoeven et

al., 1992; Solis et al., 1996; Lu et al., 2002b) and by Smith and Martell (1976, 1982). Given this acceptance and its consistency with the more recent data (as discussed above), Beck's recommendation of $pK_a^0(\text{HCN}) = 9.21 \pm 0.02$ at 25 °C will be retained as the best available estimate at the present time, pending further high quality studies.

2.1 Effects of Ionic Strength on pK_a

The effects of ionic strength (I) on the dissociation of $\text{HCN}^0(\text{aq})$ have been studied in lithium and sodium perchlorate (Banyai et al., 1992), sodium chloride (Verhoeven et al., 1990a,b), sodium perchlorate (Gáspár and Beck, 1982; Verhoeven et al., 1990b; Solis et al., 1996a) and sodium nitrate media (listed in Beck, 1987). These data are summarized in Table 1. Note, however, that most of the values of Gáspár and Beck(1982) at high I in NaClO_4 , endorsed by Beck in his 1987 review, have been shown to be erroneous (Banyai, et al., 1992; Solis et al., 1996a) and so have been omitted.

The most comprehensive data to date on the effects of I on $pK_a(\text{HCN})$ are the determinations by glass-electrode potentiometry at $0.1 \leq I/M \leq 5$ in NaClO_4 (Solis et al., 1996a) and NaCl (Verhoeven, 1989; Verhoeven et al., 1990a) media at 25 °C. The variation of $pK_a(\text{HCN})$ with increasing I in these two media (Figure 2) is as expected from electrolyte solution theory: an initial decrease followed by a larger increase at higher I . That said, the magnitude of the changes in pK_a differs considerably between the two electrolytes, particularly at $I > 1$ M. This reflects the specific short-range interactions of the background electrolyte with the interacting species of eq. (2). It is apparent from Table 1 that very few of the values of $pK_a(\text{HCN})$ at finite I have been confirmed by independent measurements in any of the studied media. The only exceptions (Figure 2) are at $I = 3, 1$ and 0.1 M(NaClO_4) where the respective results of Persson (1971), Banyai et al. (1992) and (surprisingly; see above) Gáspár and Beck(1982), mostly obtained by glass-electrode potentiometry, are in excellent agreement with those of Solis et al. (1996a).

It is clear from even the relatively few data currently available that there is significant variation in the dissociation constant for hydrogen cyanide with ionic strength (Table 1, Figure 2). There is also a significant dependence on the nature of the background electrolyte employed, especially at concentrations above 1 M. While Banyai et al. (1992) have had some success in predicting values of $pK_a(\text{HCN})$ in various media using the semi-empirical specific interaction theory (SIT), fundamental electrolyte solution theory (i.e., without empirical parameters) is unable to estimate accurate dissociation constants in this region (Grenthe and Puigdomenech, 1997). This means that further determinations of $pK_a(\text{HCN})$ at high ionic strengths are desirable for a range of added electrolytes to better identify the most appropriate values for use in practical applications.

2.2 Enthalpies and Entropies of Dissociation

The enthalpies (ΔH_a) and entropies (ΔS_a) for the dissociation of hydrogen cyanide in aqueous solution, eq. (2), have been determined in very dilute solutions (Christensen et al., 1970; Izatt et al., 1962) and at higher I in NaCl and NaClO₄ media (Solis et al., 1996a). The results are compiled in Table 2 and show the significant dependence of ΔH_a and ΔS_a for the ionization of HCN on temperature (at infinite dilution) and on the medium (at 25 °C).

At infinite dilution, $\Delta G_a^\circ (= -RT \ln K_a^\circ)$, the standard Gibbs energy change for the ionization of HCN⁰(aq), eq. (2), remains relatively constant with rising temperature (Table 2) but this is only because the independent variables ΔH_a° and ΔS_a° both become much less positive/more negative (Christensen et al., 1970). This so-called enthalpy/entropy compensation (EEC) effect can be rationalized in terms of increased hydration and solvent ordering around the highly polar hydrogen and cyanide ions as the extent of dissociation increases. Such effects are quite common in solution equilibria (Hefter et al., 2002).

As the ionic strength is increased at 25 °C in NaClO₄ media, the ΔG_a , ΔH_a and ΔS_a values initially remain relatively constant (Table 2). However, between 3 M and 5 M, ΔG_a becomes more positive by 3.2 kJ/mol.

This corresponds to ΔH_a becoming *less* positive by 4.6 kJ/mol, but being more than compensated by ΔS_a becoming much more negative. It is apparent that significant changes in the hydration and solvent ordering around the dissolved species occur in this region. In NaCl media the situation is different, with ΔG_a essentially tracking ΔH_a , both becoming more positive with increasing I . Clearly the solvation of Cl^- and ClO_4^- ions are quite different at high I . The use of dielectric relaxation spectroscopy to better understand the exact nature of the species present and their levels of hydration (Buchner and Hefter, 2009) would be particularly useful with regard to understanding these effects.

2.3 Effect of Temperature on pK_a

There have been a number of studies on the variation of $pK_a(\text{HCN})$ with temperature (Bek et al., 1972; Boughton and Keller, 1966; Broderius, 1981; Christensen et al., 1970; Izatt et al., 1962; Tsionopoulos et al., 1976). There is general agreement (Verhoeven et al., 1990a) between the directly measured values (Boughton and Keller, 1966; Izatt et al., 1962) and those obtained by calorimetry (Christensen et al., 1970). These results are preferred to those of Broderius (1981), who used a non-equilibrium method to determine HCN concentrations in the vapour phase.

The variation of the standard dissociation constant of HCN in the near-ambient temperature range of (0 to 50) °C can be satisfactorily described using the simple van't Hoff thermodynamic relationship:

$$pK_a^\circ(T) = pK_a^\circ(T_r) + \frac{\Delta H^\circ}{2.303R} \left[\frac{1}{T} - \frac{1}{T_r} \right] \quad 4(a)$$

where T denotes the temperature in Kelvin and T_r is the reference temperature of 298.15 K. This relationship is based on the usually-reasonable assumption that $\Delta C_{p,a}^\circ$, the heat capacity change for the dissociation reaction, is zero, meaning that ΔH° is a constant and independent of temperature, over the normal liquid range of water (Kotrlý and Šůcha, 1985).

Adopting the calorimetrically-derived value of $\Delta H_a^\circ = 43.6$ kJ/mol (Christensen et al., 1970), eq. (4a) produces a straight line plot of $\text{p}K_a^\circ(T)$ vs. $1/T$ (Figure 3) that provides a reasonable fit of the experimental data (Boughton and Keller, 1966; Broderius, 1981; Izatt et al., 1962) over this limited temperature range. Nevertheless, some curvature in the $\text{p}K_a^\circ$ results (particularly the averaged values) as a function of temperature is apparent even in Figure 3. For wider ranges of temperature (Table 2) it is essential to use the more accurate equation employed by Verhoeven et al. (1990a) in which the non-zero value of $\Delta C_{p,a}^\circ$ is taken into account (note that there is a typographical error in the published equation of Verhoeven et al. (1990a): the third term on the rhs of their eq. (3) is missing a minus sign in front of the $\ln(T/T_r)$ term. This error is repeated in eq. (3) of Solis et al. (1996a)).

The correct form of the equation is:

$$\text{p}K_a^\circ(T) = \text{p}K_a^\circ(T_r) + \frac{\Delta H^\circ(T_r)}{2.303R} \left[\frac{1}{T} - \frac{1}{T_r} \right] + \frac{\Delta C_{p,a}^\circ}{2.303R} \left[1 - \frac{T_r}{T} - \ln \left\{ \frac{T}{T_r} \right\} \right] \quad 4(b)$$

Using this equation 4(b) with $\Delta C_{p,a}^\circ = 251$ J K⁻¹ mol⁻¹ (Christensen et al., 1970), gives $\text{p}K_a^\circ(T)$ values that are in good agreement with the limited data at higher temperatures (Table 2), although there is some suggestion (Tsonopoulos et al., 1976) that $\Delta C_{p,a}^\circ$ may be slightly temperature dependent.

Unfortunately, all of the preceding discussion is limited to (near) infinite dilution. Further information on the variation of $\text{p}K_a$, ΔH_a and $\Delta C_{p,a}$ with ionic strength and temperature will be required to permit more accurate calculation of $\text{p}K_a(T)$ under all conditions of practical interest.

To summarize, even though the dissociation constant for hydrogen cyanide, eq. (2), has been well studied at 25 °C and at low ionic strengths, there are few data on how $\text{p}K_a(\text{HCN})$ varies with ionic strength, solution composition and temperature. Verhoeven et al. (1990a) and Solis et al. (1996a) have made significant

contributions to measuring the variations of pK_a and ΔH_a with ionic strength and medium, but almost no further information on the effect of temperature on pK_a has been published since the work of Izatt et al. (1962), Boughton and Keller (1966) and Tsonopoulos et al. (1976) some 40 to 50 years ago. Further accurate studies in this area (and the alternative of calorimetric determinations of the corresponding enthalpies and heat capacities) are desirable.

