

# Investigation of A Metal Complex Ion by Simple Precipitation-Titration Method

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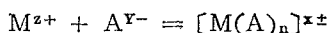
A simple precipitation-titration method for the determination of the coordination number of a metal complex ion is described. The experimental data for eight complex ions are presented along with graphical figures for four complex ions which show close approximations to the theoretical coordination numbers. This method may prove useful for student laboratories in both advanced quantitative analysis and physical chemistry.

## Introduction.

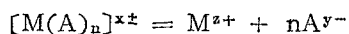
The concentration of a free metal ion in a solution containing a complexing agent is governed by the stability of the complex formed<sup>1</sup>. If a precipitating agent for this free ion is now added to the solution, no precipitate will form unless the solubility product is exceeded. The relationship between these reactions has been discussed in many analytical texts,<sup>2,3,4</sup> and various experiments concerning the dissolution of precipitate through complex formation are also suggested<sup>5</sup> to help students understand the principle of the equilibria established<sup>5,6</sup>. No simple experiments, however, concerning the structure or the coordination number of the metal complex ion are available. This paper describes a simple titration method and its application for determining the coordination number of a metal complex ion.

## Theory.

When a metal ion  $M^{z+}$  reacts with a complexing agent, either a coordination molecule ( $Y=O$ ) or an anion ( $Y=\text{small number}$ )  $A$ , a complex metal ion will form according to the following reaction:



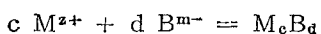
and its instability constant can be expressed as:



and

$$\frac{[M^{z+}][A]^n}{[MA]_n^{x\pm}} = K_{inst} \dots \dots \dots (1)$$

If a precipitating agent for this metal ion is added to the solution, a precipitate will not form until its solubility product is exceeded.



and

$$[M^{z+}]^c [B^{m-}]^d = K_{s.p.} \dots \dots \dots (2)$$

As long as the solution is in contact with the first particle of precipitate formed and the metal complex ion is present, metal ion  $M^{z+}$  must have the same value in both

equations (1) and (2). The equilibrium now may be expressed by dividing equation (2) by equation (1), and simplifying gives

$$\frac{[M(A)_n]^{x\pm} \cdot [B^{m-}]^d}{[A]^n} = \frac{K_{s.p.}}{K_{inst.}}$$

and after rearrangement,

$$[A]^n = \frac{K_{inst.} \cdot [M(A)_n]^{x\pm}}{K_{s.p.}} \cdot [B^{m-}]^d \dots\dots\dots(3)$$

Letting

$$\frac{K_{inst.} \cdot [M(A)_n]^{x\pm}}{K_{s.p.}} = K',$$

then, equation (3) can be simplified as:

$$[A]^n = [B^{m-}]^d \times K' \dots\dots\dots(4)$$

Taking the logarithm on both sides, then

$$n \log [A] = d \log [B^{m-}] + \log K' \dots\dots\dots(5)$$

Letting X = log [A] and Y = log [B<sup>m-</sup>], then equation (5) can be written as

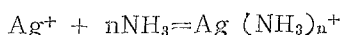
$$n X = d Y + C$$

Plotting log [A] vs. log [B<sup>m-</sup>], a straight line is expected and the slope of the equation will be the number of n, i.e., the co-ordination number of the metal complex ion.

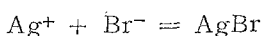
**Application.**

**I. Diamminesilver (I) complex ion.**

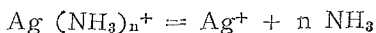
when Ag<sup>+</sup> is added to a solution containing NH<sub>3</sub>, silver ammonia complex will be formed as the following reaction shows:



If this solution is titrated with bromide as well as chloride or iodide ion, a turbidity end point will be reached after a certain amount of bromide solution is added. The reaction may be expressed as:



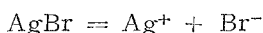
The instability constant K<sub>inst.</sub> of this complex will be



and

$$\frac{[Ag^+][NH_3]^n}{[Ag(NH_3)_n^+]} = K_{inst.} \dots\dots\dots(A)$$

The solubility product constant of silver bromide will be



and

$$[Ag^+][Br^-] = K_{s.p.} \dots\dots\dots(B)$$

As long as equilibrium is maintained and the Ag(NH<sub>3</sub>)<sub>n</sub><sup>+</sup> ion is present, [Ag<sup>+</sup>] must have the same value in both equations.

