STUDY OF SOLUTIONS OF THE SODIUM-CADMIUM CYANIDE COMPLEX

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This is to certify that the

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STUDY OF SOLUTIONS OF THE SODIUM-CADMIUM CYANIDE COMPLEX

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As stated by M. R. Tompson[1]--"During the last forty years over one hundred papers have been published dealing in one way or another with the constitution and properties of the cyanide plating baths". Of the various metals plated in this manner, formulae for the cadmium complex are less definite than those for zinc, copper, gold, silver, as well as those in the brass plating solution.

L. P. Westbrook[2] states that the cadmium complex is usually written as $Na_2Cd(CN)_4$ but continues to use $NaCd(CN)_3$ throughout his article on cadmium plating.

S. Glasstone[3] carried out an electrometric titration of cadmium sulphate with sodium cyanide. He obtained no direct evidence of the formation of $Cd(CN)_3$ but states: "The shape of the titration curve when the ratio CN:Cd exceeds 2:1, and the fact that the precipitate of cadmium cyanide dissolves completely when the ratio is 3:5:1, suggests that at least two complex ions, $Cd(CN)_3^-$, or perhaps $(Cd(CN)_3(H_2O))^-$, and $Cd(CN)_4^{--}$ are present in solution".

M. R. Tompson[1] basing his calculation upon Corbit's[4] phase rule study of the cadmium cyanide complex, shows that the content of $Cd(CN)_3^-$ in a saturated solution containing KCN and $Cd(CN)_2$ is appreciable although in this case, the complex ion is chiefly $Cd(CN)_4^{--}$.

Britton and Dodd[5] have studied the formation of the complexes in several different ways:

(1) The glass electrode

(2) Metal electrode potentials

(3) Conductivity measurements.

By all methods they found definite complex formations for silver, zinc, etc., but cadmium was an exception.

Their pH measurements with the glass electrode suggested the formation of $Cd(CN)_3^-$ and $Cd(CN)_4^{--}$ but the evidence was not pronounced.

Their study of metal-ion concentration by means of potential measurements and the electrode potential equation gave a very irregular curve in the case of cadmium. A slight inflextion was obtained between the points which would correspond to formation of $Cd(CN)_3^-$ and $Cd(CN)_4^{--}$.

The conclusion they draw from conductivity measurements states: "In the cadmium curve, the end-point is not difinite". This curve was a conductrimetric titration of $CdSO_4$ with KCN.

N. Hall's[6] work most closely resembles the present investigation. He determined by volumetric analyses, the formula of the cadmium cyanide-sodium cyanide complex in a sodium cyanide solution saturated with cadmium oxide. He found the mole ratio-NaCN:CdO to be 3.8 and concludes there from that this ratio may be used in the analyses of cadmium plating baths. For industrial purposes, this empirical constant, which was also proposed by S. Wernick[7] in 1929, may prove satisfactory. However, there are several circumstances which may change the above factor as this investigation will show.

In order to fully interpret the meaning of such an empirical constant, it is necessary to consider the influence of such factors as: the mole ratio in an unsaturated solution of NaCn plus CdO, the combined ratio change with change in the total concentration of NaCN and CdO, change in unsaturated solutions if the NaCN concentration is held constant but the CdO concentration varies, change with ageing of solutions, pH, the effect of electrolysis upon the complex formula, the cadmium salt in combination with NaCN, temperature, the effect of Na_2CO_3 which is always present in cyanide plating baths, and alteration of the complex during the process of volumetric titration. No attempt is made to discuss all these details because of the limited time allotted to this research.

A study of these matters by volumetric analysis presents several difficulties in that there is to date no accurate dependable method for the analyses needed.

ANALYSES

All titrations were carried out at room temperature.

Free NaCN -- A widely used method for determination of "free" NaCN in the cadmium plating bath is the direct titration of the solution with $AgNO_3$ using KI as indicator. N. Hall[6] adequately discusses this procedure but as he points out, the results are not sufficiently reproducible, and they are generally high. He explains these high results as follows: "Because of the very high cyanide content, there is some decomposition resulting in the formation of sodium carbonate and ammonia, the reaction being represented as follows[8]:

$$2NaCN + 2H_2O + 2NaOH + O_2 = 2Na_2CO_3 + 2NH_3$$

In the presence of ammonia, the endpoint does not occur when all the free cyanide has been titrated, this is probably due to the formation of the soluble cadmium ammonia complex which may be representated by the reversible reaction:

$$Na_2Cd(CN)_4 + 4NH_3 \rightleftharpoons Cd(NH_3)_4(CN)_2 + 2NaCN$$

some of the combined cyanide being liberated and titrated as free cyanide, thus giving high results."

