

**THERMODYNAMIC AND KINETIC PROPERTIES OF  
METAL IONS IN AQUEOUS SOLUTION**

by

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**A Dissertation Submitted to the  
Graduate Faculty in Partial Fulfillment of  
The Requirements for the Degree of  
DOCTOR OF PHILOSOPHY**

**Major Subject: Physical Chemistry**

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## INTRODUCTION

The modern model of the physical structure of pure liquids is characterized by the order-disorder concept, wherein a short range ordered arrangement of the molecules of the liquid is encompassed with a long range disorder or chaos. Recent experiments<sup>1</sup> studying the effect of pressure on the behavior of sound in water indicate that water normally has a loose crystalline structure which absorbs sound waves, while under high pressures water transmits sound waves with little absorption, indicating a disordered, amorphous structure. Various theories have been proposed to explain the order-disorder model of liquids; and their validity, in view of the high-pressure experiments, must be reinvestigated, but for our purposes the observation of the probable presence of short range order suffices. A priori, since the motion of a molecule is determined by its interaction with surrounding molecules, it appears inevitable that with a dipolar liquid such as water some degree of electrostatic interaction and resultant structure should follow.

When an ion is placed in water, charge densities opposite in sign necessarily induce a form of order where

the neighboring water molecules tend to orient with their oppositely charged poles toward the central ion. A similar tendency exists between a dipolar molecule, either permanent or induced, and its water environment. Thermal agitation tends to disrupt the orientation, but the tendency towards ordering must inherently exist. This physical interaction has been termed hydration, or, more generally, solvation, of the ion or molecule, and was first recognized by Bredig<sup>2</sup>, who explained by hydration the anomalous observation that the ionic velocities of the alkali metal ions increase with increasing atomic weight, whereas lithium ion, with the smallest radius, should be expected to have the highest velocity. It appears that the small lithium ion is better able to attract to itself water molecules than the larger cesium ion which possesses the same charge but a lesser surface charge density. Cryoscopic measurements<sup>3</sup> have indicated that for aqueous KCl solutions, the average amount of total hydration per potassium plus chloride ions is: 1N KCl, 8.6 H<sub>2</sub>O; 0.5N KCl, 10.2 H<sub>2</sub>O.

Considering a dilute aqueous solution of a strong electrolyte, e.g., NaCl, in water, Arrhenius demonstrated that the salt was completely dissociated into sodium and chloride ions. The immediate neighborhoods of the ions

will possess some ordering of the water molecules, but the presence of anions in the solution indicate that very probably the sodium ion will surround itself with an atmosphere of chloride ions together with the usual oriented water molecules, and similarly, a chloride ion will tend to electrostatically induce an ionic atmosphere of sodium ions together with water molecules. If a quantity of alien salt, say KCl, were now to be introduced into this solution, the chloride atmosphere surrounding a sodium ion would be augmented over the original situation, and any properties of the sodium ion in the two cases would most certain differ. The concept of ionic strength,  $\mu$ , of a solution is concerned with such variations in properties with total quantity of salt in solution. The ionic atmosphere is the fundamental concept of the Debye-Hückel theory, which quantitatively relates the active mass of ion present in solution to its actual mass as a function of the quantity of electrolyte present in the solution. The Debye-Hückel theory will be discussed later, but the idea of an ionic atmosphere surrounding each ion in a dilute solution is today almost universally accepted as valid. A similar electrostatic attraction will exist between an ion and a dipolar neutral molecule, although the effect is secondary or

tertiary in magnitude.

The above discussion is not entirely true, for in solvents of low dielectric a minimum equivalent conductance is sometimes observed at a particular concentration.<sup>4</sup> Bjerrum<sup>5</sup>, and later Fuoss and Kraus<sup>6</sup>, explained such anomalies by the existence of ion pairs and triplets caused by electrostatic interaction. The concentrations of these pairs and triplets are dependent upon the sum of the radii of the ions and upon the dielectric of the solvent. Water has such a high dielectric that any ion pairs or triplets are negligible in quantity.

Polissar<sup>7</sup> considers a molecule or ion to be surrounded by approximately twelve closest-packed solvent molecules or oppositely charged ions. This cage constitutes a potential barrier, and the central particle must possess energy of the order of magnitude of five kcal/mole to pass the boundary. The mean diameter of the cage has been estimated at about  $10^{-8}$  cm for its highest value.<sup>8</sup> The cage model of liquids and solutions, although intriguing, has not been widely accepted.

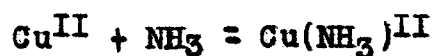
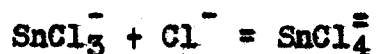
The ionic atmosphere has a loose, electrostatic structure with no stable configuration, but there is often a tendency for the anion to so closely approach the



cation and interact with it that it proves advantageous and even necessary to consider them as an intimate combination. This combination is termed a complex and acts as a single entity with innate properties which differ from the sum of the individual properties of the components. The three criteria which distinguish between an anion in the ionic atmosphere and one which can be considered as complexed to the cation can immediately be inferred as: 1) closer juxtaposition, 2) stable configuration (if a multimolecular combination), and 3) subsequent properties which differ from the sum of the components. The first two criteria are required of chemical bonding, a state which cannot be directly measured or calculated under the circumstances, and can only be indirectly inferred<sup>9</sup> after the existence of the complex is confirmed. The third criterion is likewise a direct result of chemical bonding and, therefore, not independent of the first two requirements, but if this difference in properties is macroscopically measureable and can be correlated, more or less exactly, to the microscopic conditions which prevail, then these measurements and their correlation are precisely what our attention must be focused upon.

## GENERAL OBSERVATIONS

We have seen that a metal ion in aqueous solution often forms complexes with anions, but complexing also takes place between a much wider variety of molecular and ionic species than has been indicated, e.g.,



Denoting the metal ion as M and the species to which it complexes as A, the complex may be written as  $\text{MA}_n$ , where, for convenience, valences are ignored.

It may be observed that the various species, complex or otherwise, in solution are in equilibrium, and the proportions of species may be related by an equilibrium constant,  $k_n'$ , where

$$k_n' = \frac{(\text{MA}_n)}{(\text{MA}_{n-1})(\text{A})} \quad (1)$$

where the parentheses indicate actual molar concentrations of the indicated species.

Two subjects must now be discussed, for they are relevant to equation (1). First, complexing has been observed with such a wide variety of anions that it has become customary to assume that water molecules are also

chemically bonded to the metal ion in accordance with the observed maximum complexing power of M. This coordination of water has actually been observed for the hexaaquo-complexed trivalent ions of the iron group, cobalt (III)<sup>10</sup> and chromium (III)<sup>11</sup>. Purportedly, the hexaaquo complexes of magnesium<sup>12</sup> and calcium<sup>13</sup> also exist. Thus, the essentially constant concentration of water should enter into (1), it is customary to include that term in  $k_n'$ . The question of whether alkali metal and the alkaline earth ions chemically complex with water is still undecided, but since in the crystalline state these ions are usually only electrostatically\* bonded to anions, it seems most probable that the ions exert only a similar attraction on the solvent and undergo no definite chemical bonding. An unsuccessful attempt<sup>14</sup> was made to distinguish by dialysis between the chemically bound, and the more loosely bound hydrated, water molecules.

Second, and more important, it has been noticed that the properties of an ion or molecule in solution are affected by the presence of other ions in the solution through the nature of the ionic atmosphere. The intrinsic tendency of  $MA_{n-1}$  to complex with A is a function of its effective, rather than actual, concentration,

---

\*In this paper the term electrostatic interaction is used to denote a classical electrostatic interaction.

and the effective molar concentration or activity,  $a$ , of a species may be defined as:

$$a = fc \quad (2)$$

where  $f$  is called the activity coefficient and  $c$  is the actual molar concentration of the species. At infinite dilution ion atmosphere effects vanish and effective and actual concentrations may be considered identical. Thus,  $f$  can further be defined as:

$$\lim_{c \rightarrow 0} \left( \frac{a}{c} \right) = f \Big|_{c=0} = 1 \quad (3)$$

The Debye-Huckel theory quantitatively related effective and actual concentrations by considering the work against electrostatic attraction involved in diluting a solution. After considerable approximations which are valid only in very dilute solution, the theoretical value of the activity coefficient was calculated to be:

$$-\log f_i = 0.51 \cdot z_i^2 \quad (4)$$

where the ionic strength is a measure of the electrostatic effect of ions in the solution on the activity coefficient. This formula has been found to hold for concentrations less than 0.01 molar, while various extensions of the theory are valid in more concentrated solutions. Empirical equations such as<sup>15</sup>:

$$-\log f_{\pm} = 0.51 \cdot z_1 z_2 \left( \frac{\sqrt{\mu}}{1 + \sqrt{\mu}} - C \right) \quad (5)$$

hold up to  $\mu = 0.1$ , where  $f_{\pm}$  is the mean activity coefficient and  $C \approx 0.20$  and varies from salt to salt.

Utilizing the concept of activity, the means are now at hand for eliminating salt effects on the equilibrium in (1), for the substitution of (2) in (1) gives:

$$k_n = \frac{a_{MA_n}}{a_{MA_{n-1}} \cdot a_A} = \frac{(MA_n)}{(MA_{n-1})(A)} \cdot \frac{f_{MA_n}}{f_{MA_{n-1}} \cdot f_A} \quad (6)$$

$$k_n = k'_n \cdot \frac{f_{MA_n}}{f_{MA_{n-1}} \cdot f_A} \quad (7)$$

where  $k_n$  is a true, or thermodynamic, constant for the various species, and  $k'_n$  is termed the concentration constant. The activity coefficients may be calculated, e.g., (4) or (5), when the solution is sufficiently dilute, thus for sparingly soluble salts. When more concentrated solutions are required by the nature of the experiment,  $k'_n$  may be determined as a function of the ionic strength and extrapolated to zero salt concentration to evaluate the true constant:

$$\log k'_n - 0.51 \left( z_{MA_n}^2 - z_{MA_{n-1}}^2 - z_A^2 \right) \sqrt{\mu} = \log k_n + C'\mu \quad (8)$$

Equation (8) demonstrates the course of such an extrapolation and it is obviously advantageous to measure  $k'_n$  in solutions as dilute as possible to simultaneously

reduce the extrapolation and approach the region where the assumptions are less drastic. It is evident that if A is a neutral molecule, the extrapolation should be of zero slope, and such a slope is observed with neutral A in dilute solutions.

Having found a property,  $k_n$ , which depends only on the intrinsic properties of the various species in solution and the relation of these species to their aqueous environment, it should prove enlightening to investigate the magnitudes of these constants, and, if possible, draw conclusions as to cause and effect.

Kossel (1916), and later Fajans, theorized that the formation of complexes was entirely determined by classical electrostatic interaction which existed between metal ions and anions, considering both as charged spheres. The existence of complexes such as  $\text{Sn}(\text{Cl})_4^{\equiv}$  does not necessarily disprove an electrostatic interaction, for attraction between dipoles, either permanent or induced, could account for interaction between two negatively charged or neutral species. Such complexes as the ferric or aluminum (III) fluorides are partially explained on such grounds, but more general comparisons to experiment have reduced the classical electrostatic attraction theory to obsolescence, although it is no doubt true that electro-

statics plays some role in the stability of complexes. N. Bjerrum<sup>16</sup> has calculated the electrostatic effect between ions considered as spheres on the ratio of  $k_n$  to  $k_{n-1}$  as:

$$\log \frac{k_n}{k_{n-1}} = 0.434 \frac{\phi_{n,n-1}}{kT} \quad (9)$$

where  $\phi_{n,n-1} = \frac{e^2}{Dr}$ , the simple coulombic interaction between two charged particles. The expression for electrostatic attraction has been further extended by others<sup>17</sup>, but the results are largely empirical and are therefore considered inadequate.

N. Bjerrum also developed the statistical effect on the ratios of the two constants. If  $N$  is the maximum value of  $n$  for the complex  $MA_n$ , and assuming that the  $N$  positions are uniform with respect to energy, the probability that  $MA_n$  splits off an  $A$  is proportional to  $n$ , and the probability that it takes up an  $A$  is proportional to  $N-n$ . The  $N$  consecutive constants are therefore proportional to

$\frac{N}{1}, \frac{N-1}{2}, \dots, \frac{N-n+1}{n}, \frac{N-n}{n-1}, \dots, \frac{2}{N-1}, \frac{1}{N}$ , and

$$\frac{k_n}{k_{n-1}} = \frac{(N-n+1)(n-1)}{(N-n)(n)} \quad (10)$$

Bjerrum extends this treatment to include non-uniform bonding. For a di-hydrogen acid, with the two hydrogens bound with different strengths,  $\frac{k_1}{k_2} = \frac{(q-1)^2}{q}$ , where  $q$  is how many times more readily one rather than the other acid

hydrogen is split off.