Dividing eq. (B) by eq. (A) and simplifying gives

$$\frac{[Ag(NH_3)_n^+][Br^-]}{[NH_3]^n} = \frac{K_{s.p.}}{K_{inst.}} \dots\dots\dots(C)$$

After rearrangement, equation (C) can be expressed as

$$[NH_3]^n = \frac{K_{inst.} [Ag(NH_3)_n^+][Br^-]}{K_{s.p.}}$$

Keeping the final volume of each determination nearly the same to make the concentration of  $[Ag(NH_3)_n^+]$  almost constant, the above equation becomes

$$[NH_3]^n = \frac{K_{inst.} [Ag(NH_3)_n^+]}{K_{s.p.}} \cdot [Br^-]$$

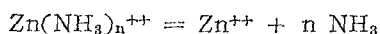
$$= K' \times [Br^-]$$

Taking logarithm on both sides of the equation,

$n \log [NH_3] = \log [Br^-] + \log K'$ , with the varied concentrations of  $[NH_3]$  and  $[Br^-]$ , and plotting  $\log [NH_3]$  vs.  $\log [Br^-]$ , the slope of the equation will be the number of  $n$ , i.e. the coordination number of the silver ammonia (diamminesilver(I)) complex.

## II. Tetramminezinc (II) complex ion

Applying the preceding derivation to a case such as tetramminezinc (II) complex when potassium ferrocyanate,  $K_4Fe(CN)_6$  is used as its precipitating agent, the related equilibria may proceed as follows:



and 
$$\frac{[Zn^{++}] [NH_3]^n}{[Zn(NH_3)_{n^{++}}]} = K_{inst.} \dots\dots\dots (E)$$

According to the reaction,



the solubility product constant of  $K_2Zn_3[Fe(CN)_6]_2$  can be expressed as

$$[K^+]^2 [Zn^{++}]^3 [Fe(CN)_6^{4-}]^2 = K_{s.p.} \dots\dots\dots (F)$$

From equation (F),

$$Z[n^{++}] = \sqrt[3]{\frac{K_{s.p.}}{[K^+]^2 [Fe(CN)_6^{4-}]^2}}$$

substituting into equation (E),

$$\frac{K_{s.p.}^{1/3} [NH_3]^n}{[Zn(NH_3)_{n^{++}}] [K^+]^{2/3} [Fe(CN)_6^{4-}]^{2/3}} = K_{inst.} \dots\dots\dots (G)$$

and rearranging,

$$\frac{[NH_3]^n}{[K^+]^{2/3} [Fe(CN)_6^{4-}]^{2/3}} = \frac{K_{inst.}}{K_{s.p.}^{1/3}} \cdot [Zn(NH_3)_{n^{++}}]$$

Considering the concentration of  $[Zn(NH_3)_{n^{++}}]$  as constant. then

$$\frac{K_{inst.}}{K_{s.p.}^{1/3}} \cdot [Zn(NH_3)_{n^{++}}] = K'' \dots\dots\dots (H)$$