The end point is not sharp in this titration. It was the experience of the present author that different lighting conditions have widely different results. Because this titration is so difficult and at times apparently inaccurate, another method was attempted.

Titration of "free" NaCN by $CdSO_4$ was next tried. The titration reactions could be

$$CdSO_4 + 3NaCN = NaCd(CN)_3 + Na_2SO_4$$

or $$CdSO_4 + 4NaCN = Na_2Cd(CN)_4 + Na_2SO_4$$

The end point is determined by the formation of a slight turbidity caused by one of the following reactions:

$$CdSO_4 + Na_2CO_3 = CdCO_3 + Na_2SO_4$$

or $$CdSO_4 + 2NaOH = Cd(OH)_2 + Na_2SO_4$$

Either of these precipitates is soluble in alkali cyanide and hence will dissolve so long as any excess NaCN remains.

This method has its disadvantages but was used for the major part of this investigation. It is difficult to fix the exact endpoint. As the stoichiometric point is approached, local excess of $CdSO_4$ causes a precipitate which is not readily soluble. This tends to make one take his endpoint too soon. Obviously too, the end point is dependant upon the solubility of $Cd(OH)_2$ or $CdCO_3$. These solubilities in turn are largely dependant upon concentration of the OH^- or CO_3^{--} ions as predicted by the law of mass action. This latter effect will be brought out later in the discussion of results.

Total NaCN.-- This analysis was quite thoroughly studied and the following facts were obtained:

(1) There is a range of ammonium hydroxide over which constant and reproducible results may be obtained. Below this range, the complex cyanide is incompletely broken down - giving low results. Above this range, silver iodide is appreciably soluble - giving high results.

(2) The magnitude of this range is dependant upon the solution being titrated.

(3) 10 ml. of 2% KI in the 100-150 ml. being titrated is the maximum allowable concentration of indicator ion. More than this maximum gives low results.

(4) Within experimental error, the $AgNO_3$-NaCN titration is independant of dilution prior to titration.

In view of these facts the following procedure was adopted:

The cyanide solution is diluted to approximately 100 ml., 5 ml. of 2% KI added, and is then titrated with standard $AgNO_3$ (0.1N) until a faint opalescence is noted.

5 ml. dilute NH_4OH is added.

A turbidity is again produced by addition of $AgNO_3$.

The last two steps are repeated until addition of 5 ml. of dilute NH_4OH causes no change in opalescence. One can then assume that he is in the constant range mentioned under (1) above.

Cadmium Analysis.--The standard method for cadmium analysis in the plating bath is the precipitation as sulphide and titration with standard potassium ferrocyanide using uranium acetate as outside indicator. This method is rather lengthy and not entirely dependable.

The following procedure for electro-analysis was adopted after trying a number of conditions;

(1) Quantitatively transfer the equivalent of less than 0.25 g. of Cd to the electrolytic beaker.

(2) Add 1 drop of phenolphthalein and then add dilute sulpharic acid (HOOD) until the last trace of pink disappears.

(3) Add two grams of NaOH pellets, dilute to approximately 100 ml. and heat almost to boiling (HOOD).

(4) Electrolyze for 14 to 18 minutes with rotating copper gauze. 5.0 amps/dm^2 for half this time and 6.0 amps/dm^2 for the remaining half.

(5) Remove cathode with current on, wash and dry in the usual manner.

Equally accurate results may be obtained by deposition on a Cu of Cd surface. Anode area was found to be important, probably because of the voltage relationship. In this investigation a platinum electrode with an area of approximately 1.5 cm^2. was used.

Voltage less than 11; greater than 7.

FORMULA OF THE CADMIUM CYANIDE-SODIUM CYANIDE COMPLEX AS FORMED BY ADDITION OF CADMIUM SULPHATE TO SODIUM CYANIDE

Experimental.--The cadmium sulphate solution was standardized according to the electrolytic method given by Classen & Hall[9] except that the current densities given under Cadmium Analysis were used. Concentration was found to be 49.58 g/l. This standardized solution was used throughout the entire research.

The sodium cyanide solution was standardized with the procedure given by Willard and Furman[10]. Concentration was found to be 384.8 g/l.

To a sample of NaCN was added 5 ml. of 20% Na_2CO_3 and enough water to make the volume 100 ml. prior to titration. The lone exception to this was the 10 ml. sample of NaCN. Only 40 ml. of water was added in this case because of the large amount of $CdSO_4$ necessary to produce an end point. Sample #1 was titrated with a cadmium sulphate solution which was exactly one-half the concentration of the above standardized $CdSO_4$ solution.

