

POLAROGRAPHIC STUDIES OF VANADIUM (II) COMPLEXES

A Thesis submitted to the committee on post-graduate studies of the University of Manitoba in partial fulfilment of the requirements for the degree of

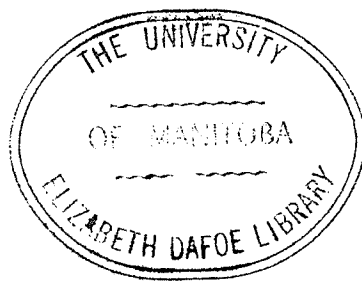
Master of Science.

by

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ABSTRACT

Investigations were carried out on the half-wave potentials and diffusion currents of the oxidation waves of vanadium (II) in thiocyanate, fluoride, chloride, bromide and iodide solutions.

The electrode reaction was shown to be reversible by plot of $\log i/(i_d - i)$ vs $E_{d.e.}$. On applying the equation described by Lingane, the ratio of the formation constants between vanadium (II) and vanadium (III) complexes of thiocyanate and fluoride were determined. It was found that the formation constants of vanadium (III) complexes are smaller than the corresponding vanadium (II) complexes.

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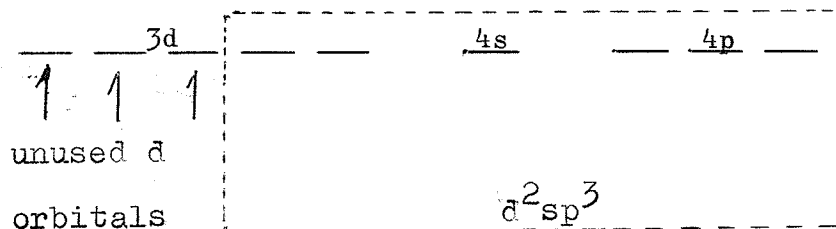
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INTRODUCTION

The electronic configuration of V^{++} is



The half-filled, unused d orbitals which are left after hybridization to obtain the bonding orbitals and thus get a stable electronic configuration for the central metal ion by coordination.

It has been qualitatively indicated by Taube (*1), that the possibility of stability of a half filled d set by covalent bonding to vanadium (II) would suggest that $[V(CN)_6]^{-4}$ should be stabilized with respect to the $[V(CN)_6]^{-3}$ state. King and Garner(*2) reported that the vanadium (II) ion forms a stable complex with $[V(diphy)_3]^{++}$. Schwarzenbach(*3) has found direct evidence for EDTA complex of vanadium (II).

Although the polarographic characteristics of +2 and +3 vanadium in complexing solution has been investigated by Lingane and Meites(*4,5,6), no quantitative work regarding the formation constants has as yet been done.

Accordingly, this research was undertaken to obtain information about the composition and stability constants of some of the halides and thiocyanate complexes of vanadium (II).

Some methods were tried but the overlap of the absorption spectrum of complex and simple ions in spectrophotometry, and failure of E.M.F. methods due to the high

reducing power of vanadium (II) on metal-salt indicator electrodes (Ag-AgCNS, Cu-CuCNS and Hg-HgCNS) made it impossible to use those methods. Finally, the dropping mercury electrode was found to be satisfactory for this work.

In the dropping mercury electrode, the considerable complexation of vanadium (II) will be expected to produce a more negative half-wave potential than the simple ion. By carefully estimating the change in the character of the redox curves, the ratio of complex formation constant between +2 and +3 vanadium complexes can be evaluated.

PRINCIPLES OF POLAROGRAPHY

The general principles and practical application of polarographic analysis with the dropping mercury electrode have been reviewed by Heyrovsky (*7), Hohn (*8), Stackelberg (*9) and Kolthoff and Lingane (*10) .

The current-voltage curves are obtained when solutions of electro-oxidizable or electro-reducible substances are electrolyzed in a cell, in which the cathode consists of easily polarized droplets of mercury emerging regularly from the end of a fine capillary glass tube and continuously exposing a fresh mercury surface to the electrolyte, thus preventing the accumulation of any products of electrolysis at the electrodes. The anode is a large unpolarized pool of mercury into which the cathode mercury is absorbed. The potential of this type of electrode is variable, depending upon the composition and nature of the electrolyte in contact with it, and is now often replaced by a saturated calomel electrode (S.C.E.) whose potential is constant and independent of the nature of the electrolyte.

The technique consists in applying a gradually increasing potential difference across the electrodes immersed in the solution under analysis, and measuring small currents of the order of microamperes produced by the reduction of ions at the dropping mercury cathode, or oxidation if the electrode is operating anodically. These currents are due to the migration of ions to this cathode in the electrical gradient set up, and to the diffusion of ions

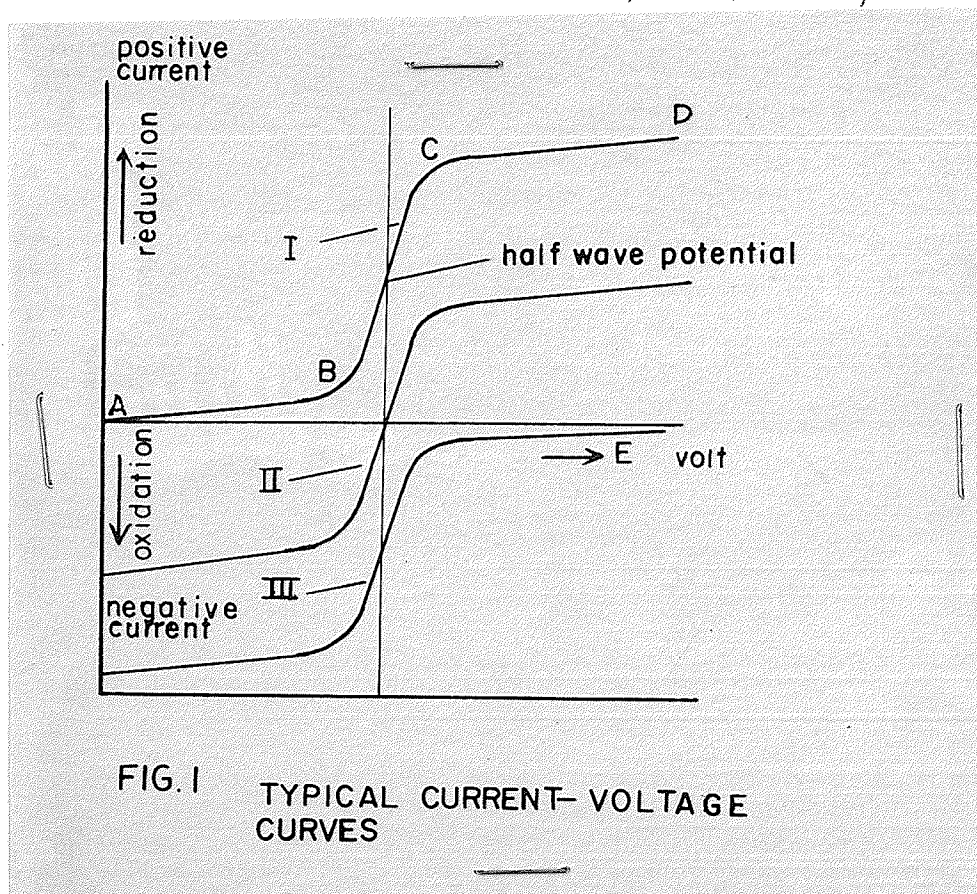
in the concentration gradient produced by the removal of ions from solution in the proximity of the cathode. Only the latter current is needed in the polarographic method, since its magnitude is dependent on the concentration of the reducible substance.

A current-voltage curve, or polarogram, is then obtained by plotting the applied voltage in volts along a horizontal axis against the observed current in microamperes along a vertical axis.

Some typical current-voltage curves are shown in Fig. 1. Curve I represents the type of cathodic wave (electro-reduction) which the electrode reaction is reducing the metal ions of higher oxidation state to lower oxidation state.