Taking logarithm on both sides of the above equation, and rearranging,

$$n \log [NH_3] = 2/3 \log [K^+] + 2/3 \log [Fe(CN)_6^{4-}] + \log K''.$$

The concentration of  $K^+$  is four times the concentration of  $Fe(CN)_6^{4-}$ , assuming the salt  $K_4Fe(CN)_6$  is completely ionized, then

$$[K^+] = 4 [Fe(CN)_6^{4-}] \text{ and}$$

$$n \log [NH_3] = 2/3 \log 4 [Fe(CN)_6^{4-}]^2 + \log K''$$

Plot  $\log [NH_3]$  vs.  $\log 4 [Fe(CN)_6^{4-}]^2$  and

$$2/3 \times \text{slope} = n \text{ (coordination number of zinc ammonia complex)}$$

## Experimental

### I. Reagents.

All chemicals used in this experiment were analytical grade, purchased from the

Baker Chemical Co., Philpsburg, N. J., U.S.A.

(1) Silver Nitrate Solution

*0.1 M AgNO<sub>3</sub> solution* by dissolving 17 grams of crystals of AgNO<sub>3</sub> in distilled water and making up to one liter.

(2) Ammonium Hydroxide Solution

*2 M NH<sub>4</sub> OH aqueous solution* by adding 13.5 ml of concentrated NH<sub>4</sub>OH to one-liter volumetric flask and making up to one liter with distilled water.

(3) Sodium Bromide Solution

*0.01 M NaBr solution* by dissolving 1.03 grams of NaBr in water and making up to one liter.

(4) Potassium Ferrocyanate Solution

*0.0025 N K<sub>4</sub>Fe(CN)<sub>6</sub> solution*, by dissolving 1.06 grams of K<sub>4</sub>Fe(CN)<sub>6</sub> · 3H<sub>2</sub>O and making up to one liter.

(5) Lead Nitrate Solution

*0.01 M Pb(NO<sub>3</sub>)<sub>2</sub> solution*, by dissolving 3.31 grams of Pb(NO<sub>3</sub>)<sub>2</sub> in water and making up to one liter,

(6) Sodium Thiosulfate solution

*0.0705 M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution*, by dissolving 17.4 grams of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> · 5H<sub>2</sub>O in water and making up to one liter.

(7) Zinc Sulfate Solution

*0.05 MnSO<sub>4</sub> solution*, by dissolving 8.1 grams of ZnSO<sub>4</sub> in water and making up to one liter.

(8) Sodium Chloride Solution

*1 M NaCl solution*, by dissolving 58.45 grams of NaCl in water and making up to one liter.

(9) Potassium Iodide Solution

*0.01 M KI solution*, by dissolving 1.66 grams of KI in water and making up to one liter.

(10) Ferric Nitrate Solution

*0.01 M Fe(NO<sub>3</sub>)<sub>3</sub> solution*, by dissolving 3.5 grams of Fe(NO<sub>3</sub>)<sub>3</sub> · 6H<sub>2</sub>O in water and making up to one liter.

(11) Sodium Fluoride Solution

*1 M NaF solution*, by dissolving 41.99 grams of NaF in water and making up to one liter.

(12) Cadmium Acetate Solution

*0.01 Cd(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub> solution*, by dissolving 2.3 grams of Cd(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub> in water and making up to one liter.

(13) Sodium Hydroxide Solution

*0.03 M NaOH solution*, by dissolving 1.2 grams of NaOH in water and making up to one liter, then standardizing against standard HCl solution.

(14) Sodium phosphate Solution

0.01 M  $\text{Na}_3\text{PO}_4$  solution, by dissolving 3.8 grams of  $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$  in water and making up to one liter.

## II. Procedure.

Pipet 2.0 ml of 0.01 M  $\text{AgNO}_3$  solution into each of three Erlenmeyer flasks. Then add 10, 20, and 30 ml of 2 M ammonium hydroxide solution, respectively, to the silver nitrate solutions and dilute each solution to 100 ml with distilled water. Fill the buret with 0.01 M sodium bromide solution and determine the volume of the titrant which produces a faint but permanent turbidity of silver bromide. Repeat the experiments just performed but dilute each solution by adding only the amount of distilled water calculated from the first titration, which will make a total volume of 100 ml at the end of the titration. This will insure that the concentration of  $\text{Ag}(\text{NH}_3)_n^+$  is always virtually the same when the  $\text{AgBr}$  starts to form.