By carrying out these titrations in this manner, the effect of concentration of the complex upon its formula may be studied.

Assume that the titration reaction is

$$CdSO_4 + XNaCN \rightarrow Complex + Na_2SO_4$$

Since the number of grams of NaCN titrated and the number of ml. of standard $CdSO_4$ are known, the X of the above equation may be solved for in the following manner:

$$X = \frac{\text{grams NaCN} \times \text{Mol. Wt. } CdSO_4}{\text{ml. } CdSO_4 \times \text{grams } CdSO_4/\text{ml} \times \text{Mol. Wt. NaCN}}$$

$$(1) \qquad = \frac{85.80 \times \text{g. NaCN}}{\text{ml. } CdSO_4}$$

Results are arranged in Table I.

TABLE I

ml NaCN	ml H_2O	g. NaCN	ml $CdSO_4$	X
1	94	0.3848	18.40(÷ 2)	3.589
2	93	0.7696	18.47	3.576
5	90	1.924	46.26	3.560
7	88	2.694	66.33	3.484
10	40	3.848	95.34	3.463

We may draw from table I at least two conclusions:

(1) The mole ratio NaCN-Cd is different in different solutions. The above values do not even closely check with the mole ratio of 3.8 obtained by N. Hall[6] and others.

(2) This ratio (coordination number) decreases upon increasing the complex concentration of the solution.

THE FORMULA OF THE CADMIUM CYANIDE-SODIUM CYANIDE COMPLEX AS FORMED BY ADDITION OF CADMIUM OXIDE TO SODIUM CYANIDE

Part 1.

Experimental.--Total NaCn was found by titration with $AgNO_3$ in the presence of dilute ammonium hydroxide plus 5 ml. of 2% KI. The amount of ammonia was determined as recommended under Total Cyanide analysis.

Cadmium oxide was weighed accurately in the solid form and then quantitatively transferred to the NaCN solution. Three different solutions were then electroanalyzed by the procedure previously given. In this manner representative results gave us the per cent purity of the CdO. This was found to be 96.39%.

12 g/l of Na_2CO_3 was added to each solution to serve as indicator for titration with $CdSO_4$ and the solutions were analyzed 81 days after preparation.

In each of these solutions the ratio of NaCN to CdO is maintained constant but the total concentration is varied.

Since the coordination number obtained for titration of NaCN with $CdSO_4$ is on the average about 3.5, this number is used in the first series of calculations (by use of equation (1)) to find the coordination number of CdO plus NaCN.

The chemical equations used are as follows:

Titration: $CdSO_4 + 3.5NaCN \rightarrow Complex + Na_2SO_4$

Original reaction: $CdO + XNaCN + H_2O \rightarrow Complex + Na_2SO_4$

Results are organized in Table 2.

Table 2

Free NaCN	Total NaCN	Combined NaCN	X
8.62	17.74	9.12	4.86
30.82	69.42	38.60	5.15
67.58	142.4	74.82	4.98
111.5	210.9	99.40	4.42
136.7	279.9	143.2	4.78
169.6	346.1	176.5	4.71
211.7	435.2	223.5	4.77
		Av. =	4.81

It is evident from these data the confirmation of an earlier conclusion; namely, "The mole ratio NaCN-Cd is different in different solutions". This follows from the fact that a coordination number greater than four is unlikely for this compound, which means that a different titration reaction takes place in this solution than was assumed.

It should be noted further that although widely varying solutions are studied, a fairly constant coordination number X is obtained. This is to be expected for two reasons.

The ratio of NaCN to CdO is constant in each solution.

The amount of sample taken from each solution was varied and diluted to approximately the same concentration so that at the time of analysis, each solution was almost identical. The fact that each solution was not exactly identical at the time of titration probably accounts for the large part of the discrepencies obtained and indicates that concentration may have some effect. The effect may be (a) the stoichiometry of the titration or (b) the complex may actually be different.

These solutions therefore present us with three unknowns:

(1) g/1 of free cyanide

(2) mole ratio in the original reaction

(3) mole ratio in the titration reaction

and since one cannot obtain three unknowns from two equations, a further assumption must be made.