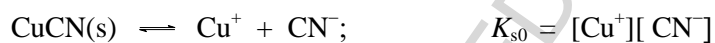
3. Aqueous Chemistry of Copper(I)-Cyanide Complexes

The documented coordination chemistry of copper(I) is rather limited (see for example, Greenwood and Earnshaw, 1997), particularly with regard to changes in equilibrium constants with ionic strength (Hefter et al., 1993). This is mostly because Cu(I) is generally unstable in aqueous solutions being readily oxidised to Cu(II) ($E^\circ = 0.168$ V) and having a tendency to disproportionate to Cu(II) and Cu⁰ ($K_{\text{disp}} \sim 10^5$, Greenwood and Earnshaw, 1997). However, Cu(I) can be stabilised in aqueous solution by the addition of certain ligands such as cyanide, or by changes in the electrolyte medium, e.g., by using chloride (Hefter et al., 1993).

At relatively low cyanide concentrations, Cu(I) forms the sparingly soluble cuprous cyanide, CuCN(s) (Vladimirova and Kakovskii, 1950; van Deventer et al., 2014). In excess cyanide, CuCN(s) dissolves to form di-, tri- and tetra-cyanocuprate(I) species (Chantry and Plane, 1960; Solis, 1995). These complexes are also formed when potassium tetracyanocuprate, $K_3Cu(CN)_4$, is dissolved in aqueous solutions (Baxendale and Westcott, 1959; Izatt et al., 1967; Kappenstein and Hugel, 1974; Penneman and Jones, 1956; Simpson and Waing, 1958). Copper(I)-cyanide complexes can also be formed by mixing aqueous solutions of Cu(I), stabilised in 1 M(NaCl(aq)), and sodium or potassium cyanide (Hefter et al., 1993). Note that, consistent with the stepwise formation of metal-ligand complexes (Greenwood and Earnshaw, 1997), most authors have assumed the existence of the monocyanocuprate(I) species, $CuCN^0(\text{aq})$. However, this species is extremely difficult to detect, let alone quantify (Hefter et al., 1993; Solis, 1995), although a reasonable estimate has been achieved using solubility data (Akilan et al., 2015).

Depending on the total concentrations of Cu(I) and CN^- , pH, ionic strength and temperature, Cu(I)- CN^- solutions will typically contain a mixture of (suspended) CuCN(s) and the aquated species CuCN^0 , $\text{Cu}(\text{CN})_2^-$, $\text{Cu}(\text{CN})_3^{2-}$ and $\text{Cu}(\text{CN})_4^{3-}$ in dynamic equilibrium with each other, along with free CN^- and undissociated HCN^0 . A typical species distribution diagram for the Cu(I)- CN^- complexes in aqueous solution at 25 °C is presented in Figure 1. Of course free OH^- and possibly Cu(I)- OH^- and ternary Cu(I)- OH^- - CN^- complexes may also be present under some conditions, although the latter species have never been reported in the literature. Accordingly, such species will not be considered in the following discussion.

Thus in addition to equilibria (1) and (2), the following equilibria (with all species taken to be aquated unless otherwise specified) and their corresponding overall (β_n) or stepwise (K_n) formation constants must be accurately characterised under relevant conditions for the quantitative modelling of Cu(I)/ CN^- mixtures:



Alternatively, the last three equilibria can be written in their mathematically equivalent ‘stepwise’ form:



The most reliable values for the solubility product, K_{s0} , for CuCN(s) are given below (Section 3.1) and, for a related solubility constant, in Table 3. The formation constants for the Cu(I)/CN⁻ complexes ($\log \beta_n$ and $\log K_n$) are given in Table 4, together with details of the medium used in their determination. Data deemed to be less reliable by the present reviewers are not listed in the tables but where appropriate are discussed in the text that follows.

The equilibrium constants for the Cu(I)/CN⁻ complexes have been measured using a range of techniques under widely differing experimental conditions (Table 4). This situation, along with different methods of processing the data so obtained, has produced a number of discrepancies in the reported values. Nevertheless, the data have tended to become more consistent over time, especially under standard conditions ($I = 0$, 25 °C). This is due in large part to the availability of better quality stepwise formation constants and the other thermodynamic data on which they depend, i.e., the dissociation constants for hydrogen cyanide and water under equivalent conditions.

3.1 Solubility of Copper(I) Cyanide

At low cyanide concentrations, Cu(I) will be mostly present as the sparingly soluble white cuprous cyanide solid, CuCN(s). The solubility product for CuCN(s) at 25 °C and infinite dilution was determined after an extensive study by Vladimirova and Kakovskii (1950) to correspond to $\text{p}K_{s0}^{\circ} = 19.50$. This equates to a solubility of CuCN in pure water of 2×10^{-8} M. This value was endorsed by Fritz and Königsberger (1996) in their critical review as being more reliable than the solubility of 2.6×10^{-3} M at 15 °C reported by Ragg (1950). The value of Vladimirova and Kakovskii (1950) was corrected to 19.74 by Lu et al. (2002b) using Beck's (1987) recommended value of $\text{p}K_a^{\circ}(\text{HCN}) = 9.21$. Akilan et al. (2015) have estimated $\text{p}K_{s0} = 19.49 \pm 0.02$ at $I = 1$ M(NaCl) and 25 °C using the solubility data of Königsberger et al. (1994).

In aqueous HCN solutions, the solubility of CuCN(s) varies with the square root of the HCN concentration, which has been interpreted in terms of the following reaction (Vladimirova and Kakovskii, 1950):



with the corresponding solubility constant

$$^*K_{s2} = [\text{Cu(CN)}_2^-][\text{H}^+]/[\text{HCN}] = 1.22 \times 10^{-5} \text{ M.}$$

This equilibrium is much more easily characterized than the solubility product because of the greater stabilization of Cu(I). Indeed, the value obtained by Vladimirova and Kakovskii (1950), $p^*K_{s2}^0 = 4.91$, has been quantitatively confirmed by Königsberger et al. (1994) who studied the solubility of CuCN(s) in HCN-NaCN solutions at 25 °C and $0.15 \text{ M} \leq I/\text{M} \leq 1.0$ in NaCl media (see also Solis, 1995; Akilan et al., 2015). Taking Cu(I) speciation into account by using appropriate Cu(I)/CN⁻ formation constants (Hefter et al., 1993) values of $p^*K_{s2}^0 = 4.9 \pm 0.1$ at $I = 0$ and 4.50 ± 0.01 at $I = 1.0 \text{ M}$ (NaCl) have been derived from these data (Königsberger et al. 1994; Akilan et al., 2015).

3.2 Formation of Cyanocuprate(I)

As mentioned earlier, the species CuCN⁰(aq) cannot usually be detected using the common methods of equilibrium constant determination. This is because its formation overlaps with the precipitation of CuCN(s). The value of $\log \beta_1 = 16.33$ at 25 °C and $I = 1 \text{ M}$ (NaCl) given in Table 4 was *estimated* by Hefter et al. (1993). A recent re-processing (Akilan et al., 2015) of the solubility measurements of Königsberger et al. (1994) indicated a value of $\log \beta_1 = 15.80 \pm 0.15$ gave the best fit of the data. It can be noted that while it is necessary to include β_1 in any modelling scheme, so as to anchor the numerical values of the formation constants of the higher order species (Hefter et al., 1993), the value chosen does not have much effect on those constants.

3.3 Formation of Dicyanocuprate(I)

Apart from CuCN⁰(aq), the dicyanocuprate(I) complex, Cu(CN)₂⁻(aq), is the most difficult of the Cu(I)/CN⁻ species to detect and quantify due to its relatively low concentrations under most experimental conditions

(Figure 1). The most reliable infinite dilution value of its formation constant is probably that obtained by Vladimirova and Kakovskii (1950). These authors used potential measurements with Cu and Cu(Hg) electrodes in solutions formed by dissolving $\sim 10^{-3}$ M CuCN(s) in acidic (pH = 4.2) HCN solutions, which maximised the concentration of $\text{Cu}(\text{CN})_2^-$. Their reported value of $\log \beta_2^\circ = 24.3$ at $I = 0$ was later corrected to 23.9 by Izatt et al. (1967) using $\text{p}K_a^\circ(\text{HCN}) = 9.21$ and an extended Debye-Hückel equation. Subsequently, Bek et al. (1972) obtained a similar value of $\log \beta_2^\circ = 23.8$ at 25 °C, also corrected to $I = 0$ using an extended Debye-Hückel equation, by measuring Cu electrode potentials in 0.15 M Cu(I) solutions at $0.84 \leq I/M \leq 1.21$ in $\text{Na}^+/\text{Cu}^+/\text{CN}^-$ media. More recently, Hefter et al. (1993) used glass electrode potentiometry with Cu(I) stabilised in 1 M (NaCl) solution and obtained $\log \beta_2 = 23.97 \pm 0.01$ at 25 °C. An almost identical result (albeit from the same laboratory and using the same technique) has recently been determined by Akilan et al. (2015).

A significantly lower value of $\log \beta_2 = 21.7 \pm 1.0$ from solubility measurements of CuCN(s) dissolved in solutions containing up to 4 M KCN at 20 °C, was reported by Rothbaum (1957) but without considering activity coefficients. Hancock et al. (1972) similarly found $\log \beta_2 = 21.7 \pm 0.2$ from Cu-electrode potentials measured at $\text{CN}^-/\text{Cu}(\text{I})$ ratios from 2.5 to 10 and an ionic strength of 0.01 M at 25 °C, again without considering activity coefficients. The UV spectrophotometric measurements of Kappenstein and Hugel (1974) at low $\text{CN}^-/\text{Cu}(\text{I})$ ratios and low pH gave an even lower value of $\log \beta_2 = 16.26$ at 25 °C. However, this result is thought to be unreliable because $\text{Cu}(\text{CN})_2^-$ is more readily oxidized than the higher-order complexes (Cooper and Plane, 1966). None of the foregoing values were considered to be sufficiently reliable to be included in Table 4.