The simple statistical treatment is valuable in that a clue is given to the uniformity of the bonding. For the cupric ammines,  $(\text{Cu}(\text{NH}_3)_n)^{\text{II}}$ ,  $n = 1, 2, 3, 4$ , and  $5$ , the first four  $k_n$ 's are in the ratios of approximately  $4, 3/2, 1, 2/3, 1/4$ , thus indicating that the first four ammonia molecules are similarly bound to the cupric ion, but the fifth complexed ammonia is apparently much more weakly bonded.

Since the magnitudes of  $k_n$  can be completely explained by neither electrostatic nor statistical grounds, or a combination thereof, Bjerrum then turns to what he calls the ligand effect, the mutual influence of the ligands taken up and the influence on the forces binding the ligands to the central group. A combination of statistical, electrostatic, and ligand deliberations still proved unsatisfactory to account for the magnitudes of  $k_n$ .

It has been stated previously that the M-A bond is strictly chemical in nature. A quantitative investigation of the nature of bonding is quite outside the realm of this paper, but it may be said, with more or less exactness, that the presence of electrons in orbitals mutually compatible to the juxtaposition of M and A results in a MA



combination which has previously been termed a complex. The mutual compatibility is obviously the key to chemical bonding, but it is equally obvious that the words are descriptive only, and give no insight into the actual nature of the bond.

Proceeding, however, from such a description, the tendency towards complex formation must be some function of the electron structure of M and A. The Abegg-Bodländer rule<sup>18</sup> states that the relative electronegativities of M and A are of primary importance in discussing the stability of the MA complexing, and the tendency to complex must as a whole increase with increasing electro-affinity of the metal ion. This rule applies in comparing cadmium and mercuric ions, but does not account for the observed stabilities of complexes of metals in the zinc and copper groups. Another a priori rule, that the tendency towards complex formation decreases with increasing the size of the central metal ion, combines electrostatic and electro-negativity influences and prophesies the complexes of the Zn and Cu groups but fails in some other cases.

The Abegg-Bodländer rule indicates that there is at least a partial electron displacement from ligand to metal, and although the rule is not completely satisfactory, it

is reasonable to pursue such a line of thought to conclusion. Since the transition metals and elements such as Al and Si display considerable complexing, it is not unlikely that vacant, low-energy orbitals are necessary for complexing. Also, since the ligand invariably has a free, or reasonably free, pair of electrons, it is not immoderate to assume, as Sidwick does, that the MA bond is a coordinate-covalent type, where the ligand contributes both electrons to the bond. This view is supported, for example, by the stabilities of the cobalt(II) and (III) hexammines (See Pauling, reference 9, p. 96). It is logical, therefore, to postulate that the stability of a  $MA_n$  complex per given metal ion M is indicated by the availability of a pair of electrons, Lewis basicity, of the ligand A. If M is varied with a given A, the stability is correlated with the potential availability of a vacant, low-energy orbital, Lewis acidity, of M (or  $MA_n$ ). It is evident that this hypothesis is consistent with and includes the rules of the previous paragraph.

The first postulate qualitatively explains the slight complexing tendencies of ions such as  $NO_3^-$ ,  $SO_4^{2-}$ , and particularly  $ClO_4^-$ , for they are comparatively saturated and contain relatively firmly bonded electrons which are not

available for sharing to a metal ion. Cyanide ion, however, is quite unsaturated, and forms very stable complexes, per  $\text{Fe}(\text{CN})_6^{4-}$  and  $\text{Ni}(\text{CN})_4^{2-}$ , while  $\text{PO}_4^{3-}$  is partially saturated and forms only moderately stable complexes in comparison.

These comments are consistent with respect to metal ions, but a viewpoint may be taken where the anions which display little complexing ability with metal ions do so mainly because they are themselves complexed to saturation with water molecules. This attitude is consistent with a probable tendency for the saturated oxy-anions to form hydrogen bonds with water and is substantiated by a reported tetra-aquo perchlorate complex.<sup>19</sup> However, from the standpoint of the metal ion, perchlorate is non-complexing.

The second postulate, the potential availability of a vacant, low-energy orbital of M, is difficult to verify even qualitatively due to the lack of data, but the  $k_1$ 's of the zinc and cadmium ammines may be compared. The electronic structure of the zinc ion is  $\dots 3s^2 3p^6 3d^{10}$  and that of the cadmium ion is  $\dots 3d^{10} 4s^2 4p^6 4d^{10}$ . The complexing of an ammonia molecule would require placing the unshared pair of electrons of the ammonia into a vacant

orbital of  $M^{II}$ , probably an s orbital for both metal ions. Since the filled 5s orbital is of lower energy than the filled 4s orbital, the 5s orbital complex should be the more stable. The observed stabilities conform to such conclusions. The relative stabilities of these amines cannot be explained by electrostatic attraction, for if the crystal radii ( $Zn^{II} = 0.74^{\circ}_A$ ,  $Cd^{II} = 0.97^{\circ}_A$ ) (See Pauling, reference 9, p. 346) are indicative of the actual mean radii of the ions in aqueous solution, and this will be shown later to be true, the surface charge density of  $Cd^{II}$  is less than that for  $Zn^{II}$  and therefore should be less liable to induce an interaction with the dipolar ammonia molecule.

To accept the previous paragraph at face value would indeed be a paragon of naiveness for several reasons. First, cadmium ion apparently coordinates six ammonia molecules and zinc ion only coordinates four<sup>20</sup>, whereas equal maximum coordination should be observed. If steric hinderance alone prevents zinc from complexing more than four ammonia molecules, the above deliberations are insufficient. Second, the metal ions are very probably coordinated to water molecules, and it would be more proper to consider the energy difference between the aquo and

amine complexes, rather than between the metal ions alone and the ammine complexes. Third, solvation energies cannot be ignored. And fourth, the propriety of speaking of orbitals as such is, ipso facto, questionable. An investigation of the relation of available orbitals to stability of the complex has been pursued by Pauling<sup>9</sup>, and qualitative answers have resulted. A complete description of the energetics of the system offers insight into the problem, for systems tend to decrease in energy, but this description is attainable at the present time only by quantum mechanics and requires mathematical tools which have not yet been devised.

In general, the various theories which have been outlined are attempts to approximate a complete energetic treatment of the system, but while they appear in some instances to predict the correct stabilities, as often as not the predications are incorrect. Combinations of theories give predictions more often correct, but a general theory of stability remains to be conceived.

Meanwhile, certain empirical rules have been formulated. One rule which appears to be quite useful is: the higher oxidation states of metal ions form the stronger complexes. This is probably due to the greater

charge and greater availability of orbitals in the higher oxidation state. A purely empirical rule for stabilities was formulated by Sidgwick<sup>21</sup>, who observed that if the ligands can be considered as uniformly bound to the central ion, then values of the expression

$$\frac{N}{Z} \log k + \log 55 \quad (11)$$

for  $\text{CN}^-$ ,  $\text{NH}_3$ , and pyridine as ligands are approximately in the ratio of 1.7:1:0.6 respectively. The quantity  $k$  in equation (11) is the mean of  $k_N$ , thus  $k = \sqrt[N]{k_1 k_2 \dots k_N}$ , and  $Z$  is the characteristic maximum coordination number of the metal ion. The term  $\log 55$  arises from the separation of the water activity factor from  $k_N$ . This method can be utilized to estimate equilibrium constants which have not been measured or are difficult to determine.

## METAL COMPLEXES AND THERMODYNAMICS

Attempts to explain the tendencies of metal ions toward complexing proved generally unproductive from the microscopic viewpoint and finally appeared to be futile, especially in view of the interaction of the ions with the environment. It is now proposed that the macroscopic, or thermodynamic, viewpoint be investigated, for thermodynamics offers several conceptual, extensive quantities which may then be identified to the average microscopic physical situation.

Thermodynamics concerns itself with differences in properties, thus, the difference in properties of the system  $(MA_n)_{aq}$  and the original system  $(MA_{n-1})_{aq}$  and  $A_{aq}$ . One property, the ability to do work (other than pressure-volume work), should certainly differ between the two systems, for the chemical energies, defined as the ability to do adiabatic work, of the two systems differ, and likewise the hydrations of the two systems differ, since hydration expends energy and therefore does work. The extensive thermodynamic quantity free energy,  $F$ , has been correlated to the available work in a chemical change (isothermally at constant pressure) in a system, and the

decrease in free energy of the system is equal to the work available in that change:

$$\Delta F = -w \quad (12)$$

If the change in free energy between two given states is negative, the process towards the state having lower free energy content proceeds spontaneously, although nothing can be said about the rate of the process. For an equilibrium system, the concept of free energy is particularly useful in that it can be precisely determined by the activities of the reactants and products, combined with a knowledge of the activities of the species when equilibrium is established.

If it is desired that the product,  $MA_n$ , be formed at unit activity from reactants,  $MA_{n-1}$  and A, initially at unit activity, the change in free energy is given by

$$-\Delta F^0 = RT \ln k_n \quad (13)$$

where  $\Delta F^0$  is the standard free energy change at temperature T of the replacement of a water molecule by a ligand molecule.

Free energies are measureable by several different methods, and a determination of  $\Delta F^0$  thus evaluates the magnitude of  $k_n$ . The additivity of free energies of



reactions (and therefore the additivity of the reactions) considerably enhances one's ability to determine  $k_n$ . Finally, a free energy change is related to other thermodynamic changes which can be corresponded, more or less directly, to the microscopic viewpoint. For an isothermal, constant pressure process:

$$\Delta F^0 = \Delta H^0 - T \cdot \Delta S^0 \quad (14)$$

$$\Delta F^0 = \Delta E^0 + P \cdot \Delta V^0 - T \cdot \Delta S^0 \quad (15)$$

A change in free energy therefore is composed of a change in energy, volume, and entropy. Energy signifies the total ability to do adiabatic work, and includes translational, rotational, and vibrational energies of the molecules, any energy of the molecules due to their position in a force field, such as gravitation, and the energies of the electrons and nuclei themselves, per the Einstein equation. Since most of these quantities do not change appreciably during a chemical reaction,  $\Delta E$  is largely concerned with changes in chemical energies due to the breaking of a bond or its formation.

The  $P \cdot \Delta V$  term usually proves to be negligible, and therefore is of little interest to us, but the change in entropy in a chemical reaction is of prime importance. Spontaneous processes which are accompanied by an increase

in entropy likewise show an increased randomness, or disorder, and the association of the entropy of a system with its degree of disorder was completed by means of statistical mechanics. Thus, increasing the disorder of a system also increases its entropy, and vice versa; and the dispersion of the solute in a solution increases the entropy of the system originally composed of the two separate phases. Hydration also influences the entropy change, and therefore  $\Delta F^\circ$  and  $k_n$  of a system, for the ordering of the water molecules around ions gives an aqueous solution less entropy than it would have had if the order were not present, and the formation of  $MA_n$  from  $MA_{n-1}$  and A will include a change in the hydration characteristics and therefore an entropy change.

It is evident that the magnitude of  $k_n$  of an equilibrium system is influenced not only by energy changes, which includes the chemical bonding and electrostatic interaction with the environment, but also by the entropy change, which is independent of energy considerations and was previously unnoticed. The chemical bond energy changes have been discussed, but their precise relationship to  $k_n$  were not then apparent. It was observed that the science of these changes were largely empirical and would probably remain as such. The ion-environment interaction, however, has proved more amenable to study. An absolute method for determining

ionic entropies was devised by Latimer and co-workers.<sup>22</sup> The free energy of the ion-environment interaction can be obtained by subtracting from the free energy of the ion in solution the free energy of the gaseous ion. Utilizing various thermochemical data and the Sackur equation for gaseous ion entropies, the heat of ion-environment interaction can be obtained, and therefore the entropy of interaction can be calculated. The entropies of hydration were calculated for the alkali metal ions and for the halide ions. All entropies proved to be negative, and such would be expected from the increased ordering in the reaction  $M_{(g)}^I \rightarrow M_{(aq)}^I$ . The values steadily increased towards zero with increasing radius of the ion, and such a trend would again be expected since a larger radius signifies a lesser surface charge density and a lesser aptitude for inducing order.

If a theory were now developed which would relate the probable ordering of water molecules around metal ions as a function of the ionic radius, a means would be presented for evaluating the average physical situation in the neighborhood of metal ions. Such calculations were performed for water in ice by Pauling (See reference 9, p. 77). Proceeding from this base point, entropies of the ion-atmosphere could be calculated, and the actual

average physical system could begin to be elucidated on a microscopic scale.