We have already shown that the same salt plus alkali cyanide forms a different complex in a different solution. Therefore let us assume that that complex is indépendant of the salt; that is, assume that the mole ratios NaCN-CdO and $NaCN-CdSO_4$ are the same if present in the same solution. Our reactions will then be:

$$CdSO_4 + X NaCN \rightarrow Complex + Na_2SO_4$$

$$CdO + X NaCN + HOH \rightarrow Complex + 2NaOH$$

Let n be the grams per liter of free cyanide then,

$$(2) \quad n = \frac{ml. CdSO_4 \times g CdSO_4/ml. \times X \times Mol.\ Wt.\ NaCN \times 1000}{Mol.\ Wt.\ CdSO_4 \times ml.\ sample\ titrated}$$

$$= 11.12 \times X \times \frac{ml.\ CdSO_4}{ml.\ sample}$$

Further more, total NaCN - n = combined, therefore

$$(3)\quad \text{Total} - n = \frac{\text{g/l CdO} \times X \times \text{Mol. Wt. NaCN}}{\text{Mol. Wt. CdO}}$$

$$= 0.3818 \times \text{g/l CdO} \times X.$$

$$(4)\quad n = \text{Total NaCN} - 0.3818 \times \text{g/l CdO} \times X$$

Combining (2) and (4) we obtain

$$11.12 \times \frac{\text{Ml. CdSO}_4}{\text{Ml. Sample}} = \text{Total} - (0.3818 \times \text{g/l CdO} \times X)$$

$$(5)\quad X = \frac{\text{Total g/l NaCN} \times \text{Ml. Sample}}{(11.12 \times \text{ml. CdSO}_4) + (0.3818 \times \text{g/l CdO} \times \text{ml. sample})}$$

Using this equation we obtain the new set of values shown in Table 3.

Table 3

g/l total NaCN	g/l CdO	Ml. Sample titrated	Ml. $CdSO_4$	X
17.74	4.92	25	5.70	3.91
69.42	19.66	15	11.72	4.18
142.4	39.32	10	17.07	4.08
210.9	58.99	5	12.82	4.02
279.9	78.65	5	17.27	3.98
346.1	98.38	5	21.42	3.93
435.2	122.9	2	10.68	3.98
			Av. =	4.01
		Av. (without 2)	=	3.99

It is obvious from these data that we have a set of solutions in which the complex ion is nearly all in the form of $Na_2Cd(CN)_4$.

As evidence that these statistics are nearly correct we can present results for free NaCN as obtained by the standard method with silver nitrate.

Table 4

	Free NaCN by $AgNO_3$		Free NaCN by $CdSO_4$
	11.63 g/l		10.66 g/l
	43.83		36.51
	80.16		79.68
	124.0		119.8
	160.6		161.4
	222.3		200.2
	247.0		249.2
Av. =	127.1 g/l	Av.=	122.6 g/l