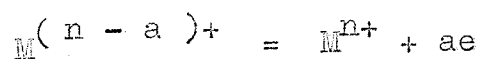
where M^{n+} symbolizes the simple, or hydrated, ions of the metal.



It will be observed that the curve falls into three separate portions. From zero applied potential to the decomposition potential (B), only a very small current, called the residual current, passes through the cell ---- this is represented by AB in the figure. At B, an appreciable rate of discharge of metal ions at the dropping mercury cathode is attained resulting in an increase of current flowing through the solution. The curve at B suddenly turns upwards and the current increases rapidly for small increase in the applied voltage until C is reached, when the current becomes constant again. After C, there is a plateau of current with the increase of the applied voltage and the steady current represented by CD is referred to as the limiting or diffusion current. Other factors remaining constant, this current is directly proportional to the concentration of metal ions in the solution.

The potential of the point on the current-voltage curve at which the diffusion current is one-half of its limiting value is known as the half-wave potential ($E_{1/2}$).

Curve II is known as an anodic wave (electro-oxidation) which the electrode reaction is oxidization of the metal ions of lower oxidation state to the higher oxidation state,



Curve III is composite cathodic-anodic wave of a mixture of the oxidized and reduced forms. According to the usual convention, a positive sign is given to a cathode current and a negative sign to an anodic current.

The mathematical theory of the polarograph has been fully worked out by J. Heyrovsky, D. Ilkovic and their co-workers. The equation resulting from the theory is known as the Ilkovic equation (*11,12)

$$I_d = 605 n C D^{1/2} m^{2/3} t^{1/6} \quad (3)$$

where I_d is the diffusion current (in microamperes), n is the number of electrons involved in the reduction process taking place at the cathode, C is the concentration of the specific metal ion in solutions (in millimoles per liter), D is the coefficient of diffusion of the metal ions (in square centimeters per second), m is the mass of mercury (in milligrams) flowing through the capillary per second, and t is the time between successive drops (in seconds).

Equation (3) can also be given as :

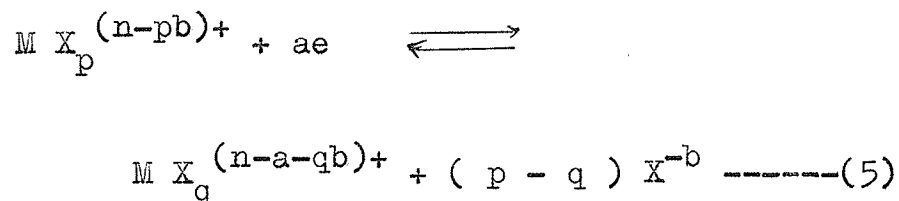
$$k = \frac{I_d}{C} = 605 n D^{1/2} m^{2/3} t^{1/6} \quad (4)$$

The numerical value of 605 was figured out experimentally.

THEORY

The polarographic method can be applied advantageously to the study of complex ions by virtue of the fact that the half wave potentials of the complex metal ions are shifted by complex formation. Lingane (*13) has described in detail the application of this technique to the determination of the formulas of Fe (II) and Fe (III) oxalate complexes under varying oxalate concentrations and to the determination of the stability constant of $\text{Fe}(\text{C}_2\text{O}_4)_3^{\equiv}$ and $\text{Fe}(\text{C}_2\text{O}_4)_2^{\equiv}$ from the dissociation constant of $\text{Fe}(\text{C}_2\text{O}_4)_3^{\equiv}$.

When the reduction at the dropping-mercury electrode takes place between two valence states of a metal ion, one or both of which are complexed, we may consider the reaction to be :



where $\text{M X}_p^{(n-pb)+}$ is the metal ion complex at lower oxidation state, $\text{M X}_q^{(n-a-qb)+}$ at a higher oxidation state, p and q are the coordination numbers, X^{-b} is the complex-forming substance and a is the number of electrons transferred in the reaction. Under these conditions, the mercury electrode behaves as an inert electrode.

A general equation for these waves will be derived on the basis of the following assumptions: (1) that the electrode reaction is reversible; (2) that sufficient supporting electrolyte is present so that the current is entirely diffusion controlled; and (3) that a sufficient excess of the complex-forming substance is present in the solution to insure that its concentration at the electrode surface will remain virtually constant and independent of the current. The potential of the dropping electrode at any point on either a cathodic, an anodic or a composite wave will then be expressible (assuming concentrations equal to activities at low concentration) by the Nernst equation (*10) as:

$$\begin{aligned}
 E_{d.e.} &= E^{\circ} - \frac{R T}{a F} \ln \frac{C_{Red.}^{\circ}}{C_{Ox.}^{\circ}} - \frac{R T}{a F} (p - q) \ln C_X \\
 &= E^{\circ} - \frac{0.0591}{a} \log \frac{C_{Red.}^{\circ}}{C_{Ox.}^{\circ}} \\
 &\quad - \left(\frac{p - q}{a} \right) 0.0591 \log C_X \quad (6)
 \end{aligned}$$

at 25° C, in this equation, E° is the ordinary standard potential of reaction(1), $C_{Red.}^{\circ}$ and $C_{Ox.}^{\circ}$ are, respectively the concentrations at the electrode surface of the complex ions in the lower and higher oxidation states, and C_X is the concentration of X^{-b} .

On the basis of Ilkovič 's equation, the cathodic diffusion current is directly proportional to the concentration of the oxidized form in the body of the solution,

$$(i_d)_c = k_{Ox.} \cdot C_{Ox.}$$

where $k_{Ox.}$ is defined by equation (4). Similarly, the anodic diffusion current is directly proportional to the concentration of the reduced form in the body of the solution,

$$-(i_d)_a = k_{Red.} \cdot C_{Red.}$$

Since the changes in the concentration of the reduced and oxidized forms at the electrode surface are directly proportional to the current, then at each value of i , we have

$$C_{Red.}^o = C_{Red.} + \frac{i}{k_{Red.}} = \frac{-(i_d)_a + i}{k_{Red.}} \quad (9)$$

$$\text{and } C_{Ox.}^o = C_{Ox.} - \frac{i}{k_{Ox.}} = \frac{(i_d)_c - i}{k_{Ox.}} \quad (10)$$

In these equations, i is to be given its conventional sign of (+) for the cathodic part of a wave and (-) for the anodic part.

Substituting the foregoing relations into equation (6), we obtain the following general equation, which is applicable to either a cathodic, an anodic or a composite wave.

$$E_{d.e.} = E_{1/2} - \frac{0.0591}{a} \log \frac{i - (i_d)_a}{(i_d)_c - i} \quad (11)$$

and the half-wave potential is given by

$$E_{1/2} = E^o - \frac{0.0591}{a} \log \frac{k_{Ox.}}{k_{Red.}} - \left(\frac{p-q}{a} \right) 0.0591 \log C_X \quad (12)$$

Since it based on Nernst equation, the relationship of equation (11) is often used as the basis of the test for reversibility. Thus a plot of E vs $\log \frac{i - (i_d)_a}{(i_d)_c - i}$ should give a straight line of slope $\frac{0.0591}{a}$.

The relative values of p and q can be obtained from the shift of half-wave potential as the concentration of the complex-forming substance is varied. If p happens to be equal to q , then it is evident according to equation (12) that the half-wave potential should be constant and independent of the concentration of the complexing forming substance.