From the data obtained in each determination, calculate the concentration of  $\text{NH}_4\text{OH}$  and  $\text{NaBr}$  solutions at the end point and plot the  $\log \text{NH}_3$  vs.  $\log \text{Br}^-$ . The slope of the resulting straight line equals the number  $n$  of the silver ammonia complex,  $\text{Ag}(\text{NH}_3)_n^+$ . Following the same procedure using the concentrations and volumes of the complexing and precipitating agents listed in Table II, the coordination numbers of metal complex ions such as  $\text{Ag}(\text{S}_2\text{O}_3)_n^{-2n+1}$ ;  $\text{Zn}(\text{NH}_3)_n^{++}$  and  $\text{Pb}(\text{S}_2\text{O}_3)_n^{-2n+2}$  may be determined.

## Results and Discussion

Eight metal complex ions were investigated. The results are listed in Table I. For those having good response, the concentrations and volumes of complexing and precipitating agents are also presented both in Table II and graphically in Fig. I-IV from which it can be seen that the coordination numbers of the metal complex ions determined by the proposed procedure agree closely with those stated in many texts.<sup>7,8</sup>

Table I. Coordination Numbers of Metal Complex Ions Tested.

| Complex ion                                 | $K_{inst.}$           | Precipitate                                       | $K_{s.p.}$             | Coordination Number |              |
|---|-----------------------|---|------------------------|---------------------|--------------|
|   |                       |   |                        | Theoretical         | Experimental |
| $\text{Ag}(\text{NH}_3)_n^+$                | $5.9 \times 10^{-8}$  | $\text{AgCl}$                                     | $2.88 \times 10^{-10}$ | 2                   | 2.30         |
| $\text{Ag}(\text{NH}_3)_n^+$                | $5.9 \times 10^{-8}$  | $\text{AgBr}$                                     | $5 \times 10^{-13}$    | 2                   | 1.93         |
| $\text{Ag}(\text{NH}_3)_n^+$                | $5.9 \times 10^{-8}$  | $\text{AgI}$                                      | $8.5 \times 10^{-17}$  | 2                   | 2.21         |
| $\text{Ag}(\text{S}_2\text{O}_3)_n^{-2n+1}$ | $6.0 \times 10^{-14}$ | $\text{AgI}$                                      | $8.5 \times 10^{-17}$  | 2                   | 2.10         |
| $\text{Pb}(\text{S}_2\text{O}_3)_n^{-2n+2}$ |                       | $\text{Pb}_3(\text{PO}_4)_2$                      | $1 \times 10^{-32}$    | 2                   | 1.97         |
| $\text{Zn}(\text{NH}_3)_n^{++}$             | $3.4 \times 10^{-10}$ | $\text{K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$ | $1 \times 10^{-95}$    | 4                   | 4.02         |
| $\text{Cd}(\text{NH}_3)_n^{++}$             | $7.5 \times 10^{-8}$  | $\text{Cd}(\text{OH})_2$                          | $2.0 \times 10^{-14}$  | 4                   | 4.68         |
| $\text{FeF}_n^{-n+3}$                       | $5 \times 10^{-16}$   | $\text{Fe}(\text{OH})_3$                          | $6 \times 10^{-38}$    | 6                   | 6.30         |

Table II. Concentrations and Volumes of Solutions of Metal ions, Complexing Agents, and Precipitating Agents.