One step in this direction has already been taken. The free energy of solution was calculated by Born,<sup>23</sup> considering ions as charged spheres, to be given by

$$\Delta F_{\text{hydr.}} = \frac{Ne^2}{2r_e} \left(1 - \frac{1}{D}\right) \quad (16)$$

where  $r_e$  is the actual radius of the ion in the aqueous solution and  $D$  the dielectric of the solvent, in this case water. Latimer obtained close agreement between experimental data and (16), if for  $r_e$   $0.85^\circ_A$  were added to the crystal radii of positive ions and  $1.00^\circ_A$  added to those for anions. Since  $r_e$  is closely related to the distance from the center of the ion to the pole of the nearest water molecule, indications are that the ion is located in a hole in the water. This model is closely similar to the cage model for solutions. Equation (16) has been extended by Yatsimirskii,<sup>24</sup> who obtained ionic entropy values slightly higher than those of Latimer. It is interesting to note that Latimer<sup>25</sup> originally used (16) as a measure of the chemical energy of hydration and concluded that the radii of ions in aqueous solution are identical with crystal radii. Another interesting feature of this problem is that the chemical energy of

hydration often cannot be approximated by the heat of hydration, or, in other words, electro-compression work is sometimes appreciable in magnitude.<sup>26</sup>

It is now proposed that a return to the quantity  $k_n$  be made, for although the existence of aqueous complex species have been recognized for some time, quantitative estimations of the proportions of the species have often been erroneous, due to confusion about ionic strength and the numbers of complexed ligands. In fact, only recently has any large amount of attention been given to the values of  $k_n$  rather than the gross equilibrium constant  $K_N$ , or  $k_1 k_2 \dots k_N$ . This earlier attitude tends to ignore the quantities of lesser complexed species, although it is mechanistically impossible for  $MA_N$  to exist without some amount of lesser complexed species present at least momentarily. From a thermodynamic point of view, the relative proportions of the complexes are merely functions of their free energy content, and if only one species is present in large amounts in the solution, this only means that its free energy content is much less than that of other complex species. Similarly, thermodynamics immediately implies equilibrium, and the existence of  $MA_N$  implies an equilibrium of  $MA_N$  with  $MA_{N-1}$  and A, although the concentrations of the latter may be small compared to  $MA_N$ . The question

is therefore one of degree of stability, or relative magnitudes in free energy content.

Exact determinations of the magnitudes of  $k_n$  would therefore increase one's knowledge of aqueous chemistry. Also, this determination should facilitate a theoretical treatment of the problem, for any empirical observation can be explained, with more or less propriety, on theoretical or judicious grounds.

It is immediately evident that gross analytical methods which disturb the equilibrium are useless to determine  $k_n^i$ .

Perhaps the most versatile method of measuring  $k_n^i$  without perturbing the system is the indirect thermodynamic technique which utilizes the free energy relation to the equilibrium constant, and the most accurate way to measure this free energy change is by its relation to the equilibrium potential of a reversible electromotive cell:

$$-\Delta F = nF'E \quad (17)$$

where  $E$  is the potential of a reversible cell,  $F'$  is Faraday's constant, and  $n$  is here the number of electrons exchanged in the isobaric, isothermal electrode process.

DETERMINATION OF STANNOUS CHLORIDE  
EQUILIBRIUM CONSTANTS

Introduction

Consider two half cells each composed of a metal electrode  $M^0$  immersed in a solution one containing the metal ion  $M$  and the other complex  $MA_n$ . If these two half cells were opposed, the electrical energy produced by the passage of one faraday is  $F'E$ , and would depend on the states of the metal ion in the two solutions. The sources of free energy change, thus  $E$ , are three in number. First, if the metal or the metal amalgam electrodes are at different activities, the transfer of a quantity of  $M^0$  from one activity to another results in a free energy change. Second, if the metals or their amalgams are at equal activity, but the aqueous activities of  $M$  differ, a similar transfer likewise results in a free energy change. And third, the junction between the two aqueous solutions often results in an appreciable  $\Delta F$ , and therefore  $E$ , or liquid junction potential. Ignoring the third source of  $\Delta F$  for the present, if both metal electrode activities are the same, the potential of a concentration cell containing different

$a_M$ 's is given by the Nernst equation as:

$$E = \pm \frac{RT}{nF} \ln \frac{a_{M_{II}}}{a_{M_I}} \quad (18)$$

where  $a_{M_I}$  is the activity of M in half cell I,  $a_{M_{II}}$  that in half cell II, and the sign readily deduced from the greater tendency of the more active solution to plate out  $M^0$ , for, in accordance with convention, it will give the more positive electrode.

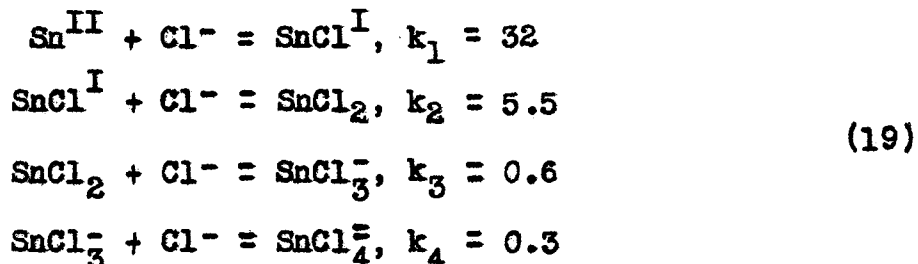
Equation (18) precisely relates the activities of M in the two half cells, and if measures are taken to ensure equal ionic strengths for the half cells, the equation will relate the disparity in metal ion activity which can be attributed to complexing.

The stannous chloride complexes and their mutual equilibriums prove to be a system to which equation (18) is applicable. An exact determination of the concentration constants of the species would prove useful, for stannous ion is a favorite mild reducing agent and often a knowledge of the nature of the species in a chloride solution would prove valuable. This knowledge would also be useful in a study of the chloride corrosion of metallic tin.



## Review of Literature

The stabilities of the stannous chloride complexes were originally determined by Prytz<sup>27</sup> as follows:

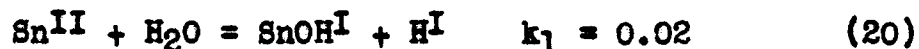


His procedure consisted of the measurement of the potential of a half cell composed of an unamalgamated tin electrode in a solution containing stannous and chloride ions. From the observed potential of the cell, its  $E^0$  (unit activities), and the stannous and chloride activities, calculated by the Debye-Hückel equations, the four constants were evaluated.

This work is of questionable value because of the very probable variation in free energy of the surface of the metal electrode due to the presence of physical strains and because of the use of the Debye-Hückel theory for solutions of ionic strength far above that for which the theory was originally derived and has been found to be applicable. Also, the standard electrode potential of the  $\text{Sn}^0\text{-Sn}^{\text{II}}$  couple is difficult to determine exactly, and Prytz did not take hydrolysis of tin(II) into account.

A later reference<sup>28</sup> contributed only a qualitative statement to the effect that stannous ion complexes with chloride ion.

The stability of a mono-hydroxyl complex of tin(II) was measured by Gorman:<sup>29</sup>



The nature of the complex species of tin(II) is therefore a function of the acid strength of the solution even if complexing anions were absent.

### Theory

It has been noticed that the e.m.f. of a concentration cell may be a measure of the change in activity of a metal ion which can be attributed to complexing, if equal ionic strengths are maintained in both half cells. The slight tendency of perchlorate ion towards complexing has already been mentioned, and, in fact, no metal perchlorate complexes have been observed. Smith and Goetz<sup>30</sup> found that the potential of the Ce(IV)-Ce(III) couple sharply varied with perchloric acid concentration, but this variation is more reasonably explained by variable aquo-complexes rather than perchlorate complexes.<sup>31</sup>

This non-complexing of perchlorate ion provides a means of maintaining an appreciable constant ionic strength without fear of complexes being formed, and it also offers a convenient base point for equation (18), for  $E$  evaluated as a function of the concentration of complexing ligand will be shown to also evaluate the magnitudes of  $k'_n$ .

If half cell I contains only perchlorate as the anion, the activity of  $M$  in I is directly proportional (equation (2)) to its total formal molar concentration,  $T_M$ , or

$$a_M = f_M \cdot T_M \quad (21)$$

But if half cell II contains a complexing ligand  $A$ , together with sufficient perchlorate to give both solutions equal ionic strength, complexing will occur, and the actual activity of  $M$  will vary with the amount of  $A$  present in the solution, although its activity coefficient, solely a function of the total amount of ions present, will remain identical with that in cell I. If  $T_M$  is equal in both half cells, then

$$T_{M_I} = T_{M_{II}} = (M)_{\text{total}} = (M) + (MA) + \dots + (MA_n) + \dots + (MA_N) \quad (22)$$

If the uncomplexed ligand concentration,  $(A)$ , is much greater than the concentration of ligand which is present in the complex species, then

$$(A) = T_A \quad (23)$$

Since,

$$k'_n = \frac{(MA_n)}{(MA_{n-1})(A)} \quad (24)$$

an evaluation of  $(M)_{II}$  as a function of  $T_A$  gives

$$(M)_{II} = \frac{T_M}{1 + k'_1 T_A + k'_1 k'_2 T_A^2 + \dots + k'_1 \dots k'_N T_A^N} \quad (25)$$

The substitution of (21) and (25) in (18) allows a cancellation of activity coefficients and

$$\exp \left[ \frac{-E}{\left( \frac{RT}{nF} \right)} \right] = \zeta = 1 + k'_1 T_A + \dots + k'_1 \dots k'_N T_A^N \quad (26)$$

An empirical determination of the curve obtained from a plot of equation (26) allows an estimation of  $k'_n$  for that particular ionic strength.

The problem of liquid junction potentials, long a thorn to electrochemists, will now be discussed, and a rationalization presented for the omission of this potential from (26). Since the cell under consideration consists of two solutions of different concentrations, a direct joining of the two solutions would produce an electrolyte-electrolyte boundary or junction of variable thickness. Across such a junction there is a diffusion of electrolytes from the solution of higher concentration to that of lower concentration, and since different ions have different mobilities a steady state is finally reached in which solutions will

become oppositely charged and a potential results. The magnitude of this junction potential is accordingly a function of the ionic mobilities and cannot be measured directly, although it has been theoretically calculated for a uni-univalent salt by Henderson,<sup>32</sup> and for the more general case by Cummings.<sup>33</sup> Attempts have been made to eliminate the junction potential by use of saturated KCl or  $\text{NH}_4\text{NO}_3$  salt bridges, for the mobilities of the cation and anion of these salts are almost equal, and the junction potential is therefore reduced to a few millivolts which is usually neglected.

For a concentration cell containing equal concentrations of all ions in both half cells, diffusions are equal in both cells and no overall junction potential results. A commendable virtue of the experimental method previously outlined is that perchlorate ions are essentially uniformly replaced by ligands, and if the ligand has approximately the same mobility as perchlorate ion, the diffusional characteristics of the two cells remain almost the same. Any junction potential which remains after using the salt bridge may be considered as negligible.

Four inherent limitations qualify use of the experimental technique as outlined. First, M must participate in a reversible electrode process; second, N, the maximum

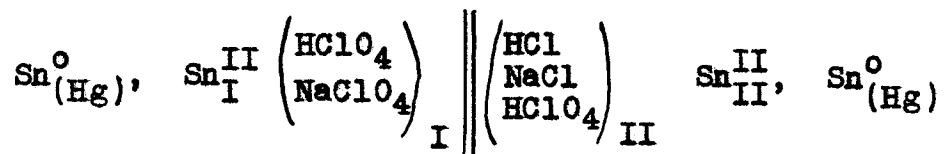
number of complexed ligands, must not be too large or the mathematical form of (26) becomes too non-unique to allow an accurate determination of  $k_n^I$  for large  $n$ ; third, the magnitudes of  $k_n^I$  must be neither too large nor too small; and fourth, since ionic strength is usually maintained at a high value, unless the activity coefficients of the species are independently known, the thermodynamic constants  $k_n$  cannot be determined. Another semi-limitation exists: if  $N$  is not previously known, the polynomial nature of (26) limits its usefulness to determine  $N$  if it is greater than three since cubic and quartic polynomials are not sufficiently dissimilar in their lower ranges to allow a distinction between them by an experimental curve.

### Experimental

The potential of a concentration cell composed of two  $\text{Sn}^0\text{-Sn}^{\text{II}}$  half cells was measured. The total concentration of tin(II),  $T_{\text{Sn}^{\text{II}}}$ , was identical in both half cells, but one half cell, I, contained only perchlorate and varying concentrations of chloride ion. Since hydroxyl complexes of stannous tin exist, a constant hydrogen ion concentration was maintained and was equal in both half cells. A constant ionic strength was also maintained. The

electrodes were tin amalgam of equal tin concentration.