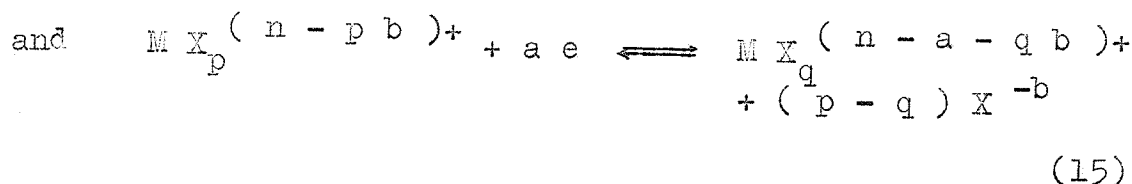
It should also be noted that the ratio of $k_{Ox.}$ to $k_{Red.}$, which is equal to $(D_{Ox.}/D_{Red.})^{1/2}$, can be derived from Ilkovic's equation and evaluated experimentally from the ratio of cathodic and anodic diffusion currents obtained with a solution containing equal concentrations of the oxidized and reduced forms.

$$\frac{(i_d)_c}{(i_d)_a} = \frac{k_{Ox.}}{k_{Red.}} = \frac{(D_{Ox.})^{1/2}}{(D_{Red.})^{1/2}} \quad (13)$$

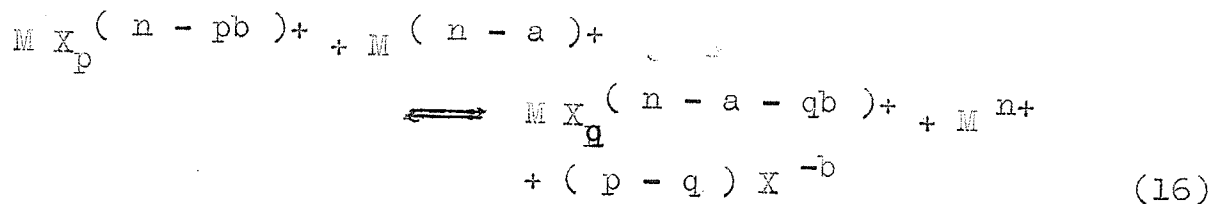
This ratio is sufficiently close to 1 in my case so that it can be neglected. When this is true, the half-wave potential observed when $C_x = 1M$ should practically coincide with the ordinary standard oxidation-reduction potential of the system.

Relation between the half-wave potential and the formation constants of the oxidized and reduced complex ions:

The difference between the half-wave potential in the partial reduction of simple or hydrated metal ions and in the reduction of a complex of the same metal can be derived by considering the two corresponding reactions:



Since the number of electrons involved is the same for both reactions, the difference between their standard potentials is equal to the standard E.M.F. of the reaction.



We have

$$E_{(16)}^{\circ} = E_C^{\circ} - E_S^{\circ} \quad (17)$$

where E_C° and E_S° are the standard potentials in the reduction of the complex and simple or hydrated metal ions. $E_{(16)}^{\circ}$ is equal to $\frac{RT}{aF} \ln K_{(16)}$ by definition of equilibrium constant K of reaction, where $K_{(16)}$ is the equilibrium constant of reaction (16). However, it follows from the definition of formation constant that

$$K_{(16)} = \frac{(M X_q^{(n-a-qb)+})(M^{n+})(X^{-b})^{(p-q)}}{(M X_p^{(n-pb)+})(M^{(n-a)+})}$$

$$K_{(16)} = \frac{K_{R.C.}}{K_{O.C.}} \quad (18)$$

Here, $K_{O.C.}$ and $K_{R.C.}$ are respectively, the formation constants of the complex ions in the higher and lower oxidation states.

It follows from (16), therefore that

$$E_C^{\circ} - E_S^{\circ} = \frac{RT}{aF} \ln K_{(16)} = \frac{RT}{aF} \ln \frac{K_{R.C.}}{K_{O.C.}} \quad (19)$$

From reasoning analogous to that in the preceding section, it can be shown that the half-wave potential in the reduction of a simple or hydrated metal ion to a lower oxidation state is related to the standard potential of the reaction E_S° by

$$\begin{aligned} (E_{1/2})_S &= E_S^{\circ} - \frac{0.0591}{a} \log \frac{(k_{Ox.})_S}{(k_{Red.})_S} \\ &= E_S^{\circ} - \frac{0.0591}{2a} \log \frac{(D_{Ox.})_S}{(D_{Red.})_S} \end{aligned} \quad (20)$$

where $(D_{Ox.})_S$ and $(D_{Red.})_S$ are the diffusion coefficients of the oxidized and reduced forms of the simple or hydrated metal ion, respectively. Concentrations have been assumed to be equal to activities. Since $(D_{Ox.})_S^{1/2} / (D_{Red.})_S^{1/2}$ is effectively unity, the last term in this equation has only minor significance, and $(E_{1/2})_S$ is practically equal to E_S° . For the same reason, we may neglect the second term in equation (12), and write as a good approximation,

$$(E_{1/2})_C = E_C^{\circ} - \left(\frac{p-q}{a}\right) 0.0591 \log C_X \quad (21)$$

From these relations, and equation (19), it follows that

$$(E_{1/2})_C - (E_{1/2})_S = E_C^0 - E_S^0 - \left(\frac{p-q}{a}\right) 0.0591 \text{ Log } C_X \quad (22)$$

or

$$(E_{1/2})_C - (E_{1/2})_S = \frac{0.0591}{a} \log \frac{K_{R.C.}}{K_{O.C.}} - \left(\frac{p-q}{a}\right) 0.0591 \text{ Log } C_X \quad (23)$$

The shift of the half-wave potential thus depends on the ratio of the dissociation constants of the oxidized and reduced complex ions, and also, of course, on the stoichiometry of the formula of the complex ion. If, as is usually the case, the oxidized complex ion is considerably more stable than the corresponding reduced form, then $K_{O.C.}$ is larger than $K_{R.C.}$, and $(E_{1/2})_C$ is more negative than $(E_{1/2})_S$, when $C_X = 1$ M. If in a particular case, $K_{O.C.}$ and $K_{R.C.}$ should happen to be equal, then $(E_{1/2})_C$ would be more positive than $(E_{1/2})_S$ when C_X was less than 1 molar; the two half-wave potentials would be equal when $C_X = 1$ M; and $(E_{1/2})_C$ would become more negative than $(E_{1/2})_S$ only when C_X was greater than 1 M. In general, when

$$(C_X)^{p-q} = \frac{K_{R.C.}}{K_{O.C.}}$$

then

$$(E_{1/2})_C - (E_{1/2})_S = 0$$

Equation (22) can be used to determine the ratio of formation constants of the complex ions in the higher and lower oxidation state. If one of the oxidized or reduced form of complex formation constant is known, then the other form of formation constant can be evaluated.

A series of solutions of constant concentration
of Vanadium (II)

were made up with various concentrations of the complex forming reagent. The ionic strength of the solution was maintained constant by adding sodium perchlorate. The reversibility of the electrode reaction was tested by plot of $\log \left(\frac{i - (i_d)_a}{(i_d)_c - i} \right)$ vs $E_{d.e.}$. From the slope of the line the reversibility and numbers of electrons transferred will be shown, and the value of $E_{1/2}$ was obtained from this graph.

The concentration of free complex forming reagent was calculated by subtracting the concentration of bound ligand from the total concentration present. A plot of $E_{1/2}$ vs $\log C_X$ gave the value of $p - q$. The ratio of the formation constants were thus determined by means of Eq. (22)

EXPERIMENTAL.

A. Materials:

Vanadium (II) sulfate was prepared, according to J. Grinnell and J. H. Colvin (* 14), 150 grams of British Drug Houses reagent grade of vanadium pentoxide was suspended in 50 ml. of concentrated sulfuric acid, diluted with about 600 ml. of water and sulfur dioxide passed through the solution until the vanadium pentoxide was completely reduced to vanadyl sulfate, as indicated by the clear blue solution. A stream of air was then passed through the solution to remove the excess sulfur dioxide from the solution, which then was filtered through a sintered glass filter.

The vanadyl sulfate was reduced at a mercury cathode in a reducing cell (Fig. 2) with the platinum anode and 2 amperes of current were crossing it. After about 20 hours, a greenish-yellow precipitate was found, presumably trivalent vanadium, which was dissolved by adding more sulfuric acid. Continuation of electrolysis for about four days resulted in a concentrated, violet colored solution. The solution was inducted into a flask containing 95% ethyl alcohol, care being taken to insure that the vanadium (II) solution was in the bottom of the flask, under the alcohol and not mixed with the alcohol, The flask was filled almost completely and then stoppered to protect from air. After a few days the crystallization of violet vanadium (II) sulfate was completed.