The values of $\log \beta_2$ at 25 °C that are listed in Table 4 are remarkably similar given that they were measured in different electrolytes and at different I . Collectively, they suggest that $\log \beta_2$ does not vary much with ionic strength or medium at least at $I < \text{ca. } 1 \text{ M}$, so until more detailed studies are made it seems best to

assume $\log \beta_2 = 24.0$ at $I \leq 1$ M in all background electrolytes at 25 °C. It may also be noted that this value is consistent with the solubility data of Königsberger et al. (1994). At higher I only the data of Akilan et al. (2015) in NaCl media are available (Table 4); they show that $\log \beta_2$ increases smoothly with increasing I .

3.4 Formation of Tricyanocuprate(I)

The tricyanocuprate complex, $\text{Cu}(\text{CN})_3^{2-}$ is formed to a greater extent in more alkaline ($\text{pH} > 5$) solutions and at $\text{CN}^-/\text{Cu(I)}$ ratios >3 , where $\text{Cu}(\text{CN})_2^-$ is present in only minor amounts. This can be seen from the species distribution (Figure 1) which shows that $\text{Cu}(\text{CN})_3^{2-}$ is the dominant complex over much of the pH range. The stepwise equilibrium between the two species:



quantified by the constant K_3 has been much investigated. A range of values has been reported, the more reliable of which are presented in Table 4 and discussed in the following paragraphs.

At $I = 0$, Izatt et al. (1967) obtained by extrapolation a value of $\log K_3^0 = 5.30 \pm 0.01$ at 25 °C using pH-potentiometric titrations at $1 \leq [\text{Cu(I)}]_{\text{T}}/\text{mM} \leq 10$. Similar values of $\log K_3 = 5.34$ at 25 °C in 0.01 M KOH and $\log K_3 = 5.39 \pm 0.03$ in 0.01 M KClO_4 were obtained respectively by Baxendale and Westcott (1959) and by Kappenstein and Hugel (1974), both using UV spectrophotometry. In the latter case, the use of very dilute solutions ($\sim 10 \mu\text{M}$) may have introduced significant errors. Hefter et al. (1993) reported $\log K_3 = 5.43 \pm 0.04$ at $I = 1.0$ M (NaCl) and 25 °C using glass electrode potentiometry; a similar result (Table 4) was obtained by Akilan et al. (2015) using the same technique. Akilan et al. (2015) also determined $\log K_3$ at $I = 3$ and 5 M in saline media and found that it *decreased* smoothly with increasing I .

The value of $\log K_3 = 5.0$ obtained calorimetrically by Brenner (1965) has been omitted from Table 4 as it appears to be too low and insufficient experimental detail was provided to enable a proper assessment of the work to be made. Similarly, the even lower value of $\log K_3 = 4.61 \pm 0.07$ in 0.8–1.2 M $\text{K}(\text{Na})\text{CN}$ at 29 °C

obtained by Penneman and Jones (1956) using IR spectroscopy has been rejected, as they used an improbably high value of $pK_a(\text{HCN}) = 9.29$ (cf. Table 2).

On the basis of the data available (Table 4), it seems that at 25 °C $\log K_3$, like $\log \beta_2$ (see above), changes only slightly with ionic strength at $I < \text{ca. } 1 \text{ M}$. The values thought to be the most reliable for $\log K_3$ are 5.30 ± 0.01 at $I = 0$ (Izatt et al., 1962) and 5.53 ± 0.10 at $I = 1.0 \text{ M}$ in NaCl, which is the average of the values reported by Hefter et al. (1993) and Akilan et al. (2015). The range for the latter is undoubtedly a reflection of the real uncertainties inherent in the measurement of the Cu(I)-CN⁻ system. At higher I , *qualitative* changes in the distribution of the di- and tri-cyano complexes with increasing salinity (up to 4 M NaCl) have been noted by Lukey et al. (1999) and quantified by Akilan et al. (2015).

3.5 Formation of Tetracyanocuprate(I)

The tetracyanocuprate complex, $\text{Cu}(\text{CN})_4^{3-}$, is formed most readily at high pH (>10) and high CN⁻/Cu(I) ratios. Under most conditions it is in equilibrium with the tricyano complex:



The stepwise formation constant K_4 , corresponding to equilibrium (7), has been the subject of much investigation (Table 4), mostly by authors investigating the di- and tri-cyanocuprate(I) equilibria under the conditions described above. Thus, Izatt et al. (1967) obtained a value of $\log K_4^0 = 1.5 \pm 0.2$ at 25 °C while Baxendale and Westcott (1959) reported $\log K_4 = 1.74$ at 25 °C in 0.01 M KOH by using UV spectrophotometry with very dilute solutions (3 to 36 μM) of Cu(I). Penneman and Jones (1956) using IR spectroscopy reported $\log K_4 = 1.6$ in 0.2 M Cu(I) at $\text{Cu}/\text{CN} \approx 3$ ratios after adjustment to 25 °C.

Values of $\log K_4$ measured at higher I (Table 4) are much larger than that of Izatt et al. (1967) at $I = 0$, which indicates that $\log K_4$, unlike $\log K_2$ and $\log K_3$, increases significantly with increasing I . Thus, Bek et al. (1972) obtained a value of $\log K_4 = 1.84$ in 0.84 to 1.21 M (Na)CuCN while Hefter et al. (1993) and Akilan

et al. (2015) reported $\log K_4 = 2.38 \pm 0.04$ and 2.51 ± 0.04 respectively in 1.0 M (NaCl). Brenner's (1965) calorimetric value of $\log K_4 = 2.64$ has been rejected as lacking in experimental detail (Beck, 1987).

The increase of $\log K_4$ with increasing I has been observed qualitatively by Raman spectroscopy on Cu(I)-CN⁻ solutions of varying salinity (Lukey et al., 1999) and quantified by Akilan et al. (2015). It should also be noted that the higher $\log K_4$ value of Hefter et al. (1993), confirmed by Akilan et al. (2015), fitted the data obtained in a modelling study of the adsorption onto activated carbon of Cu(I)-CN⁻ complexes in 1.0 M NaCl solutions (Dai et al., 2010) significantly better than the infinite dilution value of Izatt et al. (1967). The higher value of $\log K_4$ at high I is also consistent with the solubility data of Königsberger et al. (1994).

Pending further investigation, the preferred values of $\log K_4$ at 25 °C are the potentiometric results of Izatt et al. (1967) corrected to infinite dilution ($\log K_4^0 = 1.5 \pm 0.2$) and at higher I the values of Hefter et al. (1993) and Akilan et al. (2015) in NaCl media listed in Table 4, although further work is required at intermediate I to harmonize all of these results.

3.6 Effect of Temperature on Log β_n

The most extensive study to date of the variation of the formation constants of Cu(I)-CN⁻ complexes with temperature was that by Bek and co-workers (1972) whose data are presented in Table 4. From their results, Bek et al. produced straight line relationships between $\log \beta_n$ (for $n = 2, 3$ and 4) and $1/T$ (Figure 4). These data can be used to calculate, via eq. (4a), the enthalpy changes associated with the overall formation reactions in solution of the dicyano-, tricyano- and tetracyano- complexes. The values so calculated are listed in Table 5 along with the available calorimetric data. The corresponding values for ΔG and ΔS were calculated using the usual thermodynamic relationships: $\Delta G = -RT \ln K = \Delta H - T\Delta S$.

3.7 Enthalpies and Entropies of Complex Formation

Compared with the formation constants of the Cu(I)-CN⁻ complexes, rather little is known of the corresponding enthalpies and entropies (Table 5). Only three calorimetric studies appear to have been undertaken in the last fifty years: by Brenner (1965), Izatt et al. (1967) and Solis et al. (1996b). Unfortunately, the study of Brenner (1965) lacks key experimental information, which has led us to reject his calorimetrically-derived stability constants. Similar considerations apply to his enthalpy data, which also appear to have the wrong sign. The remaining studies of Izatt et al. (1967) and Solis et al. (1996b) can only be compared for the (overall) formation reaction of Cu(CN)₄³⁻ and were made at markedly different *I*. Despite the difference in media, the values reported are in reasonable agreement (Table 5). Also included in Table 5 are the ΔH and ΔS values calculated from the potentiometric ($\log \beta_n(T)$ vs. $1/T$) data of Bek et al. (1972) at $0.84 \leq I/M \leq 1.21$ in Na⁺/Cu⁺/CN⁻ media (Figure 4). While the ΔH and ΔS values obtained from the data of Bek et al. for the overall formation reaction for Cu(CN)₂⁻ are in fair agreement with the calorimetric results of Izatt et al., those for Cu(CN)₃²⁻ and Cu(CN)₄³⁻ are not (Table 5). In general, enthalpies and entropies obtained from the variation of $\log \beta_n$ with *T* are less reliable than those obtained calorimetrically (Hefter et al., 2002) so where large differences occur, the calorimetric values are preferred.