Thus, the system under consideration is:



The only source of potential is:

$$E = -0.0128 \ln \frac{a_{\text{Sn}_{\text{II}}^{\text{II}}}}{a_{\text{Sn}_{\text{I}}^{\text{II}}}} \quad (27)$$

since the tin activities are equal in both amalgams and junction potentials are assumed eliminated by a  $\text{NH}_4\text{NO}_3$  salt bridge.

The assumption of elimination of junction potentials follows from a comparison of the limiting conductances of perchlorate and chloride ions,  $\lambda_0 = 68.0, 76.3$ , respectively, and, for comparison,  $\lambda_0(\text{K}^{\text{I}}) = 73.5$ .<sup>34</sup> Since the limiting conductance of an ion can be related to its mobility, it may be inferred that the replacing of perchlorate by chloride does not produce an appreciable junction potential, especially when a salt bridge is used.

Since the stannous concentration was initially only 0.005M and decreased with increasing chloride concentration because of dilution, the assumption that the free chloride concentration is identical with the total, or formal, chloride concentration is well founded. Such species as  $\text{Sn}(\text{Cl})_5^{-3}$  and  $\text{Sn}(\text{Cl})_6^{-4}$  are not included in this treatment

since there is no evidence for their existence. Since a considerable acid concentration is maintained in the cells, the concentration of the hydroxylated stannous species can be calculated to be negligible. Therefore, from equation (26),

$$\exp\left(-\frac{E}{0.0128}\right) = \zeta = 1 + AT_{Cl^-} + BT_{Cl^-}^2 + CT_{Cl^-}^3 + DT_{Cl^-}^4 \quad (28)$$

where

$$\begin{aligned} A &= k_1' \\ B &= k_1'k_2' \\ C &= k_1'k_2'k_3' \\ D &= k_1'k_2'k_3'k_4' \end{aligned} \quad (29)$$

Reagent grade chemicals were used in this experiment. Sodium perchlorate was made by the neutralization of  $HClO_4$  with  $NaOH$ .

The  $Sn(ClO_4)_2$  was standardized against  $Ce(ClO_4)_4$ , which was previously standardized by ferrous ammonium sulfate. Any original stannic tin impurities in the stannous perchlorate were assumed to have a negligible effect since the stannous concentrations were small. The acids were standardized against weighed  $Na_2CO_3$ , and the  $NaCl$  solution prepared from weighed  $NaCl$  which had been dried.

The acids were adjusted to equal concentrations, and similarly for the salt solutions. The amalgam was made ..



by dissolving approximately one gram of tin in 100 ml. of mercury. The activity of the tin in the amalgam, being equal in both half cells, is immaterial for our purposes.

Equal volumes of a solution in which  $(H^I) = 2.00$  and  $(Sn^{II}) = 0.005$  with  $\mu = 2.03$  were added to the half cells and the potential of the system measured. In every case the original potential was within 0.3 millivolts of the correct potential of zero. Then acids, salts, and water were added to the cells, perchlorates in one cell and perchlorates and chlorides in the other, in the appropriate quantities as determined by the desired chloride concentration and the constraints of constant  $(H^I)$  and ionic strength. The required equality in concentration of the stock acid and salt solutions and initial electrode solution enabled constant  $(H^I)$ ,  $\mu$ , and  $T_{Sn}^{II}$  to be maintained in both cells while  $(Cl^-)$  was changed in cell II. This dilution lowered the total stannous concentrations in both cells from their original values, but at any time the total volumes in the cells were equal, and therefore the total tin(II) concentrations were identical. This procedure required that the partial molar volumes of the two acids, and likewise the two salts, be equal, and within the limits of this experiment the condition can be assumed satisfied.

The facility of the experimental method follows from the equalities in concentrations indicated above. The mathematics of the dilution are easily developed and therefore will only be briefly indicated. Choosing a desired increment in chloride concentration, a series of equations may be set up according to the required constraints of constant ( $H^I$ ), constant ionic strength, chloride concentration, and volume additivity. These equations are homogeneous in the first order. Since all variables, the volumes of acid, salt, and water, do not occur in all equations, they may be solved for with no great difficulty.

A salt bridge made of a three per cent agar solution saturated with ammonium nitrate was used. With a saturated KCl bridge, a potential drift was observed, for some chloride necessarily diffuses into the body of solution. The lack of drift with the ammonium nitrate bridge allowed the elimination from consideration of stannous nitrate complexes.

An inert atmosphere of nitrogen was maintained throughout the cell system to prevent air oxidation of the stannous tin. Fresh solutions of stannous perchlorate were prepared each day. All potentiometric measurements were made with a Leeds and Northrup Student Type Potentiometer. Precision was maintained to  $\pm 0.4$  mv. Temperature was held constant

to  $25.0 \pm 0.1^\circ\text{C}$ .

### Results and Discussion

The results of this experiment are given in Table 2. Values for E are the average of three determinations. The data in Table 1 were plotted, Figure 1, and the best curve was drawn through the experimental points. Figure 1 corresponds to equation (28), and the tolerances indicate the effect of the probable error in E.

Due to the unwieldiness of a fourth order determinant, A, or  $k_1^i$ , is best found by taking the limiting slope of the curve at  $T_{C1}^- = 0$  by the plane surface mirror method. With A known, three values for  $T_{C1}^-$  with their corresponding  $T_{C1}^-$  values were taken, and solution of the resulting third order determinant for B, C, and D enabled evaluation of  $k_2^i$ ,  $k_3^i$ , and  $k_4^i$  from (29). A direct solution of the fourth order determinant was found to offer fewer significant figures in  $k_n^i$ . The following values for the equilibrium constants were obtained at  $\mu = 2.03$ :

Table 1. E as a function of  $T_{Cl}$ .

$(\text{Sn}^{\text{II}})_{\text{initial}} = 0.005$   
 $(\text{H}^{\text{I}}) = 2.00$

$\mu = 2.03$   
 $T = 25.0 \pm 0.1^\circ\text{C}$

---

$T_{\text{Cl}}$	- E	$\xi = \exp\left(\frac{-E}{0.0128}\right)$
0	0	1
0.010	0.0015	1.12
0.030	0.0043	1.40
0.050	0.0068	1.69
0.080	0.0103	2.23
0.100	0.0129	2.74
0.130	0.0156	3.38
0.160	0.0189	4.40
0.200	0.0222	5.72
0.250	0.0262	7.75
0.300	0.0296	10.1
0.350	0.0327	12.9
0.400	0.0356	16.1
0.450	0.0382	19.9
0.500	0.0404	24.0
0.550	0.0428	28.3
0.600	0.0451	33.8
0.650	0.0472	39.5
0.700	0.0492	46.5
0.750	0.0507	53.0
0.800	0.0528	61.3
0.850	0.0540	68.0

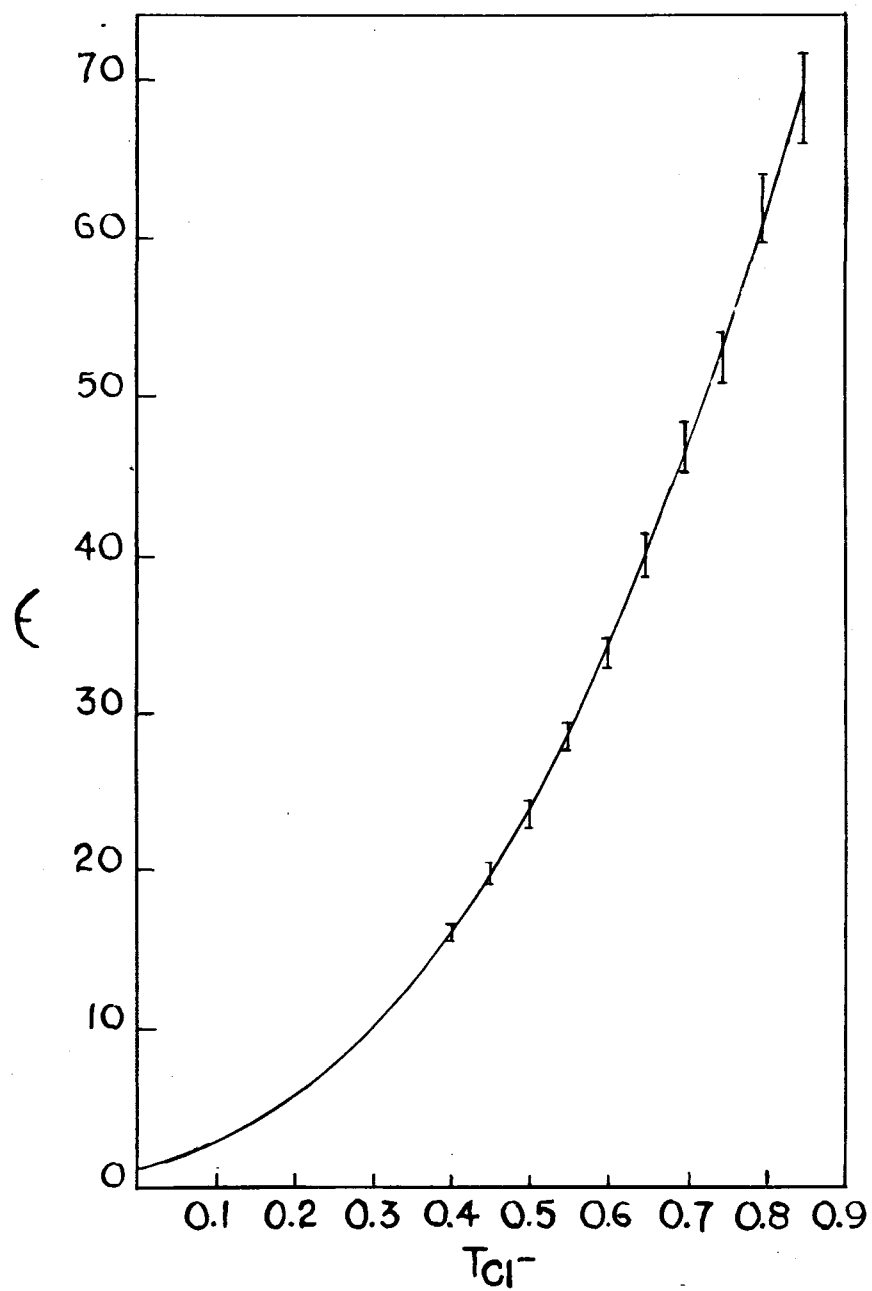


Fig. 1. Variation of  $\xi$  with  $T_{Cl-}$ , where  $\xi = \exp (-E/0.0128)$ .

$$\begin{aligned}
k_1' &= 11.3 \pm 0.2 \\
k_2' &= 5.1 \pm 0.2 \\
k_3' &= 0.24 \pm 0.005 \\
k_4' &= 1.0 \pm 0.4
\end{aligned}
\tag{30}$$

The increasing probable error in (30) resulted from the polynomial character of  $T_{Cl^-}$  in (28) and the exponential nature of  $\xi$ , although the precision of  $E$  was maintained throughout. These probable errors were calculated from the probable error in  $k_1'$  together with values from best curves drawn through the extremities of the tolerances. The values of  $k_n'$  in (30) generally correspond to those of Prytz for  $\mu = 0$  when allowance is made for trends in activity coefficients, but it is believed that  $k_n'$  in (30) was the more accurately determined.

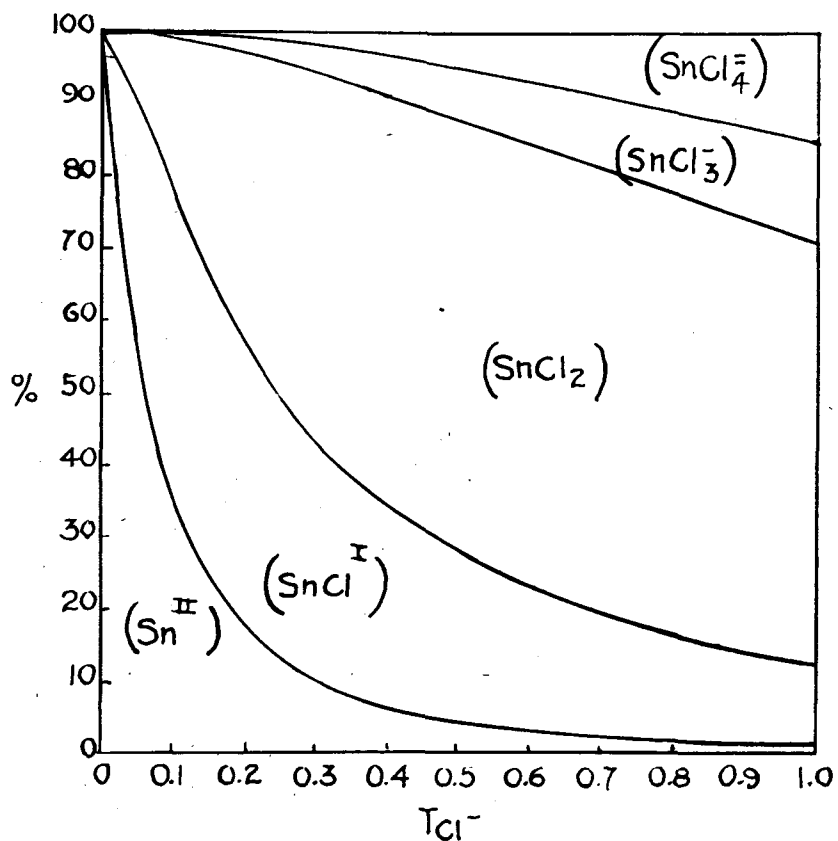
The relative proportions of species in an acidic stannous chloride solution of  $\mu = 2.03$  can be calculated by the following equations, assuming  $(Cl^-) = T_{Cl^-}$ :

$$\begin{aligned}
(Sn^{II}) &= \frac{T_{Sn^{II}}}{1 + k_1' T_{Cl^-} + \dots + k_1' k_2' k_3' k_4' T_{Cl^-}^4} \\
(SnCl^I) &= (Sn^{II}) \cdot T_{Cl^-} \cdot k_1' \\
(SnCl_2) &= (Sn^{II}) \cdot T_{Cl^-}^2 \cdot k_1' k_2' \\
(SnCl_3) &= (Sn^{II}) \cdot T_{Cl^-}^3 \cdot k_1' k_2' k_3' \\
(SnCl_4) &= (Sn^{II}) \cdot T_{Cl^-}^4 \cdot k_1' k_2' k_3' k_4'
\end{aligned}
\tag{31}$$

These proportions are shown in Figure 2.