The formula of the violet crystal was shown to be $VSO_4 \cdot 7H_2O$. In order to verify that quantitative reduction to the divalent state had taken place, the vanadium and

sulfate ions were determined separately. A convenient amount of vanadium (II) sulfate crystal was dried in a vacuum desiccator over night, and dissolved in dilute hydrochloric acid. The sulfate ion content was determined by precipitation as barium sulfate and vanadium was precipitated by ammonium benzoate, according to the procedure which is recommended by Shemyakin (*15,16) and weighed as V_2O_5 . Water content was figured by difference. The analytical results are shown as Table (I)

Table I : Formula Analysis of Vanadium Sulfate.

No. / Compositions	Vanadium %	Sulfate(SO_4^-) %	H_2O %
1	18.64	35.10	46.26
2	18.61	35.14	46.25
3	18.65	35.20	46.23
4	18.68	35.12	46.20
5	18.63	35.15	46.22
Mean Value	18.64 \pm 0.02	35.14 \pm 0.03	46.23 \pm 0.02
$VSO_4 \cdot 7H_2O$ (theoretical)	18.65	35.17	46.17
group ratio	1	1	7

Sodium perchlorate, ammonium thiocyanate, sodium chloride, sodium bromide and sodium iodide were recrystallized twice from distilled water.

Baker analyzed grade perchloric acid and Merck & Co. reagent grade of sodium fluoride were used without any further purification.

Barium perchlorate was prepared from Desicchlora by recrystallizing twice from distilled water.

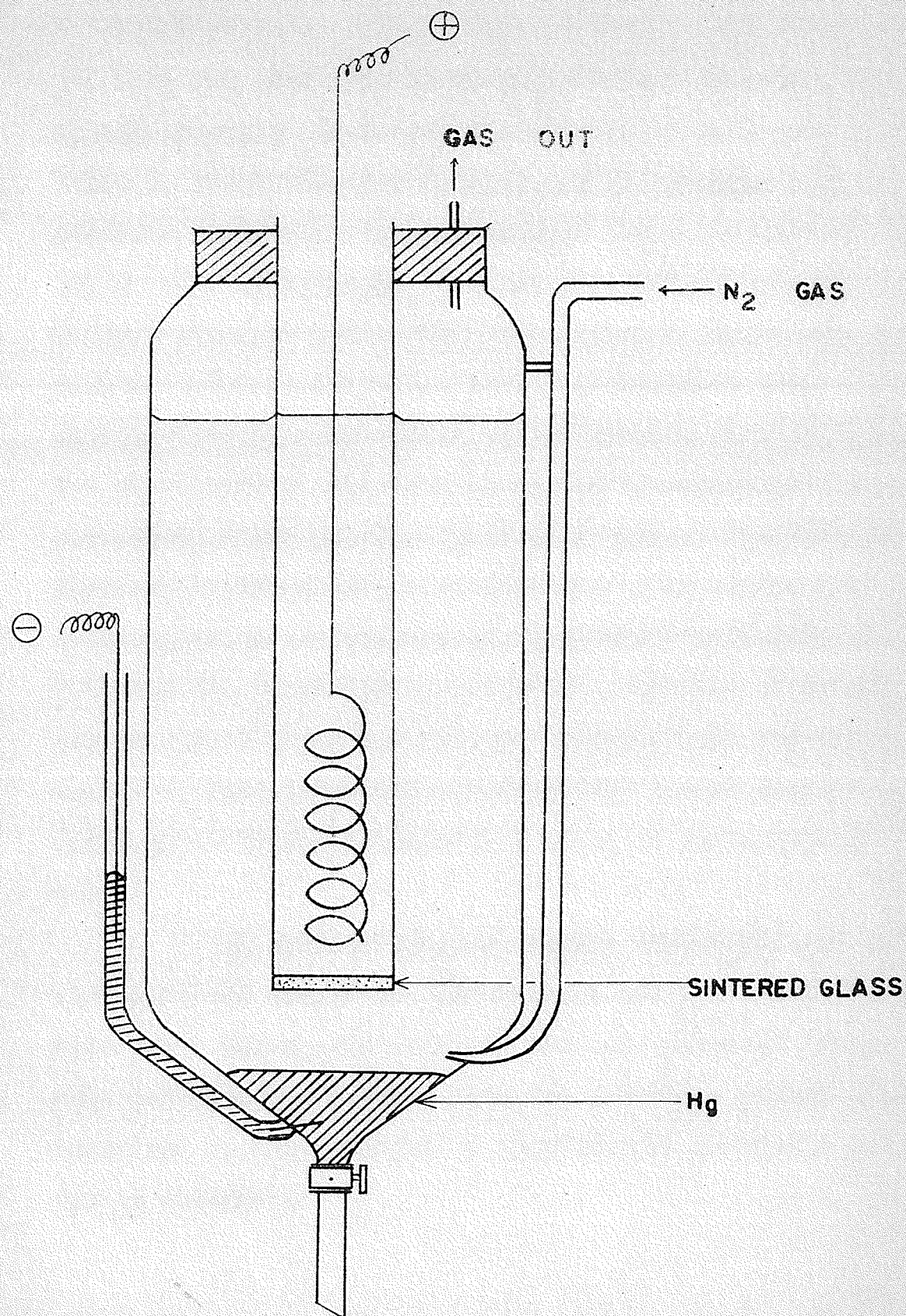
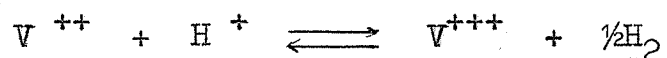


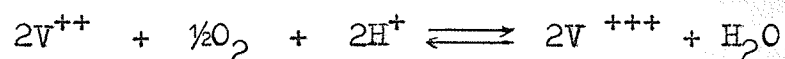
FIG. 2 ELECTROLYTIC REDUCTION CELL.

B. Solutions :

Vanadium (II) solution : Vanadium (II) is a powerful reducing agent; it is thermodynamically capable of reducing hydrogen ion in acid solution,



and is sensitive to air oxidation



Therefore, a great care had to be taken during the preparation of vanadium (II) solution. All solutions were saturated with hydrogen gas before using. Transferring of crystals and of solutions were done in an inert atmosphere (purified nitrogen gas was used) to protect from air. The solutions were prepared by dissolving a desired amount of vanadium (II) sulfate crystal into 0.1 N perchloric acid. The solution in the reservoir was preserved by continuous bubbling of hydrogen gas through it, and was prepared freshly each day in the course of investigation. Vanadium (II) concentrations were established by titration with a standard permanganate solution.

All complex forming reagent solutions were made up in volumetric flasks by dissolving a weighed amount of salt into 0.1 N perchloric acid and the concentration factor of each solution was checked with the titration method which is described in the Textbook of Quantitative Inorganic Analysis by Kolthoff.

C. Apparatus :

As shown in Fig. 3, A titration type of polarographic cell was used in this investigation. It was developed to facilitate the preparation of vanadium (II) electrolytic solutions and to carry out the polarographic oxidation in an atmosphere of inert gas. The 500 ml. cell employs a separate permanent anode: a layer of mercury on the bottom of the flask serves as the permanent anode, and a saturated calomel electrode is used as the external anode. The outer vessel, which is separated by a sintered glass and agar plug, contains a saturated solution of potassium chloride that is also saturated with calomel. A gas inlet tube is placed just on the surface of the mercury pool, passing hydrogen gas to stir and protect the solution. Two necks on the top of the cell are used to insert the mercury dropping electrode and buret. Addition of any reagent solutions are through the buret and are also protected from air.