| Complex ion                                 | Concentration<br>(M)                      | Volume<br>(ml) |       |       |
|---|---|----------------|-------|-------|
|   |   | 1              | 2     | 3     |
| $\text{Ag}(\text{NH}_3)_n^+$                | $\text{AgNO}_3$ 0.01                      | 2.00           | 2.00  | 2.00  |
|   | $\text{NH}_4\text{OH}$ 2.00               | 10.00          | 20.00 | 30.00 |
|   | $\text{NaBr}$ 0.01                        | 1.54           | 6.20  | 13.60 |
| $\text{Ag}(\text{S}_2\text{O}_3)_n^{-2n+1}$ | $\text{AgNO}_3$ 0.01                      | 2.00           | 2.00  | 2.00  |
|   | $\text{Na}_2\text{S}_2\text{O}_3$ 0.07    | 30.00          | 40.00 | 50.00 |
|   | $\text{KI}$ 0.20                          | 3.02           | 6.33  | 9.45  |
| $\text{Zn}(\text{NH}_3)_n^{++}$             | $\text{ZnSO}_4$ 0.06                      | 2.00           | 2.00  | 2.00  |
|   | $\text{NH}_4\text{OH}$ 2.00               | 25.00          | 40.00 | 50.00 |
|   | $\text{K}_4\text{Fe}(\text{CN})_6$ 0.0025 | 2.04           | 7.94  | 14.42 |
| $\text{Pb}(\text{S}_2\text{O}_3)_n^{-2n+2}$ | $\text{Pb}(\text{NO}_3)_2$ 0.01           | 1.00           | 1.00  | 1.00  |
|   | $\text{Na}_2\text{S}_2\text{O}_3$ 0.40    | 10.00          | 20.00 | 30.00 |
|   | $\text{Na}_3\text{PO}_4$ 0.01             | 2.50           | 7.92  | 25.50 |

To obtain a distinct and sharp end-point of the titration a suitable precipitating agent must be selected. From the data listed in Table I it can be seen that the solubility product constant of the precipitate must be smaller than the instability constant of the metal complex ion. In the case of the complex ion  $\text{Ag}(\text{NH}_3)_n^+$ , it appears that the solubility product constant of the precipitate should be of the order of  $10^{-5}$  times the instability constant of the complex ion for an approximation of the theoretical coordination number. Thus, the use of bromide gives the best approximation, i. e., an experimental coordination number of 1.93 compared with the theoretical number of 2. The use of  $\text{Cl}^-$  with a much higher solubility product constant or the use of iodide with a much lower  $K_{s.p.}$  gives significantly greater deviations from the theoretical, 2.30 and 2.21, respectively. With  $\text{Cl}^-$  too much titrant is needed to reach the end point, and on the other hand the  $K_{s.p.}$  of  $\text{I}^-$  is so small that a few drops of the titrant will produce turbidity no matter how much complexing agent is used.

Another factor to be considered in selecting a suitable precipitating agent is that there must be no reaction effecting a shift of the equilibrium between the complexing and precipitating agents. For the metal complex ion  $\text{Cd}(\text{NH}_3)_4^{++}$ ,  $\text{OH}^-$  is used as a precipitant to determine its coordination number. The  $K_{s.p.}$  of  $\text{Cd}(\text{OH})_2$  is of the order of  $10^{-6}$  times the instability constant of this complex ion, suggesting that it might be a good choice, but a poor approximation of 4.68 for the coordination num-

ber is obtained. This error is partly due to the reaction between  $\text{OH}^-$  and  $\text{NH}_3$  in the equilibrium  $\text{NH}_3 + \text{H}_2\text{O} = \text{NH}_4^+ + \text{OH}^-$ .

The concentration of the complexing agent is not appreciably diminished by formation of the complex ion and therefore is assumed to remain unchanged throughout the determination. The fact that the close approximations to the theoretical coordination numbers were obtained for four complex ions supports this assumption.