### Summary

A general method was outlined for evaluating concentration equilibrium constants of complex ions when the parent positive ion participates in a reversible electrode reaction. This method was utilized to determine the equilibrium constants of the stannous chloride species at an ionic strength of 2.03.



**Fig. 2.** Per cent of ionic species in a stannous chloride solution, assuming excess chloride. Vertical distances between curves denote per cent of tin(II) present as the indicated species.



## METAL COMPLEXES AND KINETICS

Up to this point our attention has been thermodynamically focused upon equilibrium systems composed of aqueous metal complexes and their products. Since thermodynamics is concerned only with net changes in properties between states, it can say nothing about the mechanisms of such changes. It is now proposed that the mechanistic or kinetics of these changes when applied to aqueous metal ions and their complexes be investigated.

The reactions involved in thermodynamic equilibria between complex species are usually rapid and a relatively small free energy of activation for the reaction is concluded. Since the entropy of activation may contribute appreciably to the rate if the formation of the activated complex requires considerable rearrangement of energy, the chemical energy of activation may be quite small but the reaction will still be slow. Some equilibria, however, are only slowly established. Among these are the "robust" amines of cobalt, chromium, and platinum. The low value for  $k$  indicated a considerable free energy of activation.

The rapidity of the establishment of most complex equilibria have not allowed a study of their kinetics,

but reactions involving change in oxidation state are often sufficiently slow so that the mechanism of the reaction may be studied.

Previous to now we have been concerned only with thermodynamic and kinetic systems which undergo no gross change in oxidation state, but it is obvious that a discussion of the behavior of metal ions in aqueous solution would be quite incomplete if oxidation changes were omitted. Indeed, the mechanism of electron exchange is perhaps the most interesting facet of the chemistry of metal ions.

Consider the oxidation-reduction reaction involving an exchange of one electron:



An electron exchange between the bare, colliding metal ions is conceivable, but electrostatic repulsion between the ions would tend to oppose this mechanism. Although such a possibility should not be considered refuted, it is labeled as improbable. Another possible mechanism is the "tunneling" of an electron through the free energy barrier which would exist between the state of the two metal ions in fairly close proximity, but not colliding, and a similar juxtaposition but with the electron transferred to the other metal ion.

Another mechanism offers itself, for the tendencies of metal ions to complex and thus lower their free energy, tenders a variety of possible reactants, each of which may pursue different reaction paths. The diversity of paths due to complexing arises from the increased complexity of the complex species over a bare metal ion. If a mechanism is observed which involves a complex of one of the metal ions in the activated state together with the other metal ion in some form, the problem arises as to whether the change in oxidation state is actually due to atom transfer and whether the name of electron transfer is a misnomer. But the term oxidation state was not designed to be relevant on a microscopic scale, and the question of whether a trivalent metal ion complexed to a univalent anion is actually in its trivalent oxidation state or in its divalent state and complexed to a neutral atom is quite nebulous and will hereafter be ignored as much as proves to be feasible. The convention henceforth will be to attribute to the atoms of a complex the oxidation state which they originally had before complexing unless evidence proves otherwise. This technique is the simplest one and is common procedure, but it is admittedly only a bookkeeping device.

MECHANISM OF  $\text{Cu(II)-CN}^-$  REACTION

## Introduction

Studies of the mechanism of electron transfer have demonstrated that complexes often play a pertinent role in the oxidation reaction, e.g.,  $\text{Fe(III)-I}^-$ ,<sup>35</sup>  $\text{Ce(IV)-glycol}$ ,<sup>36</sup>  $\text{Ce(IV)-Cl}^-$ ,<sup>37</sup>  $\text{Fe(III)-SO}_3^-$ ,<sup>38</sup>  $\text{Mn(III)-C}_2\text{O}_4^-$ ,<sup>39</sup> and numerous others, and a possible generalization may be stated: coordination complexes are involved mechanistically as intermediates in homogeneous ionic oxidation-reduction reactions. This hypothesis appears to be particularly applicable to reactions involving cationic oxidizing agents and anionic reducing agents.

A further point of interest in connection with coordination intermediates is any relationship which might exist between the number of oxidizable anions in the complex and the rate of electron transfer. For example, the complex  $\text{FeI}_2^{\text{I}}$  forms ferrous ion much more rapidly than does the complex  $\text{FeI}^{\text{II}}$ , while  $\text{Mn(C}_2\text{O}_4)^{\text{I}}$  yields manganous ion very much more rapidly than does  $\text{Mn(C}_2\text{O}_4)_2^-$ .

The present work examines the  $\text{Cu(II)-CN}^-$  reaction from the points of view outlined above. This reaction is suitable for our purposes since the oxidizable anion is such a

strong complexing agent that if the reaction were found to not involve an intermediate complex, the postulate of necessary intermediates would have to be discarded. But more important, the numerous cyanide complexes of both Cu(I) and (II) indicate that in this reaction any relationship between the intermediate and its rate of reaction could perhaps be recognized more easily than for other reactions.

### Review of Literature

The experimental procedure required an investigation of the literature pertaining to the copper (I) and (II) complexes of ammonia and cyanide.

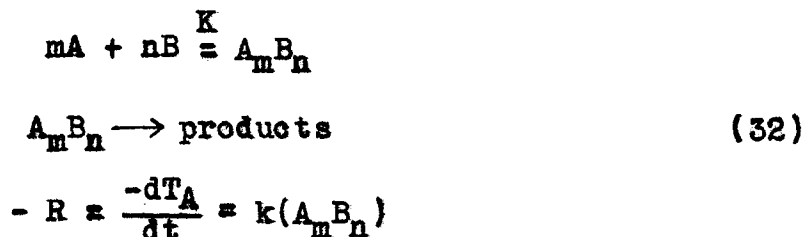
The existence of stable blue cupric-ammonia complexes is well-known, and a voluminous literature reports various species and various stabilities of the species. Rechler<sup>40</sup> and Gauss<sup>41</sup> reported the major constituent of a copper(II)-ammonia solution as  $\text{Cu}(\text{NH}_3)_4^{\text{II}}$ . Ephraim<sup>42</sup> later reported di-, tetra-, and pentaammine cupric complexes. Studies with the glass electrode by J. Bjerrum<sup>43</sup> found the species  $\text{Cu}(\text{NH}_3)_n^{\text{II}}$  for n equal to 1, 2, 3, 4, and 5, and he reports their relative stabilities,  $k_n^{\text{I}}$ , for solutions one molar in ammonium nitrate. Bjerrum found no evidence for a hexamine

complex, even in liquid ammonia, but the hexammine has been reported by Kubota<sup>44</sup> and Dey<sup>45</sup>. More recent work by Vosburg and Cooper<sup>46</sup> found only the di- and tetrammine complexes, although their variation technique is insensitive to small quantities of complex species. The entire concept of chemical cupric-ammine complexes has been questioned by various workers<sup>47</sup> who believe the blue color is due to physical adsorption of ammonia molecules on colloidal cupric hydroxide. The work by Bjerrum was chosen to most truly represent the cupric-ammonia complex system, partly because his experimental technique proved to be the most exacting and partly because he supplies values for the equilibrium constants at an ionic strength of one, data which later proves useful.

The literature relating to the copper cyanide complexes is similarly confusing, but the best evidence reports the complex species to be: cupric with two<sup>48</sup> and four<sup>48</sup> cyanides; and cuprous with one<sup>49</sup>, two<sup>50,51,52</sup>, three<sup>50-54</sup>, four<sup>51,52</sup>, and five<sup>52</sup> cyanides. A further reference<sup>55</sup> cites  $\text{Cu}(\text{CN})_4^=$  as colorless and  $\text{Cu}[\text{Cu}_2(\text{CN})_8]_2^=$  to be violet in color. This latter work used freezing point, vapor pressure, and similar methods. The rapidity of the reaction casts strong doubt upon the ability to accurately measure such properties.

## Theory

The reaction of copper(II) with cyanide is known to produce cyanogen. Postulating that the reaction proceeds through the necessary formation of an intermediate complex, a general kinetics equation may be derived. Since coordination equilibria are usually rapidly established, the slow reaction is very likely the disproportionation of the intermediate complex:



where  $T_A$  is the total concentration of A, either oxidant or reductant, at time  $t$ ,  $k$  the first order specific rate constant of the disproportionation,  $(A_m B_n)$  the concentration of the intermediate complex in equilibrium with A and B, oxidant and reductant, and the coefficients  $m$  and  $n$  the number of corresponding atoms in the complex. If  $K$  is the equilibrium constant of the equilibrium prior to the slow reaction, then

$$-R \approx kK(A)^m(B)^n \tag{33}$$

Also,

$$T_A = (A) + m(A_mB_n) \quad (34)$$

$$= (A) + mK(A)^m(B)^n \quad (35)$$

and similarly for B. If  $m$  differs from one, the virtue of the following treatment is questionable, due to the complexity of the resulting expression, but for  $m$  equal to one, equation (33) becomes

$$-R = kK T_A \frac{(B)^n}{1+K(B)^n} \quad (36)$$

If the reaction is sufficiently slow that B may be administered in large excess and (B) therefore remain essentially constant, equation (36) can be integrated directly.

If excess B is not allowed, then the nature of the denominator determines the form of further substitution. If  $K(B)^n \gg 1$ ,  $R$  is thus only a function of  $T_A$  and an integration may be made at once. If  $K(B)^n \approx 1$ , then (B) must be solved by the same technique as was (A), and the resulting expression, though complicated, must be integrated. It is often true, however, that  $K(B)^n \ll 1$ , and in this case (36) becomes

$$-R = kK T_A (B)^n \quad (37)$$

If the quantity of B in the complex species is much less than that in the free ion form, then  $T_B = (B)$  and

$$-R = kK T_A T_B^n \quad (38)$$

which contains known quantities and can be integrated directly.



Equation (38) follows directly from (33) if the quantities of both A and B in the complex is negligible.

If more than one intermediate complex,  $X_1$ , were disproportionating, then

$$-\frac{dT_A}{dt} = \sum_i k_i X_i \quad (39)$$

and the summation can be resolved by the technique indicated above.

The ionic strength of the reacting solution should be maintained by inert salts to a degree considerably in excess of any contributions attributable to the relevant ions. In this case the activity coefficients of all species will remain constant.

### Experimental

Reagent grade chemicals were used. Acidified cupric chloride stock solution was standardized through thiosulfate against potassium dichromate with a small quantity of sodium carbonate added, and potassium cyanide was standardized against silver nitrate with the opalescent iodide end point. Concentrated ammonia was cooled to  $0^\circ\text{C}$ , diluted, standardized against HCl, and thereafter kept in an ice box, as were all solutions containing ammonia. Kinetic runs were

made at  $0^{\circ} \pm 0.1^{\circ}\text{C}$ , maintained by a bath of melting ice in a Dewar flask.