The ΔG and ΔH values corresponding to the overall reactions for the formation of Cu(I)-CN⁻ complexes in solution are all markedly negative (Table 5). This shows that the high stability of these complexes (i.e., their large formation constants and strongly negative ΔG values) is due predominantly to their highly favourable (i.e., strongly negative) ΔH values. These in turn reflect the great strength of the Cu(I)-CN⁻ bonds relative to the Cu(I)-OH₂ bonds in the aquo complex that they replace during the complex formation process. The former is often attributed to strong $d_{\pi}-p_{\pi}^*$ (metal-to-ligand) ‘back-bonding’ which is apparently highly favourable for the d^{10} Cu⁺ ion bonded to C≡N⁻. Using the infinite dilution results of Izatt et al. (1967), the corresponding ΔS° values also become more negative (increasingly less favourable) as the number of

cyanide ligands attached to the Cu(I) increases. This can be attributed to the increased ordering around the central Cu(I) ion (Solis et al., 1996b).

The overall enthalpy change for the formation of the tetracyanocuprate(I) complex in solution (corresponding to β_4) is much larger (more negative, by ~ 100 kJ/mol) than for the formation of the isoelectronic zinc(II)- and the analogous cadmium(II)-complexes measured under similar conditions (Table 5). The greater (negative) magnitude of ΔH is responsible for the much larger overall formation constant (β_4) for $\text{Cu}(\text{CN})_4^{3-}$ compared with $\text{Zn}(\text{CN})_4^{2-}$ and $\text{Cd}(\text{CN})_4^{2-}$. This difference in ΔH occurs because the enthalpies of hydration of the zinc(II) and cadmium(II) ions (-2052 and -1815 kJ/mol respectively) are much more negative than for the copper(I) ion (-576 kJ/mol) and also because of the back bonding referred to above, which appears to be particularly favourable for the Cu(I)- CN^- complexes. The negative entropy change for the overall formation of $\text{Cu}(\text{CN})_4^{3-}$ in solution, is more unfavourable (more negative) than those for the corresponding Zn(II) and Cd(II) complexes. This has been attributed to the decrease in the coordination number of the central metal atom from six (in the aquo ions) to four (in the complexes), which appears to be less important for the latter two species (Solis et al., 1996b).

4. Conclusions

When copper minerals are present in gold cyanidation systems, especially those where remnant gold is recovered from copper sulfide flotation tailings, the cyanide-soluble copper is generally present in much higher concentrations than the gold, and can therefore compete with the gold for both available cyanide and for adsorption sites on activated carbon. This can cause significant processing problems both from excessive cyanide consumption and reduced gold adsorption onto carbon, thereby increasing overall treatment costs and reducing recoveries. The equilibria between Cu(I) and CN^- in aqueous solutions are thus of critical importance in the study and modelling of real copper-gold-cyanide processes. The formation constants for Cu(I)- CN^- complexes, except for the difficult-to-detect $\text{CuCN}^0(\text{aq})$, are well documented at 25°C and at low ionic strengths. However, there is limited systematic knowledge on how these formation constants vary with

ionic strength, solution composition and temperature. Further careful measurements of these effects are highly desirable because such constants are essential for modelling a variety of observed effects under actual hydrometallurgical conditions. A similar case can be made with regard to the corresponding enthalpies and entropies of reaction. The solubility of $\text{CuCN}(s)$ in NaCN/NaCl solutions at varying ionic strengths has been studied at $25\text{ }^{\circ}\text{C}$ (Königsberger et al., 1994) but that work needs to be extended to other background electrolytes and temperatures.

5. References

- Akilan, C., Königsberger, E., Solis, J.S., May, P.M., Kyle, J.H., Hefter, G.T., 2015. Measurement of complexation and solubility equilibria in the copper(I)/cyanide system at 25 °C, unpublished results.
- Anderegg, G., 1957. The cyanide complexes of mercury. *Helv. Chim. Acta*, 40, 1022-1026.
- Ang, K.P., 1959. Determination of the ionization constant of hydrocyanic acid at 25 °C by a spectrophotometric indicator method. *J. Chem. Soc.*, 3822-3825.
- Baes, C.F., Mesmer, R.E., 1976. *The Hydrolysis of Cations*, Wiley, New York.
- Banyai, I., Blixt, J., Glaser, J., Toth, I., 1992. On the dissociation of hydrogen cyanide in aqueous solutions containing different ionic media. A combined potentiometric and carbon-13 NMR study. *Acta Chem. Scand.*, 46, 138-141.
- Barter, J., Lane, G., Mitchell, D., Kelson, R., Dunne, R., Trang, C., Dreisinger, D., 2001. Cyanide management by SART. In Young, C.A., Tidwell, L.G., Anderson, C.G. (Eds.), *Cyanide: Social, Industrial and Economic Aspects*, 2001 TMS Annual Meeting, New Orleans, LA; USA, 12-15 February 2001. Minerals, Metals and Materials Society/AIME, Warrendale, PA, USA, pp. 549-562.
- Baxendale, J.H., Westcott, D.T., 1959. Kinetics and equilibria in copper(II)-cyanide solutions. *J. Chem. Soc.*, 2347-2351.
- 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, A. I., Poddubnyi, N. P., 1972. Electrodeposition of copper from cyanide electrolytes. Part II. Formation constants for copper cyanide complexes. *Izv. Sib. Otdel. Akad. Nauk SSSR, Ser. Khim. Nauk* (4), 52-56.

- Blixt, J., Gyori, B., Glaser, J., 1989. Determination of stability constants for thallium(III) cyanide complexes in aqueous solution by means of ^{13}C and ^{205}Tl NMR. *J. Amer. Chem. Soc.*, 111, 7784-7791.
- 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. and Bouchard, J. (Eds.), *World Gold 2011*, CIMM, Canada, 285-301.
- Boughton, J.H., Keller, R.M., 1966. Dissociation constants of hydropseudohalic acids. *J. Inorg. Nucl. Chem.*, 28, 2851-2859.
- Brenner, A., 1965. Determination of the composition of complexes and their instability constant by calorimetry. *J. Electrochem. Soc.*, 112, 611-621.
- Breuer, P.L., Hewitt, D.M., Jeffrey, M.I., Rumball, J.A., 2007. The leaching and oxidation of sulfide minerals in cyanide solutions – quantification of reaction products and the effect of lead and oxygen. In *World Gold Conference, Cairns, 22-24 October, 2007*, AusIMM, Parkville, Victoria, pp. 183-189.
- Broderius, S.J., 1981. Determination of hydrocyanic acid and free cyanide in aqueous solution. *Anal. Chem.*, 53, 1472-1477.
- Buchner, R., Hefter, G.T., 2009. Interactions and dynamics in electrolyte solutions by dielectric spectroscopy. *Phys. Chem. Chem. Phys.*, 11, 8984-8999.
- Cabani, S., Gianni, P., 1972. Comments on simultaneous determination of K and ΔH . *Anal. Chem.*, 44, 253-259.
- Chantry, G.W., Plane, R.A., 1960. CN stretching bands in the Raman spectra of some group Ib and group IIb complex cyanides. *J. Chem. Phys.*, 33, 736-740.

- Christensen, J.J., Johnston, H.D., Izatt, R.M., 1970. Thermodynamics of proton ionization in aqueous solution. Part XII. ΔH° , ΔS° , and ΔC_p° values for hydrocyanic acid dissociation at 10, 25, and 40°. *J. Chem. Soc. (A)*, 454-455.
- Cooper, D., Plane, R.A., 1966. Cyanide complexes of copper with ammonia and ethylenediamine. *Inorg. Chem.*, 5, 1677-1682.
- 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.
- Donato, D., Nichols, O., Possingham, H., Moore, M., Ricci, P., Noller, B., 2007. A Critical Review of the Effects of Gold Cyanide-Bearing Tailings Solutions on Wildlife. *Environment International*, 33, 974-984.
- Dutra, A.J., Rocha, G.P., Pombo, F.R., 2008. Copper recovery and cyanide oxidation by electrowinning from a spent copper-cyanide electroplating electrolyte. *J. Hazardous Mater.*, 152, 648-655.
- Fernando, K., Tran, T., Laing, S., Kim, M.J., 2002. The use of ion exchange resins for the treatment of cyanidation tailings. Part 1 – process development of selective base metal elution. *Miner. Eng.* 15, 1163-1171.
- Finch, A., Gardner, P.J., Head, A.J., Xiaoping, W., Yefimov, M.E., Furkaluk, M.U., 1993. The standard enthalpy of formation of the aqueous cyanide ion. *J. Chem. Thermodyn.*, 25, 1385-1390.
- Fleming, C.A., 2005. Cyanide recovery. In Adams, M.D. (Ed.), *Advances in Gold Ore Processing*, Elsevier, Chapter 29, 703-728.

Fritz, J.J., Königsberger, E., 1996. IUPAC Solubility Data Series, Volume 65, Copper(I) Halides and Pseudohalides., Oxford University Press, Oxford, pp. 261-275.

Gáspár, V., Beck, M.T., 1982. The influence of the ionic strength on the dissociation constant of hydrogen cyanide. *Acta Chim. Hung.*, 110, 425-427.

Greenwood, N.N., Earnshaw, A., 1997. *Chemistry of the Elements*. Butterworth-Heinemann, Oxford, 2nd Edn, pp. 1194-1197.