### References

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## 沉澱滴定法測定金屬錯離子配位數之研究

鄭 得 安

### 摘 要

本論文提供測定金屬錯離子配位數之沉澱滴定法。其理論根據及應用經予詳細討論；並以八種不同之金屬錯離子作為實驗，其中四種經實驗結果求出之配位數與理論者極為接近。實驗數據及求出之結果均以圖表表示之。此種測定金屬錯離子配位數之滴定法可供大學高級定量分析或物理化學等課程作為講演及實驗之用。

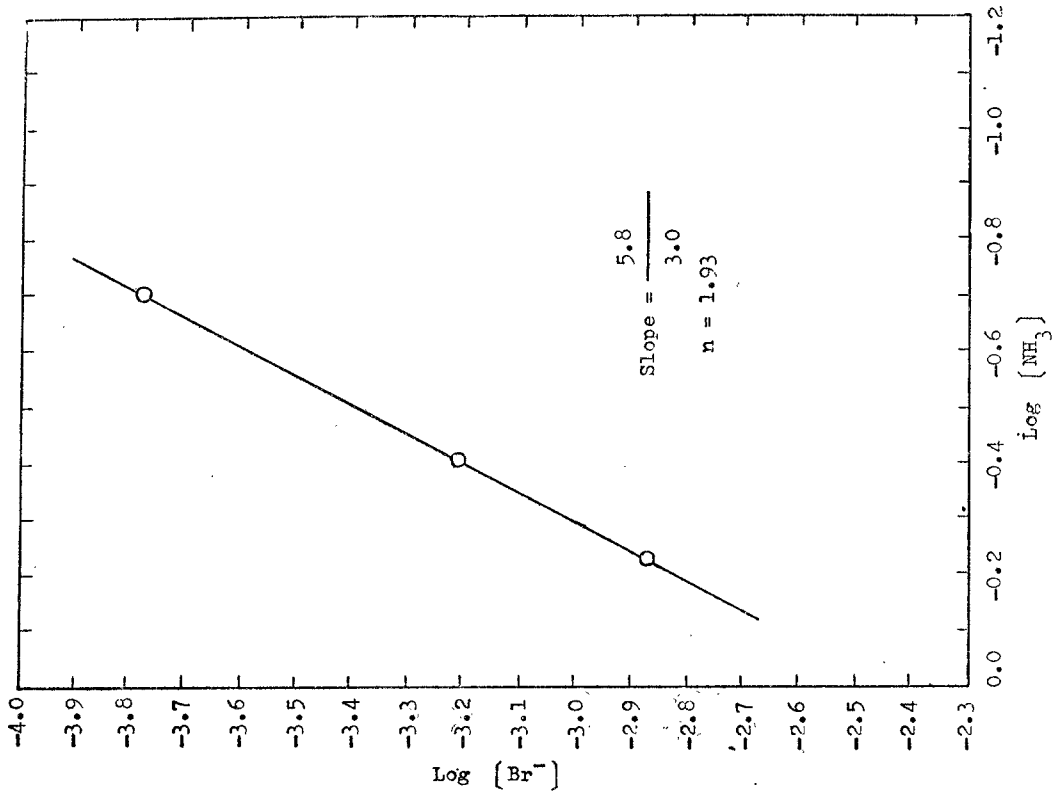


Fig. I A Plot of log [NH<sub>3</sub>] vs. log [Br<sup>-</sup>]