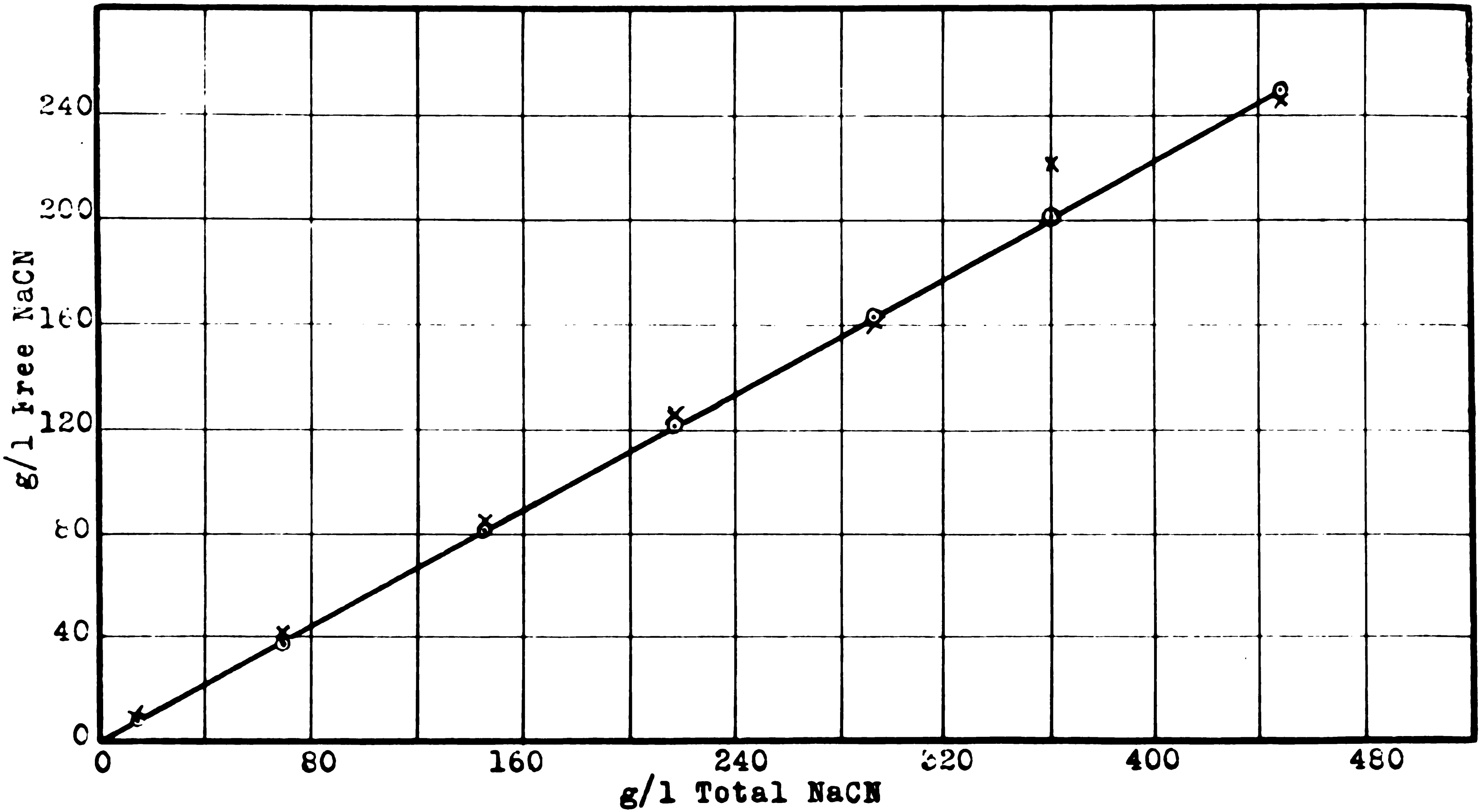

Fig. 2. - x = free NaCN by $AgNO_3$; 0 = free NaCN by $CdSO_4$

Table 4 shows that free NaCN as obtained by $AgNO_3$ gives on the average a high result. This verifies the statement made by N. Hall which was quoted previously. It should be noticed that titrations by $AgNO_3$ give somewhat irratic results. To bring out this matter more clearly, Fig. 2 has been drawn. Titration reactions assumed for this figure are:

$$AgNO_3 + 2NaCN \rightarrow NaAg(CN)_2 + NaNO_3$$

$$CdSO_4 + 3.99NaCN \rightarrow Na_{1.99}Cd(CN)_{3.99} + Na_2SO_4$$

When we remember that this set of seven solutions were prepared so that the ratio of NaCN to CdO was constant and that titrations by $CdSO_4$ brings out this straight line relationship quite accurately, we have further substantiated the precision possible by this method.

Part 2

Experimental.--A set of nine solutions were made by adding various amounts of CdO to sodium cyanide solutions, each of which contained 200 g/l. The solutions were allowed to come to equilibrium for three days and were then filtered to obtain an absolutely clear solution.

No sodium carbonate was added.

Titrations were made with standardized $CdSO_4$ after dilution to 100-150 ml.

Calculations were made using equation (5) and results are tabulated in Table 5.

Table 5

g/l CdO	Ml. Sample titrated	Ml. $CdSO_4$	X
4.82	2	10.48	3.33
9.64	2	10.06	3.36
14.46	2	9.22	3.53
19.28	2	8.41	3.69
24.05	2	7.59	3.89
48.20	5	13.31	4.17
71.29	5	9.15	4.20
96.39	10	9.92	4.17
120.4	25	7.19	4.06

To draw any conclusions from Table 5, we must remember that all considerations must be made in terms of the solutions which were actually titrated; that is, after samples have been diluted and the endpoint determined.

In this series there are at least five factors which may be changing the coordination number.

(1) Change in sodium hydroxide content

(2) Differences in concentration of the complex at the end of the titration

(3) Difference in metal content

(4) Change of the cyanide ratio

(5) Radical change in concentration of the indicator ion may be affecting the end point.

Numbers (3) and (4) are listed only because of statements made by M. R. Tompson[1]. He makes the following two generalizations:

"(1) Increasing the metal content of the solution necessarily increases the concentration of both metal-bearing anions and metal cation. There will be a tendency for a lowering of the coordination number when this is possible.---

(2) Addition of alkali cyanide, that is, an increase in the cyanide ratio, decreases the metal ion concentration and tends to cause a shift toward a higher coordination number, when higher compounds are possible.---"

These two factors do not enter into our considerations because (a) at the time our titration endpoint is taken, the cyanide ratio is supposedly the same; i.e., there is no excess cyanide in any case and (b) for this reason the metal content is also, supposedly, relatively the same in each solution.