Grenthe, I., Puigdomenech, I., 1997. *Modelling in Aquatic Chemistry*, NEA-OECD, Paris.

Hancock, R.D., Finkelstein, N.P., Evers, A., 1972. Stabilities of the cyanide complexes of the monovalent group IB metal ions in aqueous solution. *J. Inorg. Nucl. Chem.*, 34, 3747-3751.

Hedley, N., Tabachnick, H., 1958. *Chemistry of Cyanidation*. Mineral Dressing Notes 23. American Cyanamid Company, New York.

Hedwig, G.R., Powell, H.K.J., 1973. A re-investigation of the enthalpy changes for the interaction of the sulfate ion with some transition-metal ions in aqueous solution. *J. Chem. Soc. Dalton Trans.* 798-801.

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.

Hefter, G.T., Marcus, Y., Waghorne, W.E., 2002. Enthalpies and entropies of transfer of electrolytes and ions from water to mixed aqueous organic solvents. *Chem. Rev.*, 102, 2773-2836.

Högfeldt, E., 1982. *Stability Constants of Metal-Ion Complexes, Part A: Inorganic Ligands*, Pergamon, Oxford, pp. 79-84.

Ibrado, A.S., Fuerstenau, D.W., 1989. Adsorption of the cyano complexes of Ag(I), Cu(I), Hg(II), Cd(II) and Zn(II) on activated carbon. *Miner. Metall. Process.*, February, 23-28.

Izatt, R.M., Christensen, J.J., Pack, R.T., Bench, R., 1962. Thermodynamics of metal cyanide coordination: I. pK , ΔH° , ΔS° values as a function of temperature for hydrocyanic acid dissociation in aqueous solution. *Inorg. Chem.*, 1, 828-831.

Izatt, R.M., Johnston, H.D., Watt, G.D., Christensen, J.J., 1967. Thermodynamics of metal cyanide coordination. VI. Copper(I)- and silver(I)-cyanide systems. *Inorg. Chem.*, 6, 132-135.

Jianming, L., Dreisinger, D.B., Cooper, W.C., 2002. Thermodynamics of the aqueous copper-cyanide system. *Hydrometallurgy*, 66, 23-36.

Johnson, C.A., 2014. The fate of cyanide in leach wastes at gold mines: an environmental perspective. *Appl. Geochem.* in press; available online at doi:10.1016/j.apgeochem.2014.05.023.

Kappenstein, C., Hugel, R., 1974. The cyanocuprate(I) ions in neutral and acidic aqueous solutions. *J. Inorg. Nucl. Chem.*, 36, 1821-1825.

Königsberger, E., Solis, J.S., May, P.M., Hefter, G.T., 1994. 6th International Symposium on Solubility Phenomena, Buenos Aires, Argentina, cited in Fritz and Königsberger (1996), p. 274.

Kotrlý, S., Šůcha, L., 1985. *Handbook of Chemical Equilibria in Analytical Chemistry*. Ellis Horwood: Chichester, UK, pp. 18-20.

Kovács, L., Csupor, D., Lente, G., Gunda, T., 2014. *100 Chemical Myths: Misconceptions, Misunderstandings, Explanations*, Springer, Cham, Germany, pp. 298-300.

Korte, F., Spitteller, M., Coulston, F., 2000. The cyanide leaching gold recovery process is a nonsustainable technology with unacceptable impacts on ecosystems and humans: The disaster in Romania. *Ecotox. Environ. Safety*, 46, 241-245.

Kron, I., Marshall, S.L., May, P.M., Hefter, G., Königsberger, E., 1995. The ionic product of water in highly concentrated aqueous electrolyte solutions. *Monatsh. Chem.*, 126, 819-837.

Leao, V.A., Ciminelli, V.S., 2002. Application of ion exchange resins to cyanide recovery. *Metalurgia & Materials ABM* 58.

Leao, V.A., Lukey, G.C., van Deventer, J.S., Ciminelli, V.S., 2001. The dependence of sorbed copper and nickel cyanide speciation on ion exchange resin type. *Hydrometallurgy* 61, 105-119.

Leaver, E.S., Woolf, A., 1931. U.S. Bureau Mines Technical Paper No. 494, U.S. Government Printing Office, Washington DC.

Lemos, F.A., Sobral, L.G., Dutra, A.J.B., 2006. Copper electrowinning from gold plant waste streams. *Miner. Eng.* 19, 388-398.

Lu, J., Dreisinger, D.B., Cooper, W.C., 2002a. Copper electrowinning from dilute cyanide solution in a membrane cell using graphite felt. *Hydrometallurgy* 64, 1-11.

Lu, J., Dreisinger, D.B., Cooper, W.C., 2002b. Thermodynamics of the aqueous copper-cyanide system. *Hydrometallurgy* 66, 23-36.

Lukey, G.C., van Deventer, J.S., Chowdhury, R.L., Shallcross, D.C., 1999. The effect of salinity on the capacity and selectivity of ion exchange resins for gold cyanide. *Miner. Eng.* 12, 769-785.

Lukey, G.C., van Deventer, J.S., Shallcross, D.C., 2000. Selective elution of copper and iron cyanide complexes from ion exchange resins using saline solutions. *Hydrometallurgy* 56, 217-236.

Marsden, J.O. and House, C.I. 2006. *The Chemistry of Gold Extraction*, 2nd ed. Society for Mining, Metallurgy, and Exploration, Littleton, Colorado. Chapter 6.

May, P.M., 2000. A simple, general and robust function for equilibria in aqueous electrolyte solutions to high ionic strength and temperature, *Chem. Commun.*, 1265-1266.

May, P.M., Murray, K., 2000. Database of chemical reactions designed to achieve thermodynamic consistency automatically. *J. Chem. Eng. Data*, 46, 1035-1040.

Penneman, R.A., Jones, L.H., 1956. Infrared absorption studies of aqueous complex ions. II. Cyanide complexes of Cu(I) in aqueous solution. *J. Chem. Phys.*, 24, 293-296.

Persson, H., 1971. Complex formation in the zinc cyanide and the cadmium cyanide systems. *Acta Chem. Scand.*, 25, 543-550.

Powell, K.J., Brown, P.L., Byrne, R.H., Gajda, T., Hefter, G.T., Sjöberg, S., Wanner, H., 2007. Chemical speciation of environmentally significant heavy metals with inorganic ligands. Part 2: The Cu^{2+} - OH^- , Cl^- , CO_3^{2-} , SO_4^{2-} and PO_4^{3-} systems. *Pure Appl. Chem.*, 79, 895-950.

Ragg, M., 1950. *Farbe und Lack*, 56, 435 (as cited in Fritz and Königsberger, 1996).

Riveros, P.A., Molnar, R., McNamara, V.M., 1993. Alternative technology to decrease the environmental impact of gold milling--a progress report on Canmet research activities in this field. *Canadian Mining and Metallurgical Bulletin* 86 (968), 167-171.

Rothbaum, H.P., 1957. The composition of copper complexes in cuprocyanide solutions. *J. Electrochem. Soc.*, 104, 682-686.

Shantz, R., Fisher, W.W., 1977. The kinetics of the dissolution of chalcocite in alkaline cyanide solution. *Metall. Trans. B*, 8, 253-260.

Sillén, L.G., Martell, A.E., 1964. *Stability Constants of Metal-Ion Complexes*, Special Publication No. 17, Chemical Society, London, pp. 107-115.

Sillén, L.G., Martell, A.E., 1971. Stability Constants of Metal-Ion Complexes, Supplement No. 1, Special Publication No. 25, Chemical Society, London, pp. 53-58.

Silva, A.L., Costa, R.A., Martins, A.H., 2003. Cyanide regeneration by AVR process using ion exchange polymeric resins. *Minerals Eng.*, 16, 555-557.

Simpson, E.A., Waind, G.M., 1958. The ultraviolet absorption spectra and stability constants of cuprous cyanide complexes. *J. Chem. Soc.*, 1746-1749.

Smith, R. M., Martell, A. E., 1976. *Critical Stability Constants*, Vol. 4: Inorganic Complexes, Plenum, New York, pp. 26-27.

Smith, R. M., Martell, A. E., 1982. *Critical Stability Constants*, Vol. 5: Inorganic First Supplement, Plenum, New York, p. 400.

Smith, R. M., Martell, A. E., 1989. *Critical Stability Constants*, Vol. 6: Second Supplement, Plenum, New York, p. 435.

Solis, J.S., 1995. *Thermodynamics of Cyanide Complexes*, Ph. D. Thesis, Murdoch University.

Solis, J.S., May, P.M., Hefter, G., 1996a. Cyanide thermodynamics. III. Enthalpies and entropies of ionization of water and hydrogen cyanide. *Aust. J. Chem.*, 49, 651-657.

Solis, J.S., May, P.M., Hefter, G., 1996b. Cyanide thermodynamics. Part 4. Enthalpies and entropies of cyanide complexation of Cu(I), Ag(I), Zn(II) and Cd(II). *J. Chem. Soc., Faraday Trans.*, 92, 641-644.

Solis, J.S., 1995. *Thermodynamics of Cyanide Complexes*. Ph.D. Thesis, Murdoch University, Australia.

Stevenson, J., Botz, M., Mudder, T., Wilder, A., Richins, R., Burdett, B., 1998. Recovery of cyanide from mill tailings. In Mudder, T.I., Botz, M.M. (Eds.), *The Cyanide Monograph*, 1st Edition, Mining Journal Books, London.