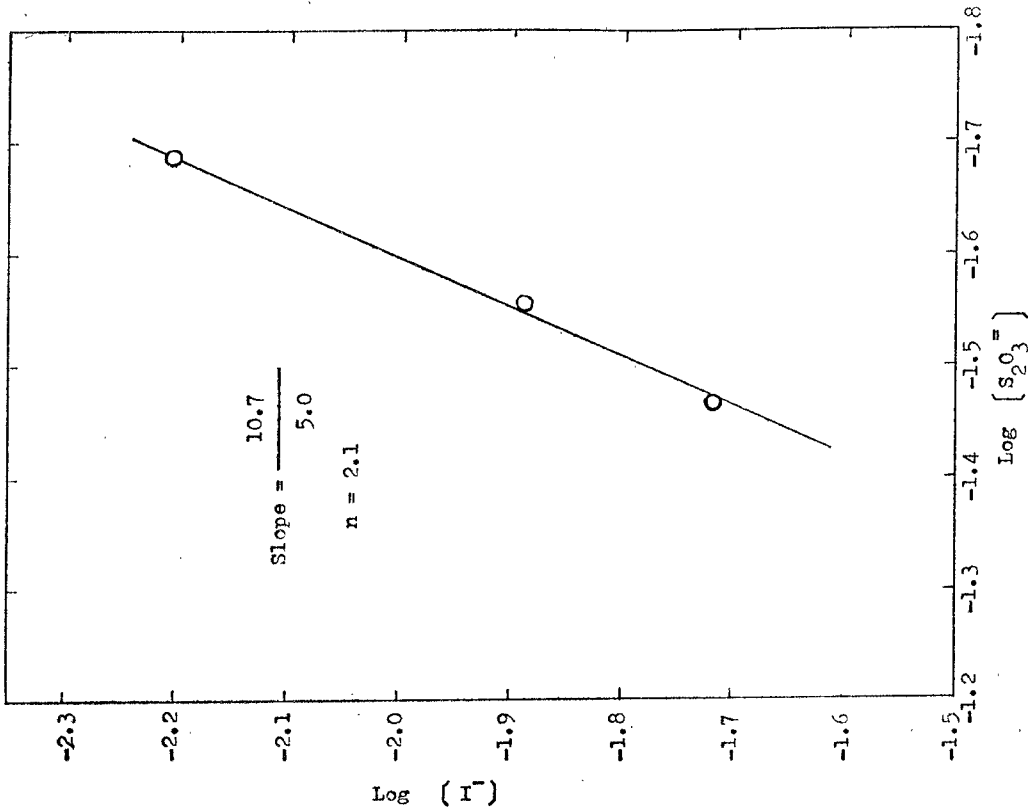


Fig. II A Plot of log [S<sub>2</sub>O<sub>3</sub><sup>=</sup>] vs. log [I<sup>-</sup>]