Numbers (1), (2), and (5) have already been shown to have an effect. Tables 1 and 2 show that increase in sodium hydroxide increases the coordination number. Table 1 shows that increase in the complex concentration decreases the coordination number. Table 5 and Fig. 3 substantuates these conclusions and also proves that our titration endpoint changes with concentration of indicator ion (OH^- in this case).

In the first place, a coordination number greater than four is thought to be unlikely since a coordination number of five "does not allow symmetrical space arrangement"[1]. Therefore some of our results indicate that Free NaCN by titration with $CdSO_4$ is not a stoichiometric titration. This can be shown to be true by calculations with the extreme values. Points between these will be

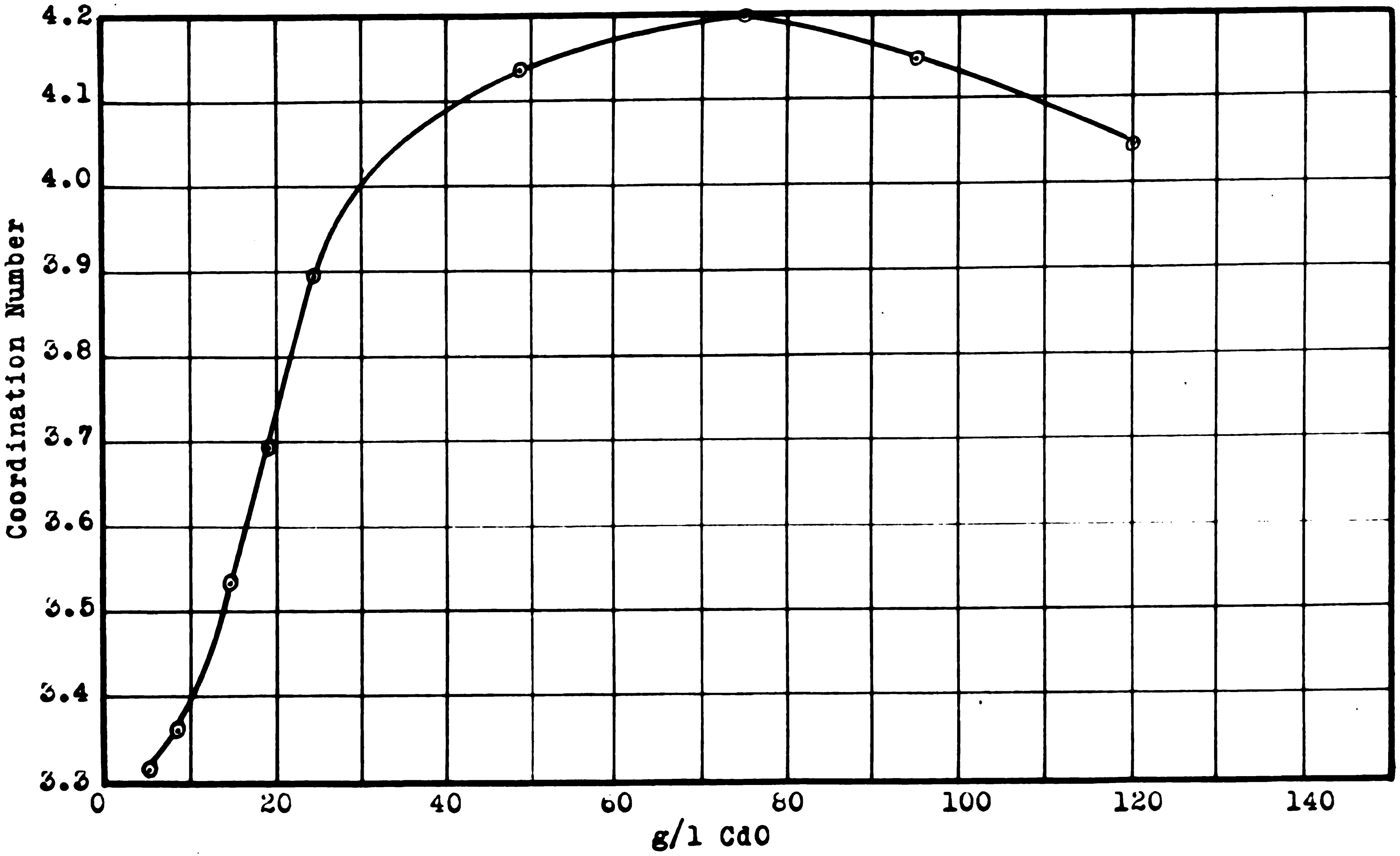

Fig. 3. - 200 g/l NaCN; No Na_2CO_3 present

proportionally more accurate.