Tsonopoulos, C., Coulson, D.M., Inman, L.B., 1976. Ionization constants of water pollutants. *J. Chem. Eng. Data*, 21, 190-193.

Van Deventer, J., Volha, B., Volha, Y., 2014. Comparison of gold-selective ion exchange resins and activated carbon for the recovery of gold from copper-gold leach liquors. *Alta Gold and Precious Metals Conference*, Perth, May, 2014, Alta Metallurgical Services, pp. 164-180.

Verhoeven, P., 1989. Speciation of the zinc(II) and cadmium(II) cyanide systems in hypersaline solution. B. Sc. Honours Thesis, Murdoch University.

Verhoeven, P., Hefter, G., May, P.M., 1990a. Dissociation constant of hydrogen cyanide in saline solutions. *Miner. Metall. Process.*, 7, 185-188.

Verhoeven, P., Hefter, G., May, P.M., 1990b. Cyanide complexes of zinc(II) and cadmium(II) in 3 M NaCl medium. *J. Coord. Chem.*, 22, 7-19.

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.

Wagman, D.D., Evans, W.H., Parker, V.B., Schumm, R.H., Halow, I., Bailey, S.M., Churney, K., Nutall, R.L., 1982. The NBS tables of chemical thermodynamic properties. Selected values for inorganic and C₁ and C₂ organic substances in SI units. *J. Phys. Chem. Ref. Data*, 11, Supplement No. 2.

Table 1

Dissociation constants of hydrogen cyanide at 25 °C in different media at various ionic strengths

Ionic Strength (M)	Medium	Method	pK_a^a	Reference
0^b		Spectrophotometry	9.22±0.02	Ang, 1959
		Potentiometry	9.21±0.01	Izatt et al., 1962
		Potentiometry	9.21±0.02 ^c	Boughton & Keller, 1966
		Spectrophotometry	9.21±0.11	Tsonopoulos et al., 1976
		Diffusion/Evaporation	9.22±0.02 ^d	Broderius, 1981
		Potentiometry	9.21	Gáspár and Beck, 1982
		Critical survey	9.21±0.02	Beck, 1987
		Gibbs energy	9.24	Finch et al., 1993
		JESS calculation	9.19	This review
1.0	LiClO ₄	Potentiometry,	9.09±0.02	Banyai et al., 1992
3.0		C ¹³ NMR	10.11±0.02	
0.1	NaClO ₄	Potentiometry	9.06±0.03	Gáspár and Beck, 1982
0.1		Potentiometry	9.03±0.01 ^d	Solis et al., 1996a
0.5		Potentiometry	9.01±0.01 ^d	Solis et al., 1996a
1.0		Potentiometry	9.04±0.01 ^d	Solis, 1995
1.0		Potentiometry	9.01±0.01 ^d	Solis et al., 1996a
1.0		C ¹³ NMR	9.09±0.02	Banyai et al., 1992
3.0		Potentiometry	9.48±0.01	Persson, 1971
3.0		Potentiometry	9.45±0.01 ^d	Solis et al., 1996a
5.0		Potentiometry	10.01±0.01 ^d	Solis et al., 1996a
0.1		NaCl	Potentiometry	9.04±0.01 ^d
0.5	Potentiometry		8.95±0.01 ^d	Verhoeven et al., 1990a; Solis et al., 1996a
1.0	Potentiometry		8.95±0.01 ^d	Verhoeven et al., 1990a; Solis et al., 1996a
1.0	Potentiometry		8.97±0.01 ^d	Hefter et al., 1993; Solis, 1995
1.0	Potentiometry		8.94±0.01 ^d	Akilan et al., 2015
3.0	Potentiometry		9.22±0.01 ^d	Verhoeven et al., 1990a,b; Solis et al., 1996a
3.0	Potentiometry		9.21±0.01 ^d	Akilan et al., 2015
5.0	Potentiometry		9.66±0.01 ^d	Verhoeven et al., 1990a; Solis et al., 1996a
5.0	Potentiometry		9.65±0.01 ^d	Akilan et al., 2015
0.1	NaNO ₃		Potentiometry	9.01±0.01 ^c
2.0		Polarography	(8.65±0.03) ^c	Beck, 1987

^a Uncertainties as stated in the original publication, where available. ^b Values of pK_a^o at infinite dilution were mostly obtained by extrapolation or correction for activity coefficients. ^c Corrected to 25 °C assuming $\Delta H_a = 43.6$ kJ/mol and $\Delta C_{p,a} = 0$ (see Table 2). ^d Reported pK_a values and their uncertainties have been rounded up.

Table 2

Thermodynamic parameters for the dissociation of hydrogen cyanide^a in different media at various temperatures and ionic strengths

Medium I / M	Method	Temp °C	pK _a	ΔG _a kJ/mol	ΔH _a kJ/mol	ΔS _a J/K.mol	Reference
0^b	Calorimetry	8	9.76 (calc)	52.5	47.3±0.8	-31	Izatt et al., 1962
		25	9.21±0.01	52.2	43.5±0.8	-16	
	Calorimetry	10	9.63 (calc)	52.2	47.40±0.16	-16.9	Christensen et al., 1970
		25	9.22 (calc)	52.6	43.64±0.13	-30.1	
		40	8.84 (calc)	53.2	40.04±0.13	-42.9	
		25	9.21±0.08	52.6			
	<i>K(T)</i> (spectro- photometry)	50	8.59±0.08	53.1			
		75	8.18±0.08	54.5			
		100	7.89±0.08	56.4			
	<i>K(T)</i> (diffusion/ evaporation)	125	7.74±0.08	59.0			Broderius, 1981
		150	7.64±0.08	61.9			
		5	9.629±0.014	51.3			
		10	9.533±0.005	51.7			
		14.9	9.421±0.007	51.9 ₅			
		20.1	9.337±0.004	52.4			
	25	9.220±0.015	52.6				
	30	9.145±0.011	53.1				
<hr/>							
NaClO₄							
0.0^b	Calorimetry	25	9.21 ^c	52.6	43.8	-30	Solis et al., 1996a
0.1			9.03	51.5	43.95±0.51	-25	
0.5			9.01	51.4	44.20±0.38	-24	
1.0			9.01	51.4	43.92±0.14	-25	
3.0			9.45	53.9	43.13±0.35	-36	
5.0			10.01	57.1	38.53±0.07	-62	
<hr/>							
NaCl							
0.0^b	Calorimetry	25	9.21 ^c	52.6	43.4	-30	Solis et al., 1996a
0.5			8.949±0.004 ^d	51.1	44.57±1.58	-22	
1.0			8.946±0.005 ^d	51.1	47.55±1.45	-12	
3.0			9.220±0.005 ^d	52.6	50.95±0.79	-5	
5.0			9.660±0.004 ^d	55.1	53.15±0.41	-6	

^a Corresponding to eq. (2). ^b Values at infinite dilution were obtained by extrapolation or by correction for activity coefficients. ^c From Beck (1987). ^d Original data and standard deviations from Verhoeven, 1989.

Table 3

Solubility constant ($\log^* K_{s2}$) for CuCN(s) at 25 °C, obtained from measurements in different media

Ionic Strength (M)	Medium	Method	Log $^* K_{s2}^0$	Reference
→0	HCN	Solubility	-4.91	Vladimirova & Kakovskii, 1950
→0	NaCl	Solubility	-4.9±0.1	Königsberger et al., 1994
1.0	NaCl	Solubility	-4.50±0.01	Akilan et al., 2015

Table 4

Overall (β_n) and stepwise (K_n) formation constants of copper(I)-cyanide complexes in different aqueous media at various ionic strengths and temperatures

Ionic Strength (M)	Medium	Temp. °C	Method	Log β_n	Log K_n	References & Comments
CuCN⁰				$n = 1$		
1.0	NaCl	25	Estimated	16.33 ^a		Hefter et al., 1993
1.0	NaCl	25	Solubility	15.80±0.15		Akilan et al., 2015
Cu(CN)₂⁻				$n = 2$		
→0		25	JESS estimate	23.7		This paper
		25	Potentiometry	23.9 ^b		Vladimirova & Kakovskii, 1950
0.84-1.21	NaCu(CN)	25	Potentiometry	24.9±1.3		Bek et al., 1972;
		10		24.5±1.3		$\beta(T)$ values calculated from line of best fit to data (Figure 3).
		15		24.2±1.3		
		20		23.8±1.3		
		25		23.4±1.3		
		30		22.7±1.2		
		40		22.1±1.2		
1.0	NaCl	25	Potentiometry	23.95±0.01		Hefter et al., 1993; Solis, 1995
1.0	NaCl	25	Potentiometry	23.76±0.01		Akilan et al., 2015
3.0	NaCl	25	Potentiometry	23.93±0.01		Akilan et al., 2015
5.0	NaCl	25	Potentiometry	24.01±0.01		Akilan et al., 2015
Cu(CN)₃²⁻				$n = 3$	$n = 3$	
→0		25	JESS estimate		5.14	This paper
→0		25	Potentiometry ^c	28.5	5.30	Izatt et al., 1967
0.01	KOH	29	UV Spectrometry			Baxendale & Westcott, 1959
0.01	KClO ₄	25	UV Spectrometry		5.34	Kappenstein & Hugel, 1974
0.84-1.21	NaCu(CN)	25	Potentiometry	29.4±1.6	5.39	Bek et al., 1972;
		10		28.9±1.6	4.54±0.3	$\beta(T)$ values calculated from line of best fit to data (Figure 4).
		15		28.5±1.6		
		20		28.4±1.6		
		25		27.6±1.5		
		30		26.9±1.5		
		40		26.1±1.5		
1.0	NaCl	25	Potentiometry	29.38±0.04	5.43±0.04	Hefter et al., 1993; Solis, 1995
1.0	NaCl	25	Potentiometry	29.38±0.04	5.63±0.04	Akilan et al., 2015
3.0	NaCl	25	Potentiometry	29.33±0.04	5.40±0.04	Akilan et al., 2015
5.0	NaCl	25	Potentiometry	29.26±0.04	5.25±0.04	Akilan et al., 2015
Cu(CN)₄³⁻				$n = 4$	$n = 4$	