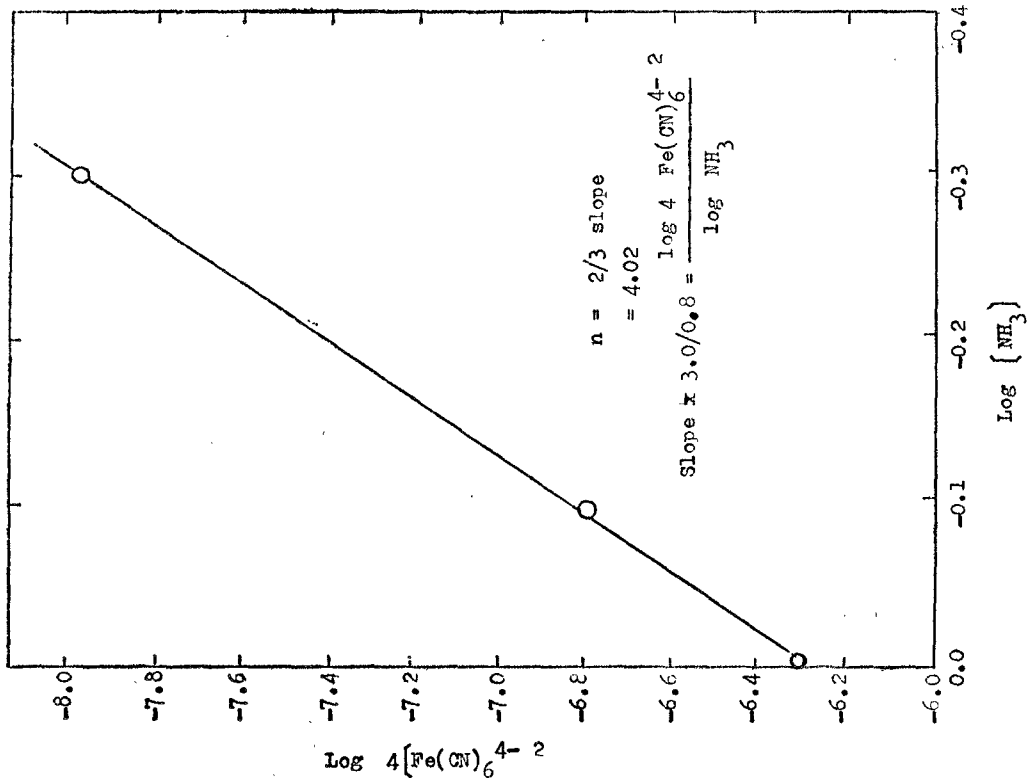


Fig. III A Plot of  $\log [\text{NH}_3]$  vs.  $\log 4[\text{Fe(CN)}_6^{4-2}]$

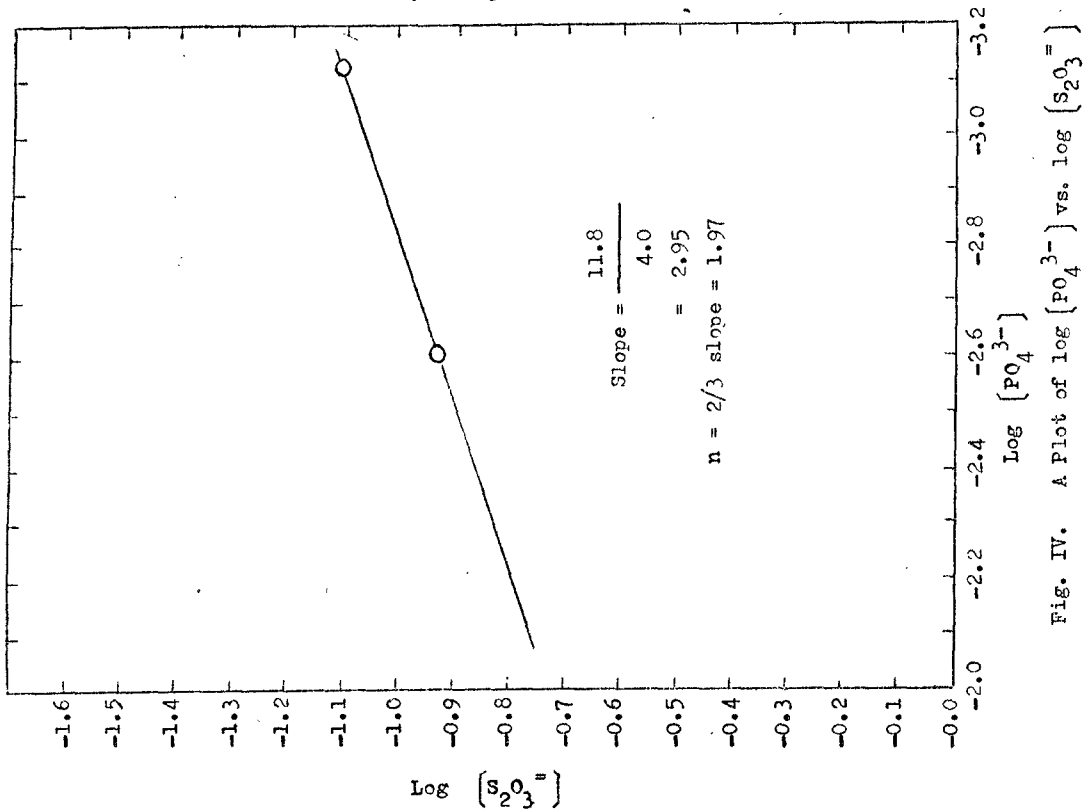


Fig. IV. A Plot of  $\log [\text{PO}_4^{3-}]$  vs.  $\log [\text{S}_2\text{O}_3^{2-}]$