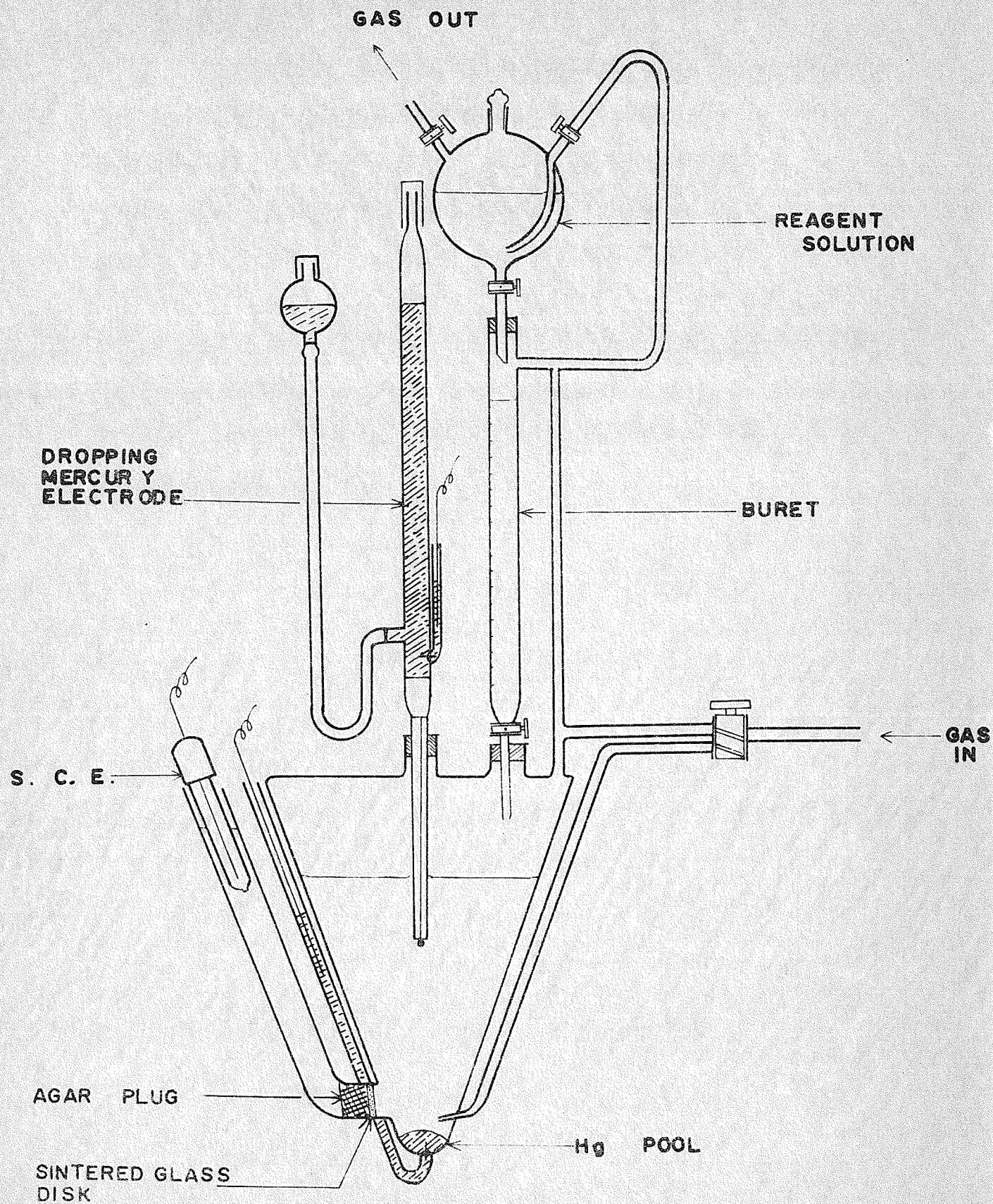


FIG. 3 TITRATION TYPE OF POLAROGRAPHIC CELL.

D. Instrument :

As shown in Fig. 4, the Sargent-Heyrovsky Model XII polarograph, Manufactured by E. H. Sargent and CO., Chicago, was used to supply the applied voltage to the cell. The polarogram was recorded by Masely X - Y recorder in which the current was measured in terms of the iR drop across the 10,000 ohms precision fixed resistance, and a variable condenser, 0 to 800 MMFD, was used to reduce the damping effect. The recorder scales of current-voltage were calibrated with the Emil Greiner CO., Model E-3043 Potentiometer.

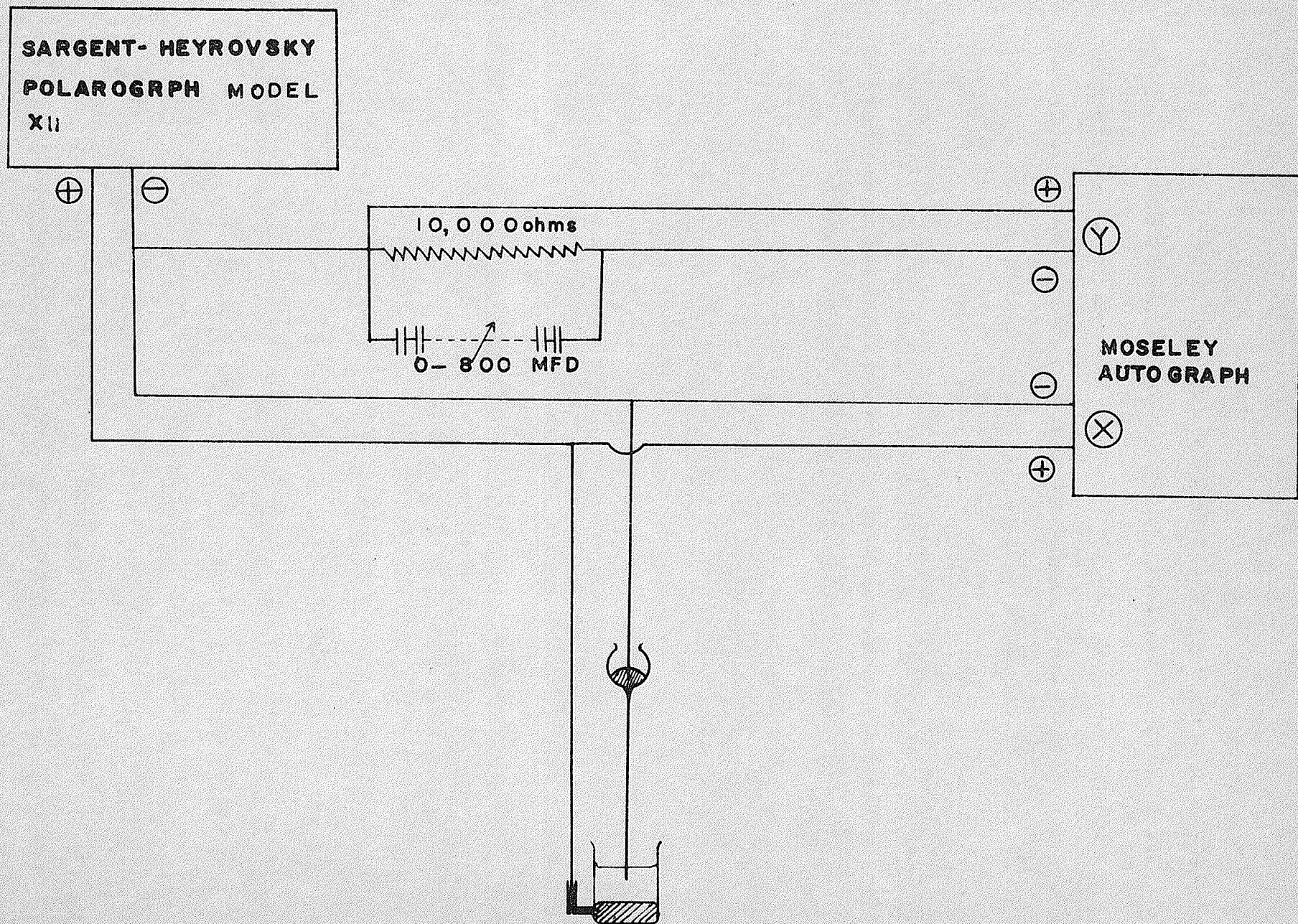


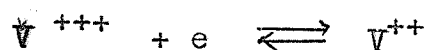
FIG. 4 SCHEMATIC DIAGRAM OF PEN-RECORDING POLAROGRAPH.