→0		25	JESS estimate	30.6	1.6	This paper
→0		25	Potentiometry ^c		1.5±0.2	Izatt et al., 1967
0.01	KOH	29	UV Spectrometry		1.74	Baxendale & Westcott, 1959
0.8-1.2	K(Na)CN	25	IR Spectroscopy		1.6	Penneman & Jones, 1956
0.84-1.21	NaCu(CN)	25	Potentiometry	30.8±1.7	1.84±0.1	Bek et al., 1972;
		10		30.3±1.7		$\beta(T)$ values calculated from line
		15		29.8±1.7		of best fit to data (see Figure 4).
		20		29.3±1.7		
		25		28.8±1.7		
		30		27.9±1.6		
		40		27.1±1.6		
1.0	NaCl	25	Potentiometry	31.78±0.02	2.38±0.04	Hefter et al., 1993; Solis, 1995
1.0	NaCl	25	Potentiometry	31.89±0.02	2.51±0.04	Akilan et al., 2015
3.0	NaCl	25	Potentiometry	32.25±0.02	2.92±0.04	Akilan et al., 2015
5.0	NaCl	25	Potentiometry	32.52±0.02	3.26±0.04	Akilan et al., 2015

^a Slightly different values have been estimated for $I = 3$ & 5 M (NaCl) media by Akilan et al. (2015). ^b Corrected by Izatt et al. (1967) using $pK_a^0(\text{HCN}) = 9.21$ and an extended Debye-Hückel equation. ^c Combined with calorimetry.

Table 5

Thermodynamic parameters for the overall formation reactions for di-, tri- and tetra-cyanocuprate(I) complexes in different media at 25 °C, with analogous data for tetracyano-Zn and -Cd complexes

Ionic Strength (M)	Medium	Method	Complex	Log β_n	$-\Delta G$ kJ/mol	$-\Delta H$ kJ/mol	ΔS J/K.mol	Reference
0 ^a		Calorimetry	Cu(CN) ₂ ⁻	23.94	137	122±1	12±0.5	Izatt et al., 1967
0.84-1.21	Na(Cu)CN	Potentiometry		23.9	136±7	125±3	[38±60] ^b	Calculated from Bek et al., 1972
0 ^a		Calorimetry	Cu(CN) ₃ ²⁻	29.24	167	168±1	-1.4±0.7	Izatt et al., 1967
0.84-1.21	Na(Cu)CN	Potentiometry		28.4	162±9	[142±4] ^b	[69±60] ^b	Calculated from Bek et al., 1972
0 ^a		Calorimetry	Cu(CN) ₄ ³⁻	30.74	175	215±2	-136±9	Izatt et al., 1967
0.84-1.21	Na(Cu)CN	Potentiometry			173±9	[165±4] ^b	[26±60] ^b	Calculated from Bek et al., 1972
1.0	NaCl	Calorimetry		31.77 ^c	181.2	237.9±1.7	-190.3	Solis et al., 1996b
1.0	NaCl	Calorimetry	Zn(CN) ₄ ²⁻	18.62 ^d	106.2	118.2±0.7	-40.3	Solis et al., 1996b
1.0	NaCl	Calorimetry	Cd(CN) ₄ ²⁻	18.62 ^d	82.4	113.9±0.6	-105.6	Solis et al., 1996b

^a Values at infinite dilution were obtained by extrapolation or by correction for activity coefficients. ^b Values in square brackets are thought to be less reliable than other listed results. ^c Value from Hefter et al. (1993). ^d Value in 3 M NaCl, from Verhoeven et al. (1990b).

Figure 1

Species distribution for the Cu(I)/CN⁻ system as a function of pH in 1 M (NaCl) at 25 °C with [Cu(I)]_T = 5 mM and [CN⁻]_T = 35 mM. Note that solutions at pH < ca. 4.5 are likely to be supersaturated with respect to CuCN(s).

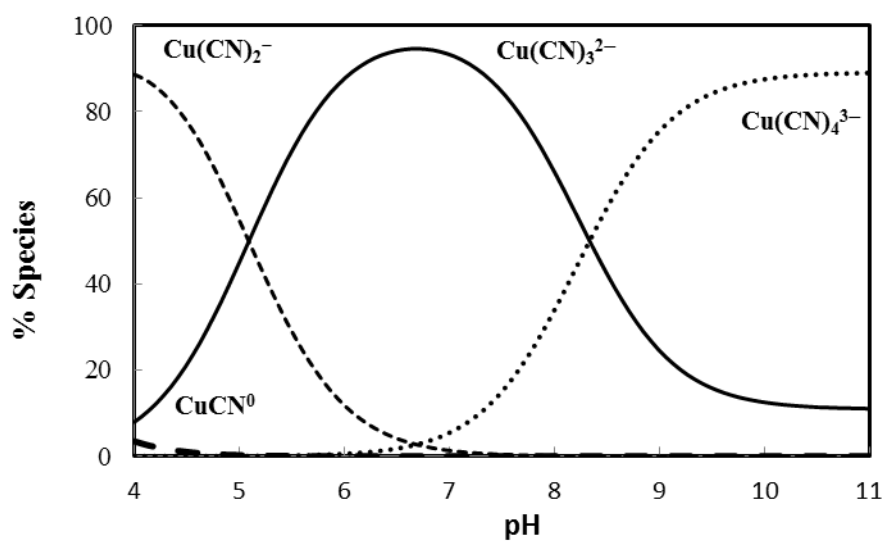


Figure 2

Ionic Strength dependence of $pK_a(\text{HCN})$ at 25 °C in NaCl (◆ Verhoeven et al., 1990a) and NaClO₄ (■ Solis et al., 1996a; □ OGáspar & Beck, 1982; + Persson, 1971).