Separate Erlenmeyer flasks containing fifty ml of the desired copper(II) ammonia solution and a cyanide solution of appropriate concentration were cooled to equilibrium in the ice bath. Five ml of the cyanide solution were then added to the rapidly shaken copper solution by means of a pipette calibrated to give  $5.00 \pm 0.2$  ml by blow delivery. Five ml portions of the reacting solution were removed by a similarly calibrated pipette at known times and quenched in two ml of a solution containing 0.2M zinc nitrate in approximately 10M ammonia. Usually ten portions were quenched per run. It was shown that the cupric ammine complexes are stable in the presence of ammoniacal zinc cyanide containing an excess of zinc ion. The optical density at  $600\text{ m}\mu$  of the quenched solution was observed and compared against an empirical curve constructed from the optical densities of known copper(II) concentrations under identical conditions except for the colorless cuprous complexes. The concentration of total cupric copper in the reacting solution was thus determined, and the degree of accuracy proved satisfactory when compared to other sources of error. Concentrations of other ions subsequently cited likewise refer to the reacting solution.

The ionic strength of the reacting solution was maintained at 1.00 with sodium nitrate. The ammonia solutions were found to remain sufficiently standard over eighteen hours, and the cyanide solutions for even longer periods.

A separate study was made to determine the cause of the distinct violet color resulting from the addition of cyanide to ammoniated cupric copper. The optical density at 615  $m\mu$  of the copper-ammonia-cyanide solution was measured as a function of time, since it proved to be unstable. Extrapolation over twenty seconds gave  $D_0$ , the extinction at zero time. The above wave length was chosen from several fast test spectrums as the approximate maximum in the absorption spectrum of the violet species. Ionic strength was varied between series of runs. These optical measurements were made with a Cary Recording Spectrophotometer, Model 12, Serial 15.

### Results and Discussion

It was noticed that a shift in absorption from blue to violet occurred when cyanide ion was added to ammonical cupric solutions. The effect of varying cyanide ion at constant initial total copper(II),  $T_{Cu}^{O} II = 0.00755$ , on  $D_0$  at 615  $m\mu$  was determined and found to be linear in total cya-

nide,  $T_{\text{CN}^-}$ . Figure 3 displays this linearity, together with the extinction at infinity,  $D_\infty$ , for comparison. Disregarding any ammonia complexed to the copper(II), the relevant equilibrium is

$$K = \frac{\text{Cu}(\text{CN})_x^{2-x}}{(\text{Cu}^{\text{II}})(\text{CN}^-)^x} \quad (40)$$

If  $D'_0$  is the absorption of the cupric-cyanide complex, then  $D'_0 = \text{Cu}(\text{CN})_x^{2-x} / k$ . The absorption at zero time is the sum of  $D'_0$  and  $D''_0$ , where  $D''_0$  is the absorption which can be attributed to the cupric-ammonia species. Since  $D''_0 = \text{Cu}(\text{NH}_3)_n / k^*$ ,  $T_{\text{Cu}^{\text{II}}}$  is held constant, and a large excess of ammonia is present so that  $k^*$  is essentially constant, then

$$D_0 = \left( \frac{K}{k} - \frac{K}{k^*} \right) (\text{Cu}^{\text{II}})(\text{CN}^-)^x + \frac{T_{\text{Cu}^{\text{II}}}}{k^*} \quad (41)$$

The straight line variation of  $D_0$  with  $T_{\text{CN}^-}$  indicates that  $x = 1$  and that  $(\text{Cu}^{\text{II}}) = T_{\text{Cu}^{\text{II}}}$ . Thus, inconsequential amounts of copper(II) and therefore cyanide are stored as  $\text{CuCN}^{\text{I}}$  at high ammonia concentrations. Since both cupric-ammonia complexes and cupric-cyanide complexes contribute unknown amounts of absorption to  $D_0$ , neither  $k$  nor  $K$  can be determined from this experiment. The decrease in slope in Figure 3 with increasing ionic strength is in accordance with the probably decrease in  $K$  with increasing ionic strength. The rapidity of the reaction limited investigation of this

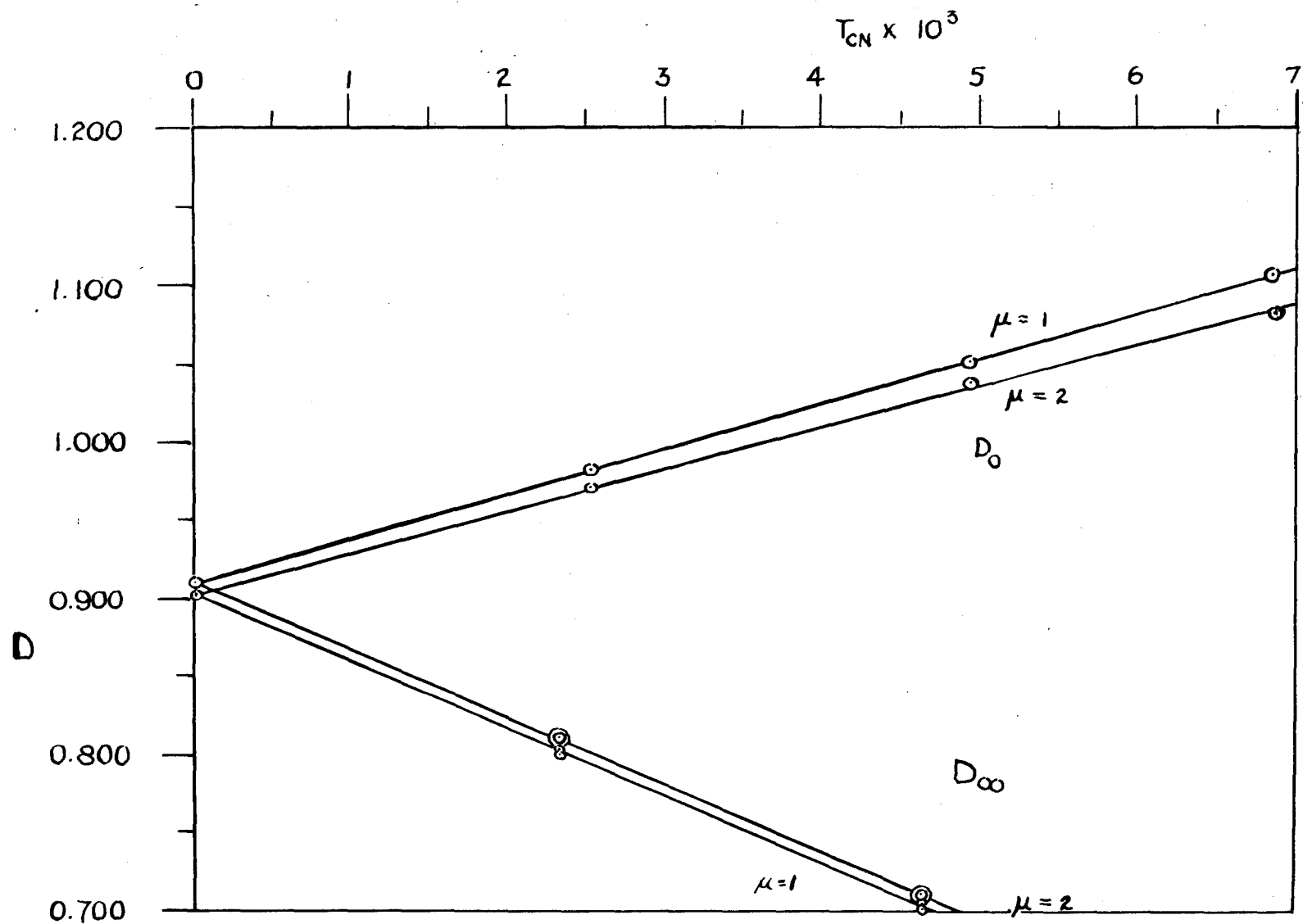


Fig. 3. Variation of  $D_0$  with  $T_{CN^-}$  with constant  $T_{Cu^{II}} = 0.00755$ .

problem. The literature had previously reported the violet color being caused by a  $\text{Cu}[\text{Cu}_2(\text{CN})_8]^\pm$  species. A kinetic treatment of the disappearance of the violet color proved inconclusive.

Stoichiometric studies showed that four moles of cyanide disappear from the reacting system for every mole of copper reduced, whereas only one mole of cyanide is oxidized, or  $2 \text{Cu}^{\text{II}} + 8\text{CN}^- = 2\text{Cu}(\text{CN})_5^\pm + (\text{CN})_2$ , in contradiction to work<sup>56</sup> showing cyanate ion as product. Cyanogen was found to hydrolyze slowly compared to the rate of the oxidation reaction, and cyanide as a hydrolysis product therefore does not re-enter into the kinetics of the reaction.

The investigation of the disappearance of total copper(II) with time was then undertaken. This change in total cupric copper proved not to have a simple first or second order dependence upon  $T_{\text{Cu}^{\text{II}}}$ . The rapidity of the reaction placed an upper limit upon the initial cyanide concentrations so that it could not be considered to remain constant, while the analytical method placed a practical lower limit on initial copper concentrations. Figure 4 indicates the course of the reaction and also indicates the stringent limitations placed upon variations in initial copper(II) and cyanide. From these plots,  $-\frac{dT_{\text{Cu}^{\text{II}}}}{dt}$  was determined by the plane surface mirror technique, both at zero times and other times. The existence of numerous

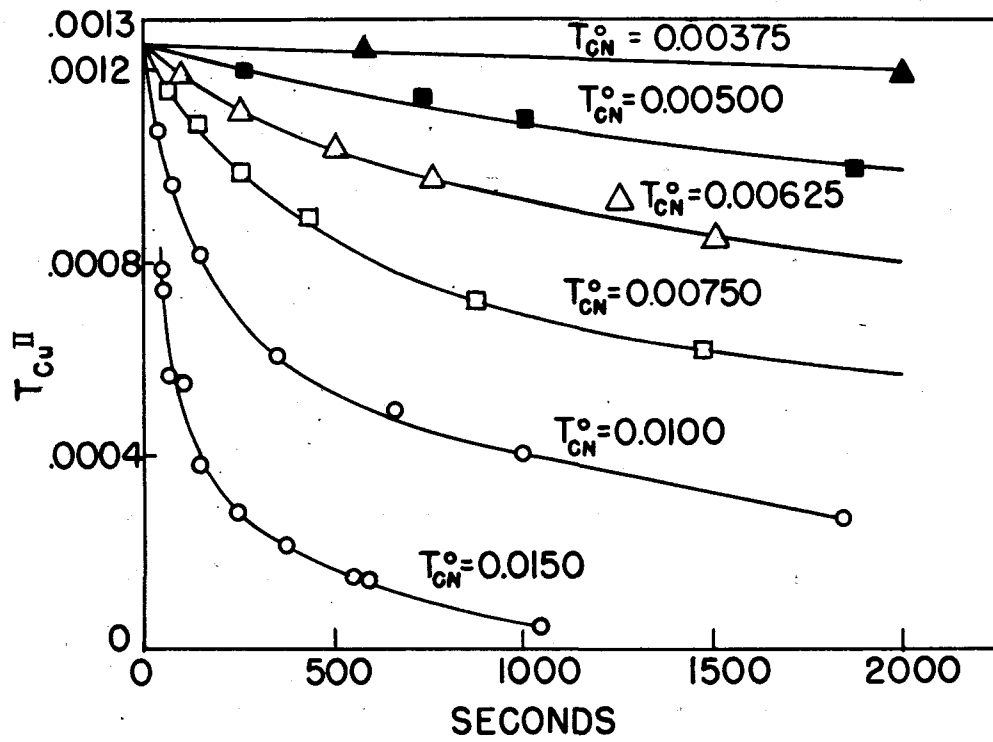


Fig. 4. Variation of  $T_{Cu}^{II}$  with time.

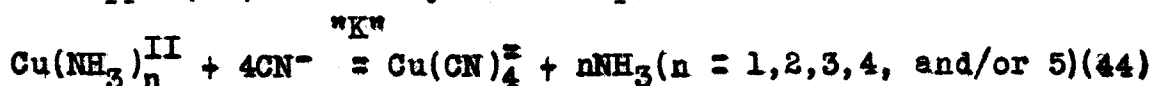
cuprous cyanide complexes and their complicating inter-equilibria pointed to an analysis of the zero time rates first. Plots were prepared, Figure 5, of  $\log (-R_0)$  vs.  $\log \alpha$  for constant initial total copper(II),  $T_{\text{Cu}^{II}}^0$ , where  $R_0$  is the initial rate of the reaction and  $\alpha$  is the zero time ratio of total cyanide to total copper(II). These plots were found to have a slope of four for a variety of  $\alpha$ 's and the intercepts appropriate to

$$-R_0 = A T_{\text{Cu}^{II}}^0 \cdot \alpha^4 \quad (42)$$

A possible initial rate expression is therefore

$$-R_0 = \left( -\frac{dT_{\text{Cu}^{II}}}{dt} \right)_{t=0} = A T_{\text{Cu}^{II}}^0 (T_{\text{CN}^-}^0)^4 \quad (43)$$

In view of the stoichiometry and equation (63), the following mechanism is postulated; with a negligible amount of copper(II) in the cyanide complex:



$$\frac{-dT_{\text{Cu}^{II}}}{dt} = k(\text{Cu}(\text{CN})_4^{\text{II}}) \quad (46)$$

This mechanism can be verified by evaluating the right hand side of (46) in terms of known quantities and then correlating the expression with experiment.