E. Procedure :

The electrolytic solution was prepared by addition of the desired amount of freshly prepared vanadium solution through the buret into a 0.1 N perchloric acid in the polarographic cell. In case of complex forming studies, a desired volume of 0.5 F complex forming reagent solution was added. The ionic strength was maintained constant at 0.2 by addition of 1 F sodium perchlorate solution. The total volume was adjusted to 400 ml, in a 0.1 N perchloric acid. A stream of hydrogen gas was passed through the solution, which was allowed to stand for one hour. The program was then recorded. All measurements were carried out in the thermostat at $25^{\circ} \pm 0.1^{\circ}$ C.

Data and Discussion :

Typical polarograms of various concentration of vanadium (II) ion in 0.1 N perchloric acid and 0.1 F Sodium perchlorate are shown in Fig. 5. These polarograms consists of three anodic waves in which only one of the waves is well-defined. Lingane^(*4) found both the reduction of vanadium (III) ion to the vanadium (II) state, and the oxidation of vanadium (II) ion to vanadium (III) ion proceeded practically reversibly at the dropping electrode in an acid medium. In 1 N sulfuric, hydrochloric or perchloric acid, both waves are very well-developed with an average half wave potential of -0.52 volt vs the S.C.E. This value is somewhat different from our result. This is not surprising owing to the different conditions, such as acidity and ionic strength of the electrolytic solution. Comparison was made by referring to the standard potential of the reaction :



Jones and Colvin^(*14) determined the reaction potential through a series of different sulfuric acid concentrations by the ordinary potentiometric method with a large stationary mercury electrode. They found that the oxidation-reduction is a function of acid concentration, and in 0.0500 molar sulfuric acid.

$E = 0.2025 + 0.0820 (C_3 + C_2)$ volt vs normal Hydrogen Electrode (N.H.E.) where C_3 and C_2 are the concentration of vanadium (III) and vanadium (II) respectively. If we take the total vanadium concentration $C_3 + C_2 = 0.005$ M, then the oxidation-reduction potential in 0.05 M and 0.10 N

acid solution is 0.2029 volt vs N.H.E. Since the potential of N.H.E. is -0.246 volt vs S.C.E., the theoretical value of the half wave potential $E_{1/2}$ is $-0.246 - 0.203 = -0.449$ vs S.C.E. This is the identical value that we get in the vanadium concentration range of 4 to 6 mM.

As shown in Fig. 6, the half-wave potential of the well-defined wave shifts more positive with an increase in the vanadium (II) ion concentration. This will be due to the different hydrated ion species of vanadium (II) at different concentrations in such a dilute acid solution.

Some of the data used in obtaining these graphs are reproduced in Table II. It is evident from this table that the anodic diffusion current is accurately proportional to the concentration of vanadium (II) ion after proper correction is applied for the residual current. The diffusion current coefficient is $2.02 \pm 0.03 \mu\text{A} / \text{millimole per liter } m^{2/3} t^{1/6}$.

For analysis of the electron changes of the reaction, $\log \frac{i}{i_d - i}$ was plotted vs $-E_{d.e.}$ at varying concentration of vanadium (II) ion. Each plot gives a good straight line. The slopes of the concentration range, 2.5 to 6 mM as shown in Table II, are very close to the theoretical value of 118.4 millivolts from Hydrovsky and Ilkovic^(*12) equation at 25.0 degree C. for a reversible, average half-electron reaction. Outside this range, that of lower or higher concentration of vanadium (II) in this electrolytic solution indicates an irreversible reaction.

The average half-electron transfer reaction indicates the ion species of vanadium (II) in this solution will be with the form of $(VO - O)^{++}$ and during the electrode oxidation,

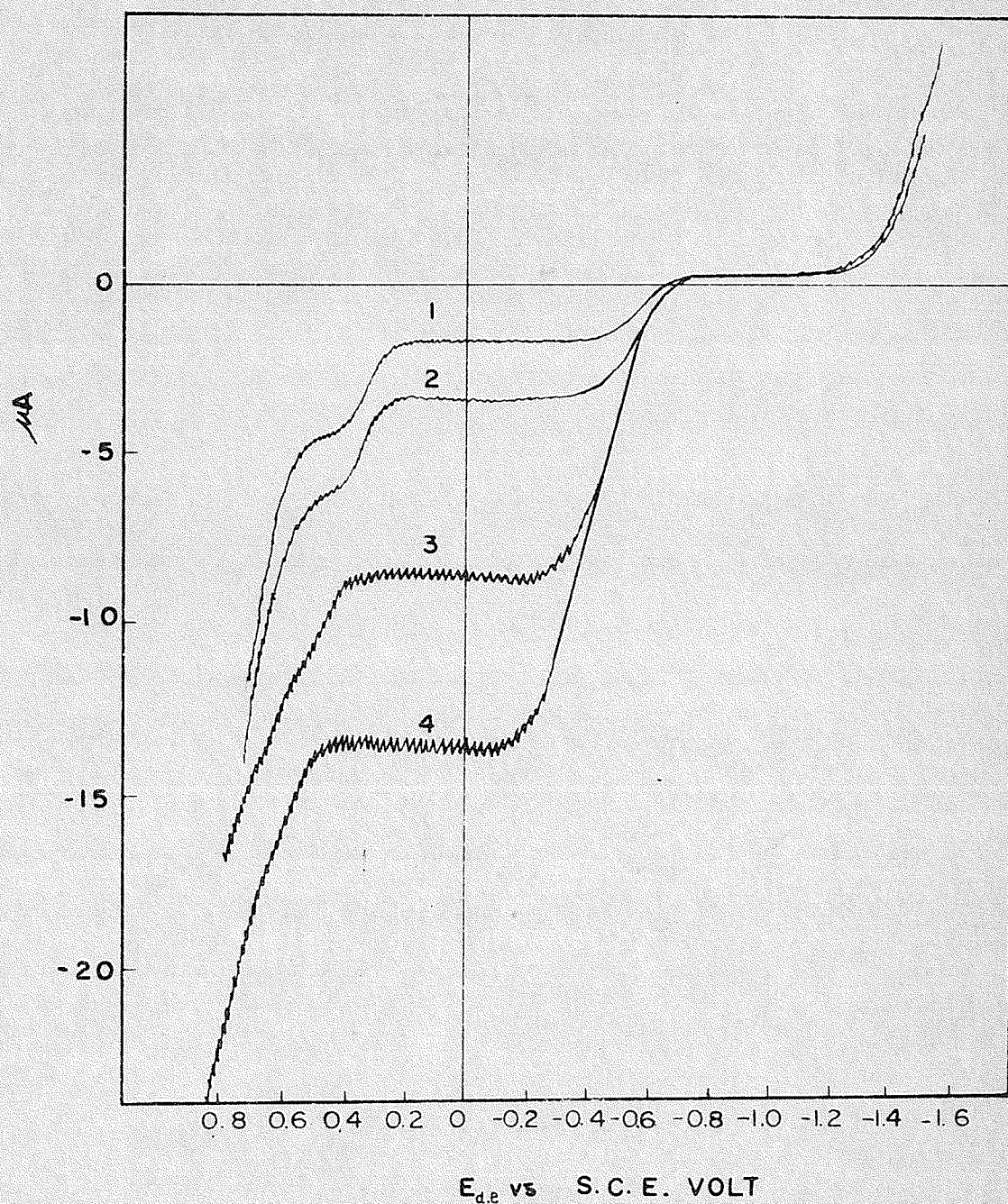


FIG 5 TYPICAL POLAROGRAMS OF VANADIUM II
AT VARIOUS CONCENTRATION.

in 0.1 N perchloric acid and 0.1 F NaClO_4 .
Concentration of V (II) : (1) 0.82
(2) 1.62 (3.) 3.94 (4) 6.36 mM

only one of the vanadium (II) atom oxidizes to V^{+++} , and with the oxidized form of $(VO - V)^{+++}$, the reaction mechanism may be expressed as follows:



The overall reaction is one electron transfer, but it corresponds to a half-electron transfer of each vanadium atom.