Let us assume that at the end of the titration, the total volume was 150 ml. This represents the maximium dilution of our titrations. Solution #1 had 4.92 g/l of CdO and since, in any case, one mole of cadmium oxide reacting with sodium cyanide yields two moles of sodium hydroxide, we have in this solution 2(4.92 /128.4) or 0.076 mole/l NaOH. Two ml. of this was taken and diluted to 150 ml. (by our assumption). Thus we have 1.5×10^{-6} moles in 150 ml. or a concentration of 10^{-5} mole/l.

The solubility product for $Cd(OH)_2$ is given by Hogness and Johnson[11] to be:

$$[Cd^{++}][OH^{-}]^2 = 1.2\times10^{-14}$$

Hence, for precipitation to take place the cadmium ion concentration must be

$$[Cd^{++}] = (1.2\times10^{-14})/(10^{-5})^2 = 1.2\times10^{-4} \text{ mole/l.}$$

Thus in 150 ml. we need 1.8×10^{-5} mole of Cd .

Now one milliliter of our standard cadmium sulphate solution contains 0.04958 g. or 2.3×10^{-4} mole. Therefore approximately 0.10 ml. must be added beyond the stoichiometric point before precipitation will begin to take place in this solution. This difference is practically negligable since calculations were made assuming maxmium silution. If dilution was less than 150 ml. the endpoint would be that much more accurate. Readings within 0.1 ml. are within experimental error.

A most interesting phenomenon is brought out by calculations with solution #3 of Table 5 and solution #2 of Table 1. In the latter case 5 ml. of 20% Na_2CO_3 was added as indicator. This is equal to 0.1g. or 10^{-3} mole or $5x10^{-4}$ equivalent. With $5x10^{-4}$ equivalent of Na_2CO_3 present in the titration beaker a coordination number of <u>3.57</u> was obtained. In solution #3 of Table 5, 14.46g. CdO was present. Reasoning as before, we find thus that 0.225 mole or equivalent of NaOH per liter is formed. Taking a two ml. sample of this gives us $4.5x10^{-4}$ equivalent of NaOH present in the titration beaker, a coordination number of <u>3.53</u> was obtained.

In view of this, it follows that coordination number is a function of pH rather than NaOH content. This follows from the fact that equivalent amounts of either Na_2CO_3 or NaOH produce the same increase in coordination number.

By use of solution #9 of Table 5 we can show that an endpoint appears before stoichiometry is reached. Once again we shall assume a total of 150 ml. at the end of the titration.

This solution contains 120.4 g/l CdO and since one mole of CdO yields one mole of complex, in any case, we have 120.4 ÷ 128.4 or 0.94 mole/l of complex cyanide. When we take 25 ml. of this solution, we take $2.35x10^{-4}$ mole. Upon diluting this to 150 ml., we have a concentration of 0.16 mole/l. The complex concentration is further increased by addition of $CdSO_4$. In this case we used 7.2ml x0.5 g/ml. which corresponds to 0.0017 mole of $CdSO_4$ or $Na_2Cd(CN)_4$. Thus the final total concentration of $Cd(CN)_4^{--}$ is 0.162 mole/l.

The dissociation constant for $Cd(CN)_4^{--}$ is given in Tompson's[1] article to be:

$$\frac{[Cd^{++}]\,[CN^-]^4}{Cd(CN)_4^{--}} = 10^{-18}$$

and we know that for each Cd^{++} formed by dissociation, there are $4CN^-$ ions produced. Therefore:

$$[Cd^{++}]\,[\tfrac{1}{4}Cd^{++}]^4 = 10^{-18} \times 0.162$$

$$[Cd^{++}]^5 = 256 \times 0.162 \times 10^{-18}$$

$$= 41.5 \times 10^{-18}$$

$$[Cd^{++}] = \underline{5.3 \times 10^{-4} \text{ mole/l.}}$$

This is the concentration of the cadmium ion at the stoichiometric point due to dissociation of the complex ion.