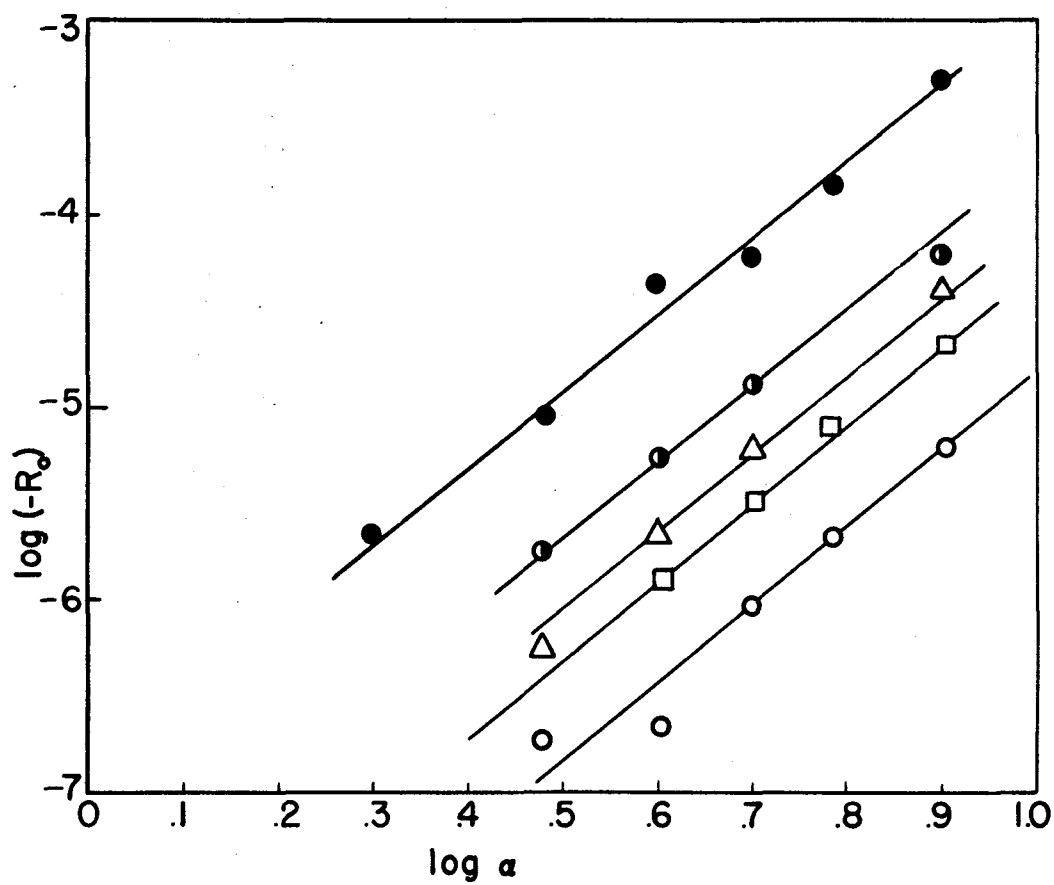
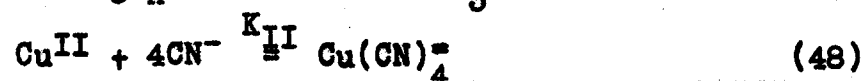
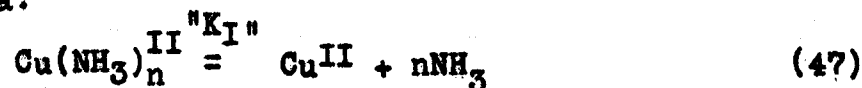


Fig. 5. Variation of  $-R_0$  with  $\alpha$ , where  $\alpha = T_{\text{CN}^-}^0 / T_{\text{Cu}^{II}}^0$ .

The prior equilibrium of (44) is intended to be only symbolic since  $n$  may be considered as a parameter of the oxidation reaction, for as copper(II) disappears from the reaction  $n$  increases, although total ammonia remains constant throughout. To facilitate a mathematical treatment, this equilibrium can be thermodynamically separated into two equilibria:



Corresponding to (33), therefore, is the equation which utilizes the second equilibrium,

$$-R = kK_{\text{II}}(\text{Cu}^{\text{II}})(\text{CN}^-)^4$$

The evaluation of  $(\text{Cu}^{\text{II}})$  is complicated by the existence of  $\text{Cu}(\text{NH}_3)_n^{\text{II}}$  species. Utilizing the cupric-ammonia stability constants  $k'_n$  where  $k'_n = (\text{Cu}(\text{NH}_3)_n^{\text{II}})/(\text{Cu}(\text{NH}_3)_{n-1}^{\text{II}})(\text{NH}_3)$ , and the relation  $T_{\text{Cu}^{\text{II}}} = (\text{Cu}(\text{NH}_3)_4^{\text{II}}) + (\text{Cu}(\text{NH}_3)_5^{\text{II}})$ , since the concentrations of less-ammoniated species can be calculated to be insignificant<sup>57</sup> and that of the cyanide complex is assumed to be insignificant, it can easily be shown that

$$(\text{Cu}^{\text{II}}) = \frac{T_{\text{Cu}^{\text{II}}}}{k'_1 k'_2 k'_3 k'_4 a_{\text{NH}_3}^4 + k'_1 k'_2 k'_3 k'_4 k'_5 a_{\text{NH}_3}^5} \quad (50)$$

Also, since  $(\text{CN}^-) = T_{\text{CN}^-} = T_{\text{CN}^-}^0 - 4T_{\text{Cu}^{II}}^0 + 4T_{\text{Cu}^{II}}$  from stoichiometry, the integrable rate equation is

$$-R = \frac{kK_{II}(T_{\text{Cu}^{II}})(T_{\text{CN}^-}^0 - 4T_{\text{Cu}^{II}}^0 + 4T_{\text{Cu}^{II}})^4}{k_1' \dots k_4' a_{\text{NH}_3}^4 + k_1' \dots k_5' a_{\text{NH}_3}^5} \quad (51)$$

$$-R = kK' (T_{\text{Cu}^{II}})(T_{\text{CN}^-}^0 - 4T_{\text{Cu}^{II}}^0 + 4T_{\text{Cu}^{II}})^4 \quad (52)$$

Equation (52) reduces to (43) at zero time. Integration of (52) gives:

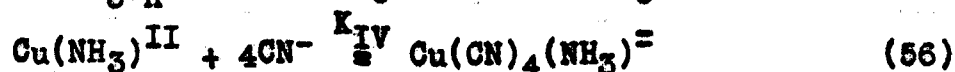
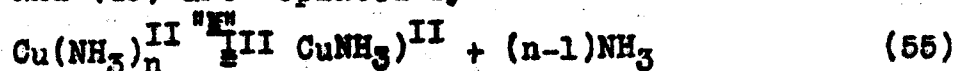
$$\ln \frac{1}{x} + 12x - 24x^2 + \frac{64}{3}x^3 - \left( \ln \frac{1}{x_0} + 12x_0 - 24x_0^2 + \frac{64}{3}x_0^3 \right) = kK'(T_{\text{CN}^-}^0 - 4T_{\text{Cu}^{II}}^0)^4 \cdot t \quad (53)$$

or,

$$x - x_0 = K'' \cdot t \quad (54)$$

where  $x = T_{\text{Cu}^{II}}/T_{\text{CN}^-}^0 - 4T_{\text{Cu}^{II}}^0 + 4T_{\text{Cu}^{II}}$  and  $x_0$  refers to zero time. Equation (54) is valid for all conditions other than  $T_{\text{CN}^-}^0 - 4T_{\text{Cu}^{II}}^0 = 0$ , when (52) must be reintegrated.

The slow reaction may involve  $\text{Cu}(\text{CN})_4(\text{NH}_3)^=$  rather than  $\text{Cu}(\text{CN})_4^=$  as the disproportionating species, and in this case (47) and (48) are replaced by



and (50) is replaced by

$$(\text{Cu}(\text{NH}_3)^{\text{II}}) = \frac{T_{\text{Cu}^{II}}}{k_2'k_3'k_4'a_{\text{NH}_3}^3 + k_2'k_3'k_4'k_5'a_{\text{NH}_3}^4} \quad (57)$$

$K'$  now becomes

$$\frac{K_{IV}}{k_2^1 k_3^1 k_4^1 a_{NH_3}^4 + k_2^1 \dots k_5^1 a_{NH_3}^4} \quad (58)$$

A similar treatment could be given for an intermediate complex of  $Cu(CN)_4(NH_3)_2^{II}$ .

The validity of the mechanism which has been postulate may be experimentally verified by the use of (54), for the product  $kK'$  should be independent of copper(II) and cyanide concentrations. The role of ammonia in the intermediate complex is carried in  $K'$ , per equation (52) or (58). For the excessive ammonia concentrations,  $K'$  is a true constant. Plots were prepared where the left side of equation (54) was calculated and graphed vs.  $t$ . Figure 6 exemplifies these plots. The lines which resulted were straight and had the slopes corresponding to  $K''$  indicated in column 4 in Table 2. The quantity  $kK'$  was calculated in column 5 and proved to be independent of initial copper(II) and cyanide concentrations.

The last two columns of Table 2 indicate the results of an attempt to determine the role of ammonia in the reaction by calculating the denominator of  $K'$  in the two mechanisms mentioned previously. With the use of van't Hoff's equation (for  $K_C$ ) and Bjerrum's data, the cupric-ammonia stability constants  $k_n^I$  were roughly estimated for  $0^\circ C$ . This process is admittedly quite improper since the

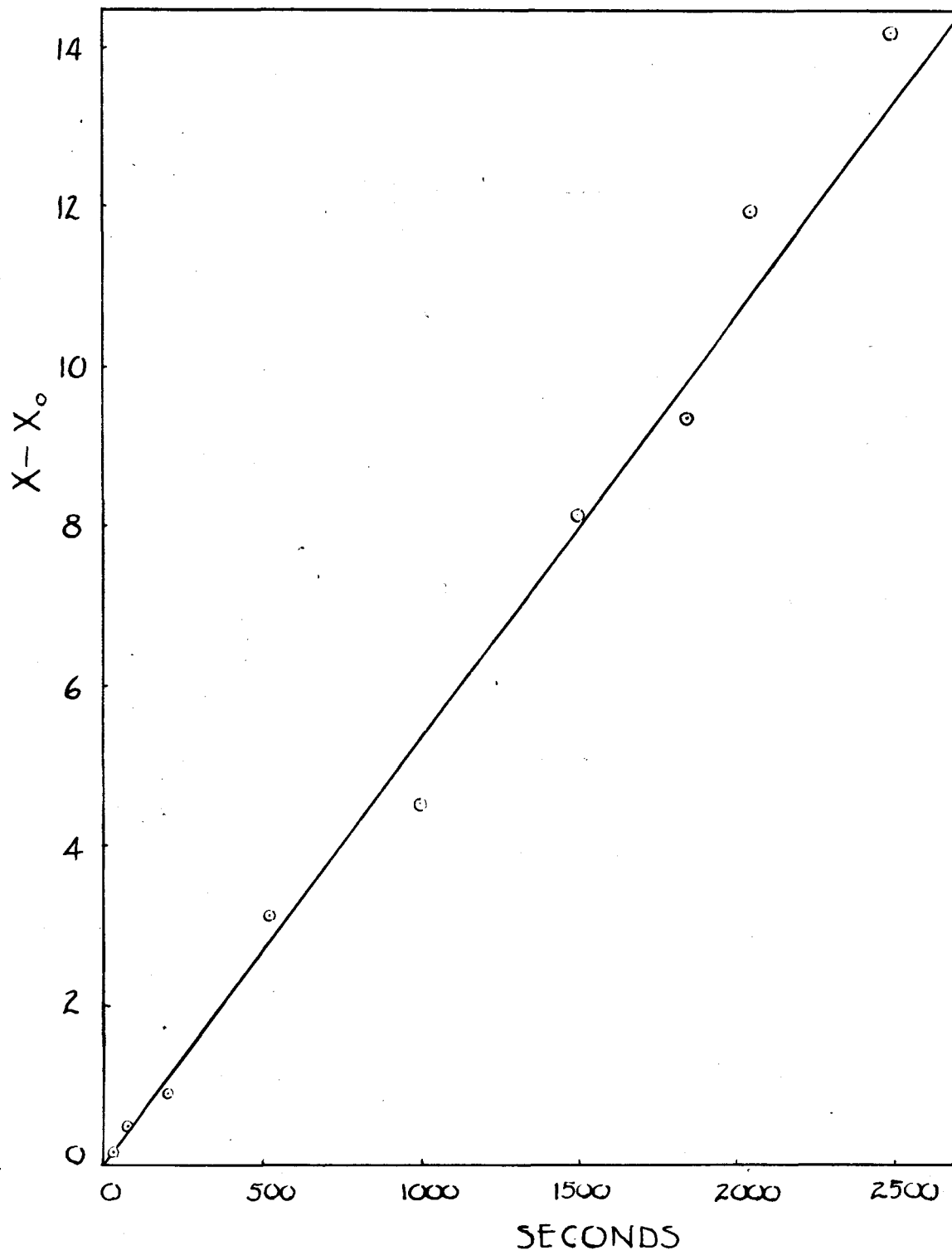


Fig. 6. Variation of  $x - x_0$  with time, per equation (54).