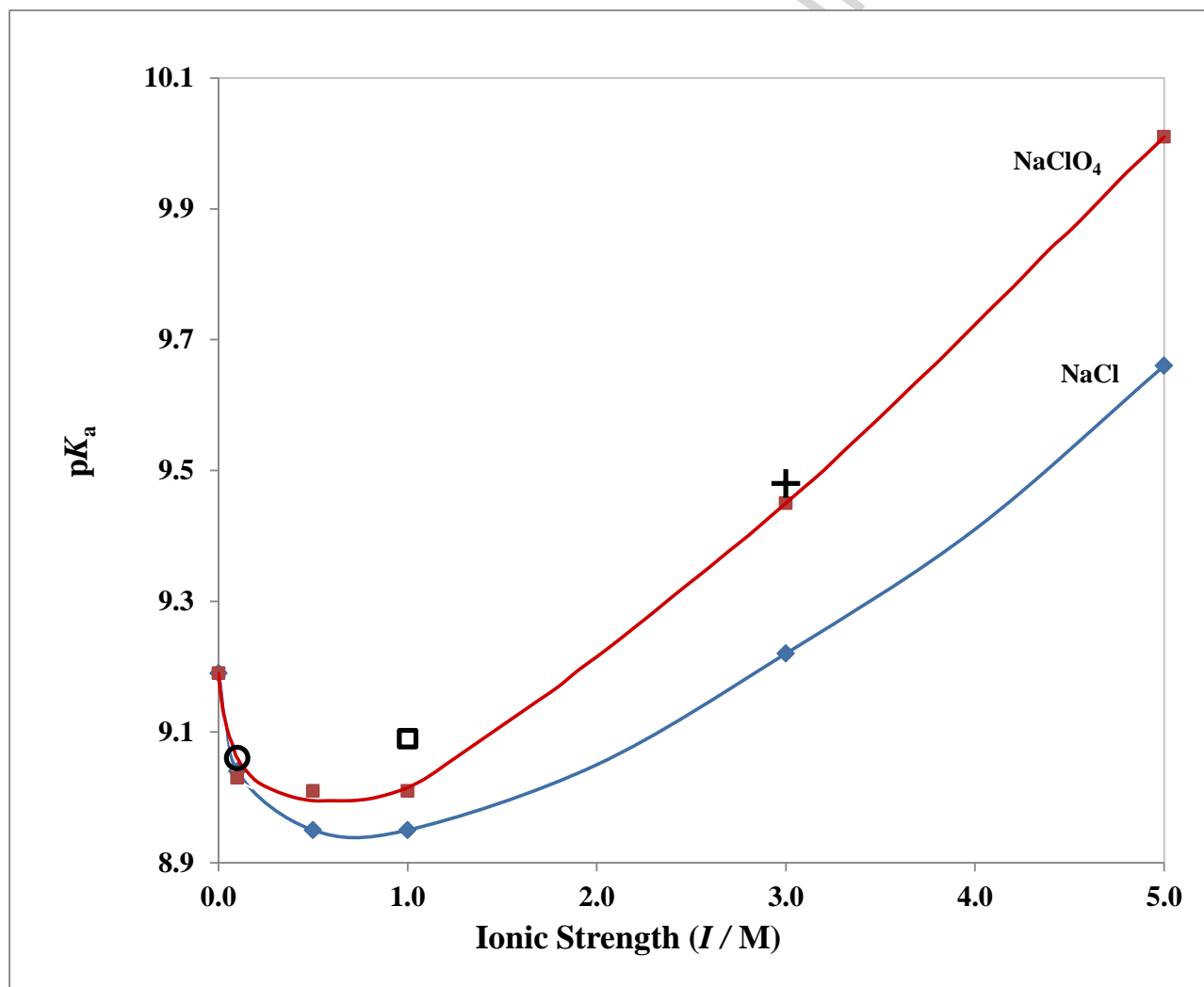


Figure 3

Temperature dependence of $pK_a(\text{HCN})$ at $I \approx 0$ and temperatures from (0 to 50) °C. The line corresponds to eq. (4) with $pK_a^0 = 9.21$ (Beck, 1987) and $\Delta H_a^0 = 43.6$ kJ/mol (Christensen et al., 1970).

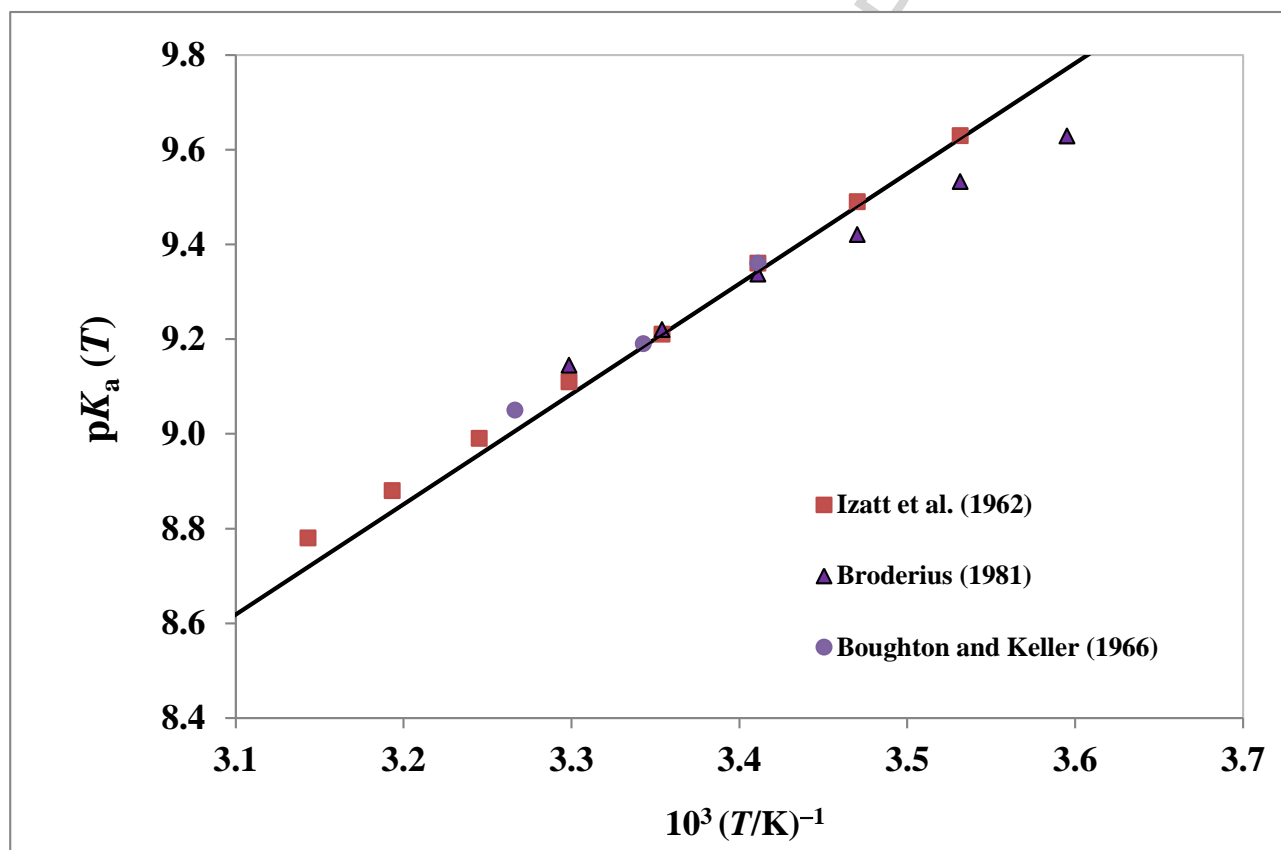
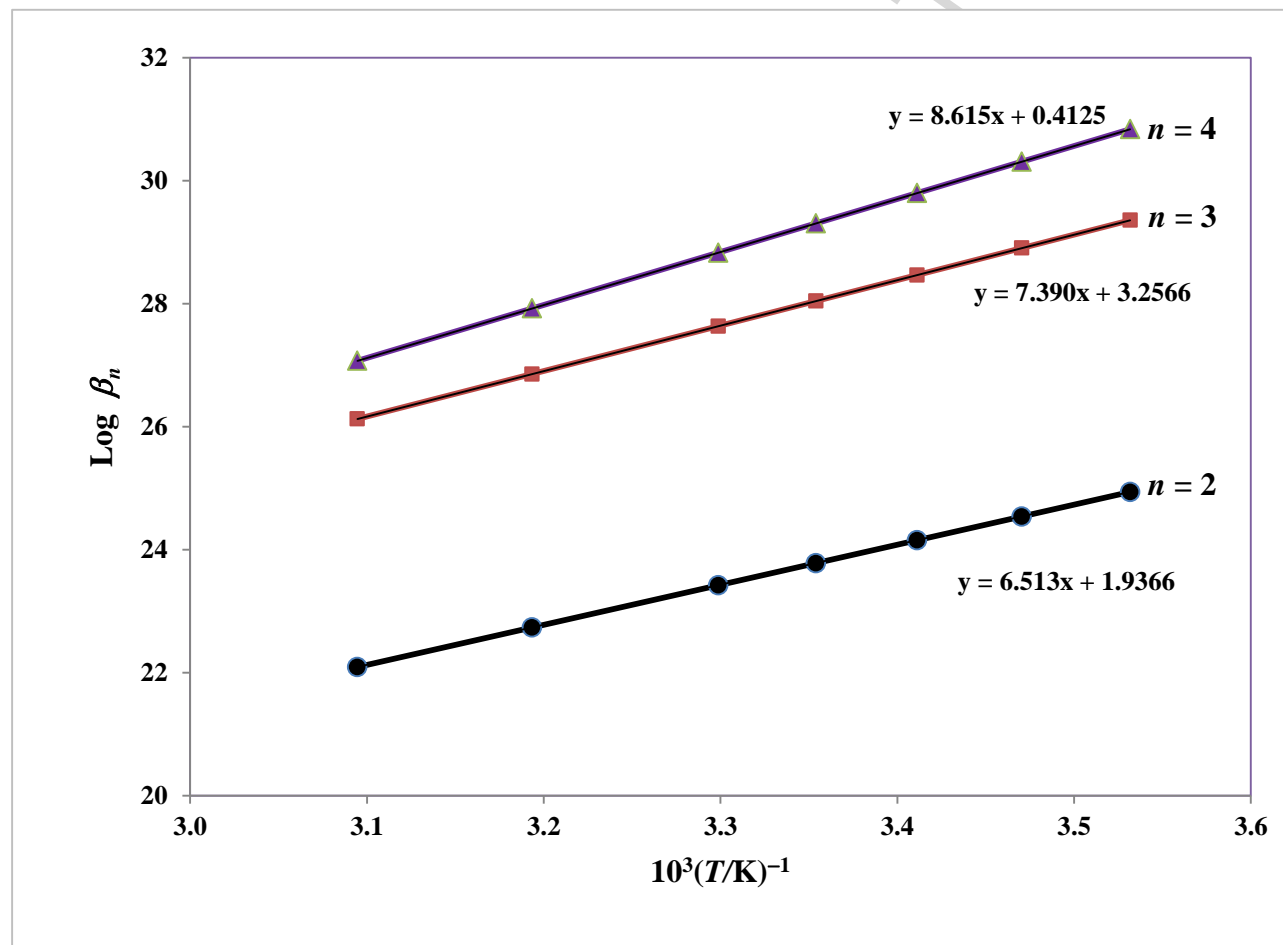


Figure 4

Temperature dependence of $\log \beta_n$ ($n = 2, 3, 4$) for cyanocuprate(I) complexes (data from Bek et al., 1972).



Highlights

- Review of formation and equilibrium constants for aqueous copper cyanide complexes.
- Includes measured dissociation constants for hydrogen cyanide and water.
- Also reviews equilibrium constants measured under non-standard conditions.
- The corresponding enthalpies and entropies of reaction are also reviewed.
- Gaps in available information determined and recommendations for further research.