In this same solution the sodium hydroxide concentration is just twice that of complex, viz., 1.88 Mole/l. Thus a 25 ml. sample diluted to 150 ml. gives us a concentration of OH^- of 0.31 mole per liter. For precipitation to take place then, the cadmium concentration must be:

$$[Cd^{++}] = \frac{1.2 \times 10^{-14}}{0.31^2} = \underline{1.2 \times 10^{-13} \text{ mole/l.}}$$

Thus we see that at the stoichiometric point the cadmium ion concentration due to dissociation is greater than that needed for precipitation. For this reason an end-point will appear too soon.

Although the dissociation constant used in this calculation was obtained in a dilute solution and therefore is most likely very inaccurate in the concentrated solution used, there can be no doubt that this solution does act in some measure in the manner shown. This may account for the values higher than four but cannot account for the decrease in coordination number obtained beyond 75 g/l. of CdO.

Because the free cyanide content of the last two solution of Table 5 were so small, large samples were taken for titration, namely 25 and 10 ml. respectively. These samples were diluted to approximately the same concentrations as were the other solutions. Therefore, the concentration of the complex at the end of the titration is very much larger. We have already shown in Table 1 that coordination number decreases with increase in concentration of the complex. This decrease is by no means negligible and very nicely accounts for the drop-off in coordination number.

From Table 5 and Fig. 3 we may then conclude:

(1) The decrease in coordination number with decrease in sodium hydroxide is greater than can be accounted for by solubility calculations.

(2) High coordination numbers at high concentrations of cadmium oxide may be accounted for by dissoc-

iation and solubility calculations.

(3) A decrease in coordination numbers at high concentrations of CdO was obtained which cannot be accounted for by such calculations.

EFFECT OF TIME UPON THE COMPLEX

Analyses on the series shown in Table 5, 145 days later gave the following results:

(1) The total cyanide content had decreased 8.6%

(2) A curve almost identical with that shown in Fig. 3 was obtained. This verified our previous results.

(3) The coordination number on the average was about 1.8% smaller.

Analyses on the series in Table 3, 80 days previous to the results given showed that:

(1) Total cyanide had decreased 3.4% in this time.

(2) The average coordination number in the last case was about 2% smaller.

Because of the lack of conclusive evidence that complexes originally formed are not the most stable, all calculations and conclusions in this paper are made on the assumption that changes in the coordination number due to dilution, increase in concentration by titration, etc. are instantaneous. In view of the above though, it appears that there might be a slight lowering of coordination number with time.

This decrease may be due to the reactions previously given under <u>Free NaCN</u> analysis:

$$2NaCN + 2HOH + 2NaOH + O_2 \quad 2NaCO_3 + 2NH_3$$

$$Na_2Cd(CN)_4 + 4NH_3 \quad Cd(NH_3)_4(CN)_2 + 2NaCN$$

These represent a decrease in NaOH as well as the mole ratio CN:Cd.

EFFECT OF ELECTROLYSIS

Several plating solutions were analyzed by the methods given earlier. Results are tabulated in Table 6. 10 ml. sample titrated with $CdSO_4$ in each case. Equation (5) is used.

Table 6

#	g/l CdO	g/l total NaCN	ml. $CdSO_4$	X
1	23.89	98.34	14.25	3.93
2	42.44	88.78	16.16	2.58
3	25.95	86.53	17.76	2.92
4	20.93	66.09	8.97	3.68
5	18.77	57.96	8.22	3.56

Numbers 1, 2, and 3 are commercial plating solutions in operation 24 hours per day. Numbers 4 and 5 are solutions from a 20 liter cadmium plating bath. Number 5 is one month later than number 4. Twenty-four hour per day electrolysis was carried on during this time.

These solutions are approximately of the same composition as those shown in Table 3. That is, at the time of titration, samples from these plating baths and from solutions in Table 3 have been diluted to approximately the same concentration.

It follows from these data that electrolysis causes a decrease in coordination number. This decrease may be due to:

(1) Impurities affecting the complex or our endpoint.

(2) Due to different migration rates, the bivalent complex may be gradually diminished in concentration.

(3) Some mono-valent cadmium may be formed in the process of electrolysis.

(4) The aging process already mentioned.

SUMMARY:

The cadmium cyanide-sodium cyanide complex is different in different solutions.

The coordination number increases with increase in pH.

The coordination number decreases with increase in concentration of the complex.

A solution of the type used in cadmium plating baths (see Table 3) contains a complex which is largely in the form of $Na_2Cd(CN)_4$.

Plating solutions have a coordination number smaller than 4 but which varies with the plating bath.

There appears to be a slight decrease of coordination number with time.

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