Table 2. Pseudo and true constants for  $\mu = 1$ ,  $T = 0^\circ\text{C}$ .

$T_{\text{NH}_3}$	$T_{\text{Cu}^{II}}^0$	$T_{\text{CN}^-}^0$	$K''$	$kK_{II}$ for $\text{Cu}(\text{CN})_4^{2-}$	$kK_{IV}$ for $\text{Cu}(\text{CN})_4(\text{NH})_3^{2-}$
12.5	0.00125	0.0150	$5.3 \times 10^5$	$2.8 \times 10^{26}$	$3.3 \times 10^{20}$
	0.00125	0.0100	$4.8 \times 10^5$	2.7	3.2
	0.00150	0.0120	$4.9 \times 10^5$	2.7	3.2
	0.00150	0.00900	$7.0 \times 10^5$	3.6	4.2
	0.00200	0.00800	--	3.0	3.6
	0.00250	0.0100	--	2.9	3.4
	0.00300	0.00900	$5.3 \times 10^5$	2.8	3.3
	0.00600	0.0120	$4.8 \times 10^5$	2.5	3.0
	0.00600	0.00900	$6.3 \times 10^5$	3.3	3.9
	0.00600	0.00600	$5.1 \times 10^5$	2.7	3.2
	0.00300	0.00900	$9.9 \times 10^5$	$2.8 \times 10^{26}$	$4.0 \times 10^{20}$
	0.00300	0.00600	$9.2 \times 10^5$	2.8	4.0
10.5	0.00200	0.00600	$1.2 \times 10^6$	$2.9 \times 10^{26}$	$4.1 \times 10^{26}$

solutions under consideration have a considerable ionic strength and since nothing is known about coefficients of thermal expansion. However, orders of magnitude are probably not too incorrect. If we now substitute the formal concentrations of ammonia,  $T_{\text{NH}_3}$ , for activities, although the concept of ionic strength was not designed to be relevant in solutions 11M in ammonia, the denominator of  $K'$  in (51) becomes  $2.4 \times 10^{-15} T_{\text{NH}_3}^4 + 1.5 \times 10^{-15} T_{\text{NH}_3}^5$  or in (58),  $3.6 \times 10^{-10} T_{\text{NH}_3}^3 + 2.3 \times 10^{-10} T_{\text{NH}_3}^4$ . The values of  $kK_{\text{II}}$  and  $kK_{\text{IV}}$  in Table 2 are calculated under these conditions and should therefore be considered as independent of variations in copper(II), cyanide, or ammonia. These values, combined with the hazardous assumptions given above and the rapidity of the reaction, which limited the lower concentrations of ammonia which was experimentally allowable, definitely disallow any categorical statements regarding the function of ammonia in the reaction, but the author feels that the intermediate species is  $\text{Cu}(\text{CN})_4^{2-}$ . The following discussion proceeds upon this assumption.

It is evident from the kinetic equation for the reaction that although a proper treatment of ammonia is assumed, only the product  $kK_{\text{II}}$  can be evaluated. Unless the stability of the cupric-tetracyanide complex is independently known the

specific rate constant for the reaction cannot be isolated. The rapidity of the reaction indicates that  $K_{II}$  cannot be evaluated directly, but with the use of equation (11) and data summarized by J. Bjerrum,<sup>20</sup> the stability of the complex was estimated at about  $10^{25}$ . This points to a magnitude for  $k$  of about ten, although perhaps not in the immediate neighborhood of that number. The devious path which was necessary to arrive at the above value of  $k$  indicated that any attempts to obtain a meaningful free energy of activation of the reaction would prove futile. But the extraordinarily high value for  $k$  does signify a low free energy of activation.

It has been shown that for a somewhat limited range in concentrations the oxidation of cyanide by copper(II) proceeds through the disproportionation of an intermediate  $\text{Cu}(\text{CN})_4^{\overline{2}}$  complex. The conclusion can therefore be drawn that the other possible paths for the oxidation, such as the unimolecular disproportionation of  $\text{CuCN}^-$  or  $\text{Cu}(\text{CN})_2$ , or the bimolecular reaction of two  $\text{Cu}(\text{CN})_4^{\overline{2}}$  molecules to form cyanogen directly, are considerably slower than the mechanism which was observed. It follows that the free energy of activation for the observed mechanism must be considerably lower than those for other paths.

The marked stability of the cuprous tri-cyanide complex



in relation to other cuprous cyanide species is evidenced by the non-appearance of other species in the kinetics of the reaction, and one may directly infer that  $\text{Cu}(\text{CN})_3^{2-}$  has considerably less free energy than the other cuprous cyanide complexes, species which do not occur to any measurable extent in the kinetic product of the reaction. If we now consider the series of reactions where various cupric complexes disproportionate to give the cuprous cyanide complexes with one less cyanide and a cyanide radical, the high free energies of the products, excepting the tricyanide complex, indicate that the energy of activation may be directly correlated to the free energy content of the product.

This correlation of free energies likewise infers a correlation of other properties, thus an identification, more or less exactly, of structural features. Such an identification of structures should not be pursued too rigorously, but when one considers the probable structure of reactant, activated complex, and product, the similarities are evident. The electronic structure of cuprous ion is  $\dots 3s^2 3p^6 3d^{10}$  and the ion has four low energy orbitals, one s and three p, available for complexing. Since an ammonia molecule is also complexed to  $\text{Cu}(\text{CN})_3^{2-}$ , a tetrahedral structure probably results from the  $sp^3$  bonding. Considering the cupric tetra-

cyanide complex, the cupric ion has a  $\dots 3s^2 3p^6 3d^9$  structure and according to Pauling, the odd d electron is promoted to a 4p orbit during covalent complexing with a  $dsp^2$  bonding and a square configuration resulting. This coplanarity has been observed for  $CuCl_2 \cdot 2H_2O$  and also for other molecules which contain  $Cu(II)-O$  bonds. Since  $dsp^2$  bonding is considered to be stronger than  $sp^3$  bonding (2.69 and 2, respectively) and since coplanarity has been observed for the covalent linkage if  $dsp^2$  bonding, one tends to conclude that the cupric tetracyanide complex has a coplanar configuration. If the activated complex, is considered to consist of a momentarily elongated  $Cu(II)-CN$  bond precursory to the  $Cu(I)-CN^O$  state, the activated complex may be allowed to have an interregnum in which it is not improbable that the structure may possess tetrahedral character.

In any case, the correspondence between activated complex and product is postulated, and the preceding paragraph should be considered as explanatory rather than apologetic. It is entirely possible that an ammonia molecule is also complexed to the reactant and it is also possible that one or two water molecules may be complexed. Under these circumstances a similar bond orbitals-configuration analysis would be questionable.

The correlation between activated complex and product in this reaction is a reversal of the general statement that for reactions of the type  $A + B \rightarrow C$  the activated complex may be expected to resemble C more than the reactants, for in the  $\text{Cu(II)}-\text{CN}^-$  reaction exactly the reverse takes place.

Reference has been made to the validity of kinetic evidence for the existence of complexes. No kinetic evidence of complexes other than  $\text{Cu(CN)}_4^{2-}$  and  $\text{Cu(CN)}_3^-$  was found in this experiment, and it follows from equation (46) and the various assumptions inherent in it that concentrations of complex cyanide species other than those mentioned are inconsequential, less than 5-10 per cent, compared to their concentrations. Kinetic evidence for the existence of non-reacting complexes is therefore to be considered as sufficient but not necessary evidence.

### Summary

The oxidation of cyanide ion by copper(II) in a concentrated ammonia solution was found to proceed most probably via the disproportionation of  $\text{Cu(CN)}_4^{2-}$  to form a cuprous tricyanide complex and a cyanide radical. The precise role of ammonia in the reaction was unable to be deter-

mined, and the intermediate complex may possibly contain one or two molecules of ammonia.

The observed mechanism of the  $\text{Cu(II)-CN}^-$  reaction was explained by an activated complex-product correspondence in terms of free energy content of the species, or, in different words, by a postulate that in a reaction of the type  $\text{A} \rightarrow \text{B} + \text{C}$ , the properties of the activated complex are more similar to  $\text{B} + \text{C}$  rather than  $\text{A}$ .

Tentative evidence was found for the existence of a violet  $\text{CuCN}^-$  species, but no evidence was found for copper cyanide complexes other than those previously noted, although the severe restrictions on kinetic evidence for complexes was observed.

## SUMMARY

It was demonstrated that the properties of an aqueous solution could not be expected to be the sum of the properties of the separate ions added to the properties of pure water. Interaction occurs between the ions and water and between the ions themselves, while a stronger interaction results in molecular entities called chemical complexes that have properties which differ from their components.

A quantity  $k_n$  was developed which related the effective concentrations of the complex species  $MA_{n-1}$ ,  $A$  and  $MA_n$ , thereby relating the concentrations of all species in the solution. This constant was found to depend not only on the tendency of  $MA_n$  to split off an  $A$ , or to further complex an  $A$ , but also on the interaction of the various species with the aqueous environment. An examination of the tendencies of species to complex supplied several semi-satisfactory empirical rules regarding the stabilities of the complex, but it was found that a complete theory of stability would require a complete knowledge of the complexing system, and this goal is unattainable at the present time.

Thermodynamics was found to offer a precise measure of the stability of the complex, and the free energy change due

to the formation of a complex was correlated to a chemical energy change in the reaction together with an entropy change in the system. A study of the entropy properties of solutions indicated that if appropriate precautions were taken, the entropies of ions could be directly correlated to the ordering of solvent molecules around the ions. A theoretical calculation of entropy, similar to that done for water in ice, could therefore elucidate the actual average physical situation of an ion immersed in water. Proceeding from this point, the measured ionic entropies in actual solutions with appreciable ionic strength could then be related to the probable numbers of ions in the ion-atmosphere.

Since such calculations have not been performed as yet, a return to  $k_n$ , or  $k_n^*$ , was proposed, for too often the nature and proportions of the species in an aqueous solution containing a moderately complexing metal ion are either unknown or unrecognized. Since an appropriate electromotive cell can measure activities of aqueous ions, the potential of a concentration cell was shown to be related to the equilibrium constants of the various aqueous complex species, and under certain conditions a determination of such a potential allows a determination of the concentration constants. This method of treatment was applied to the stannous chloride

equilibriums, and the stability constants of the four complex species were measured at an ionic strength of two.

The nature of metal ions and their complexes during the course of an oxidation-reduction reaction were then studied from the viewpoint of kinetics. It was observed that quite often such a reaction proceeds via the disproportionation of an intermediate complex, and the study of the  $\text{Cu(II)-CN}^-$  reaction was undertaken as a test for the postulate that the disproportionation of an intermediate complex is a necessary path for an oxidation reaction. Since cyanide is a strong complexing agent, if its oxidation by copper(II) does not proceed through an intermediate complex the postulate must be discarded. Also, it was hoped that a relationship between the number of oxidizable anions and the rate of reaction could be observed.

The  $\text{Cu(II)-CN}^-$  reaction was observed to proceed most probably through the disproportionation of an intermediate  $\text{Cu(CN)}_4^{\frac{2-}{4}}$  complex to form a  $\text{Cu(CN)}_3^{\frac{2-}{3}}$  and a cyanide radical. From a correspondence of the rate of reaction to the stability of the products, it is postulated that in a reaction of the general type  $\text{A} \longrightarrow \text{B} + \text{C}$ , the activated complex resembles the products more closely than it resembles the reactant. The nature of the reaction was such that the

specific rate constant could not be determined within a reasonable degree of accuracy.

Tentative evidence was found for the existence of a violet  $\text{CuCN}^-$  complex, previously unreported.



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## ACKNOWLEDGMENT

A considerable number of persons offered their aid and assistance during the course of this work, and to them gratitude is extended. In particular, Dr. Frederick R. Duke, major professor, tendered considerable enlightenment and comfort during periods of darkness.

This work was performed under the auspices of the Ames Laboratory, Institute for Atomic Research.