Table II. Half-wave Potentials And Diffusion Currents Of Vanadium (II) Sulfate In Various Concentrations.

Vanadium(II) $\times 10^4 M.$	$-E_{1/2}$ vs S.C.E. volt	i_d μA	$i_d / C m^{2/3} t^{1/6}$	$\frac{-E_{d.e.}}{\log(\frac{i}{i_d - i})}$ m.v.
8.19	0.550	1.68	1.96	84.92
16.22	0.539	3.36	1.97	87.75
26.68	0.495	5.73	2.05	129.98
39.38	0.472	8.55	2.07	126.51
44.35	0.449	9.48	2.04	128.25
49.26	0.449	10.46	2.03	130.31
54.10	0.449	11.55	2.03	129.98
58.89	0.449	12.64	2.05	131.71
63.62	0.437	13.43	2.01	134.31
75.18	0.415	15.99	2.03	138.65

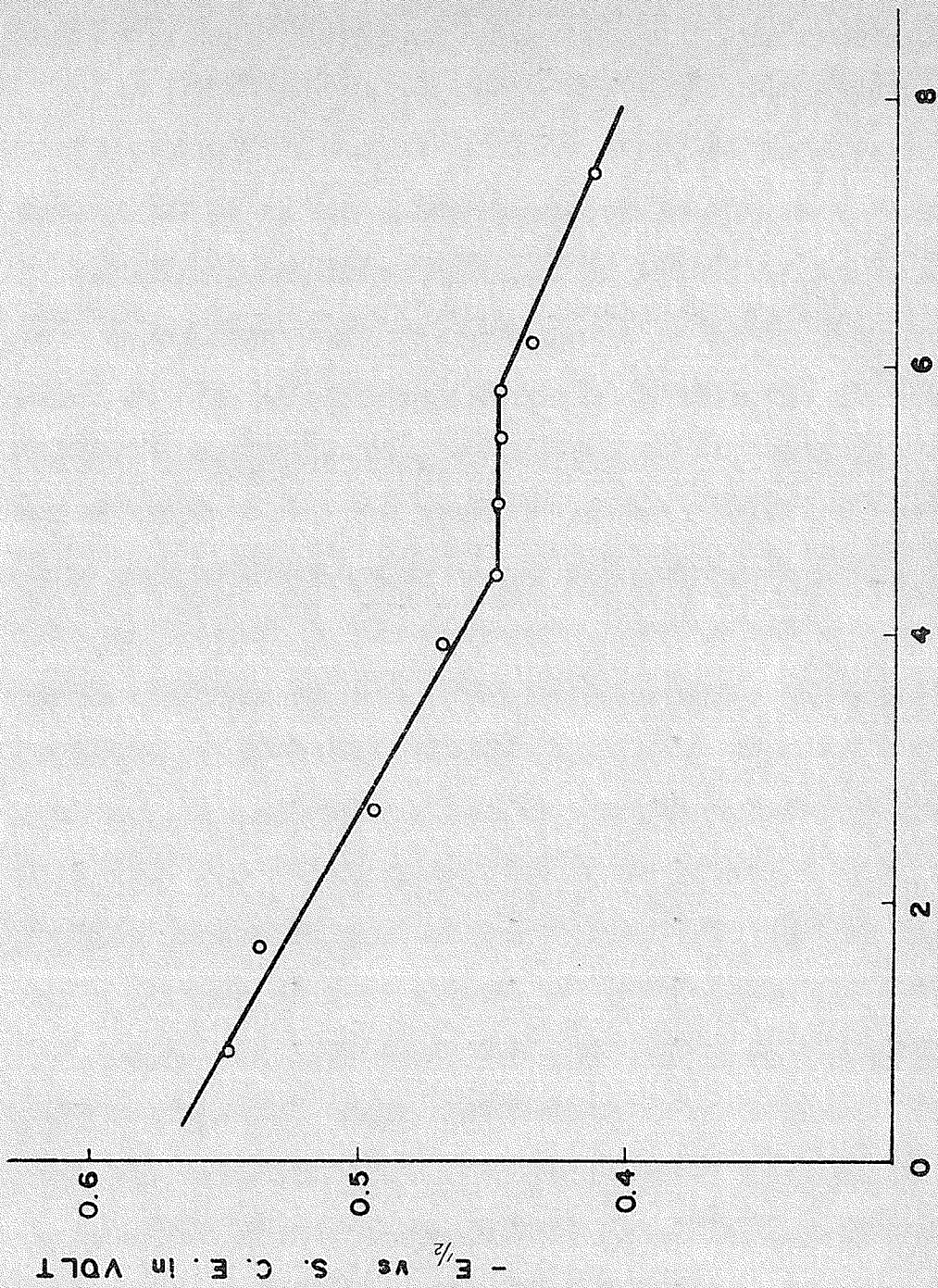


FIG. 6 RELATION OF HALF WAVE POTENTIAL AND VANADIUM (II) CONCENTRATION.

Potassium permanganate titration:

To confirm our view about the electrode reaction, a titration of vanadium (II) by standard potassium permanganate solution was polarographically studied. Some typical titration polarograms obtained by titration of 320ml of 7.5×10^{-3} M vanadium (II) sulfate in 0.1 N perchloric acid and 0.1 F sodium perchlorate with 0.1 N standard potassium permanganate solution are shown in Fig. 7. Curve 1 was taken before titration, the small cathodic diffusion current (above zero current) shows that some vanadium (III) was present initially in the solution. Curve 2 and 3 were obtained after addition of potassium permanganate solution. The increasing of cathodic diffusion current accompanied by decreasing the anodic diffusion current indicates the vanadium (II) was oxidized gradually to vanadium (III) by potassium permanganate at the first step. In the analysis of the diffusion current waves, we found that both cathodic and anodic currents have the same value of diffusion current coefficient. This fact makes it possible to determine the vanadium (II) by polarographic titration: Suppose we recorded the polarogram of v ml of an unknown vanadium (consists of V(II) and V(III)) solution, and got the anodic diffusion current $(i_a)_1$, cathodic current $(i_c)_1$. Then A ml of fN standard potassium permanganate was added. The polarogram again was recorded to get the anodic current $(i_a)_2$ and cathodic current $(i_c)_2$. From these data, we can determine the vanadium ions (II and III) concentrations in the original solution:

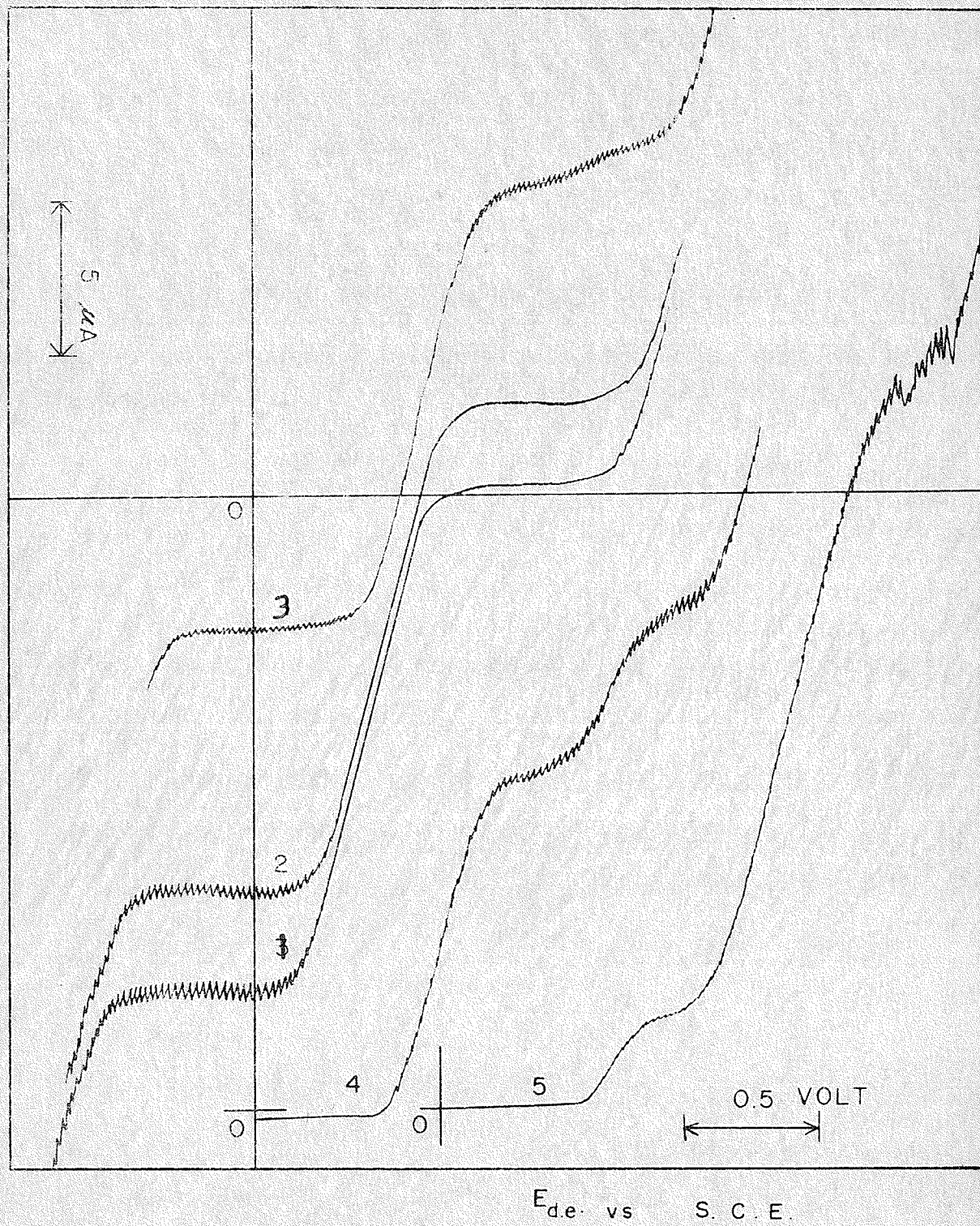
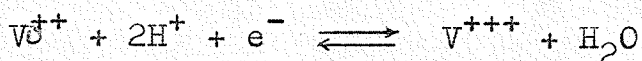


FIG. 7 $KMnO_4$ TITRATION POLAROGRAMS

$$[V(II)] = \frac{(i_a)_1}{(i_a)_1 - (i_a)_2} \cdot \frac{Af}{V + A}$$

$$[V(III)] = \frac{(i_c)_1}{(i_c)_2 - (i_c)_1} \cdot \frac{Af}{V + A}$$

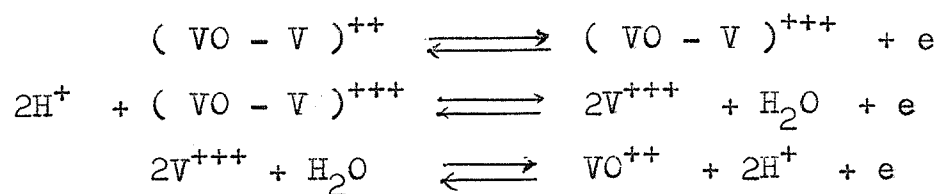
When enough potassium permanganate solution was added to reduce the anodic diffusion current to half its original value, a second cathodic wave of half-wave potential -1.2 volts vs S.C.E. appeared. The diffusion current was analyzed and it was found to be about twice that of the first wave. The wave corresponds to the reduction of VO^{++} to V^{+++} at the cathode, and the reaction was recently shown by Johns and Colvin (*14) to be :



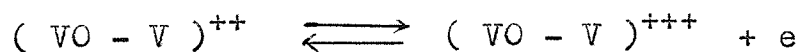
which is reversible at a platinum electrode. The titration results are shown in Table III. It is noticeable for the 0 - 7 milli normal $KMnO_4$ addition range, the addition of titration will cause a decrease in the first anodic current $(i_d)_a^1$, and increase the second cathodic diffusion current $(i_d)_c^2$. It strongly suggests that the vanadium (II) in this electrolytic solution will be in the form $(VO - V)^{++}$, in which one vanadium (II) atom becomes less labile after oxidation of the second to V(III). Therefore, in the potassium permanganate titration, the first step is oxidizing the labile vanadium atom and subsequently the oxidation of V^{+++} to VO^{++} and VO to V^{+++} will take place simultaneously.

Summarizing the reaction, the equations are re-

presented as follows:



and the dropping mercury electrode reaction of vanadium (II) and (III) couple corresponds to



This is agreeable to our conclusion in the previous section regarding the number of electrons transferred in the electrode reaction.

Table III: Half-Wave Potentials And Diffusion Currents Of Vanadium In The Potassium Permanganate Titration.

$[V(II)]$ $\times 10^4$ M.	$[KMnO_4]$ $\times 10^3$ M.	$(E_{1/2})_1$ volt	$(id)_a^1$ μA	$(id)_c^1$ μA	$(E_{1/2})_2$ volt	$(id)_c^2$ μA	$\frac{(id)_a^1 + (id)_c^2}{2}$ $(V) \mu A/mole$
75.18	0	0.415	15.99	0.20	—	—	21.28
74.05	1.405	0.472	12.65	2.96	—	—	21.08
72.97	2.769	0.485	9.49	6.10	—	—	21.10
70.80	5.379	0.623	3.75	9.53	1.235	0.79	21.00
69.89	6.629	0.674	11.54	11.01	1.275	1.98	19.37
68.90	7.844	0.651	10.20	10.32	1.291	4.58	18.59
67.96	9.026	0.629	—	7.91	1.296	9.09	18.33
67.05	10.176	0.617	—	5.18	1.291	13.54	17.82
66.15	11.296	0.607	—	2.77	1.279	19.01	18.47
65.28	12.387	—	—	0.40	1.279	24.01	19.00
64.93	12.814	—	—	—	1.178	24.70	19.02

COMPLEX FORMATION STUDIES

A preliminary test to examine the formation of sulfate complex was carried out. In order to replace the sulfate ion with perchlorate, barium perchlorate was added to precipitate the sulfate ion in vanadium (II) sulfate solution. Barium sulfate precipitate was then separated by filtering through a fine glass filter under inert gas atmosphere.

Polarograms of 5 mM vanadium (II) perchlorate in 0.1 N perchloric acid and 0.1 F sodium perchlorate, and of the same concentration of vanadium (II) ion in 0.1 N perchloric acid but of varying concentrations of sulfate ion (ionic strength was kept constant with sodium perchlorate) were recorded.

The resulting half-wave potentials were found to be constant at -0.449 volts vs S.C.E. and independent of the sulfate ion concentration up to 0.5 M. For this reason, any sulfate complex formed must be very weak and would not interfere with further investigation of thiocyanate and halide complexes with sulfate ions present in the electrolyte solution.

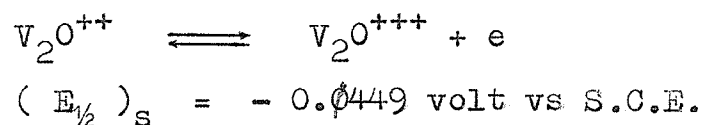
Application of the relations previously derived for the study of vanadium (II) complexes were carried out with thiocyanate, fluoride, chloride, bromide and iodide as complexing agents.

1) Fluoride complex: Table (IV) demonstrates that $E_{1/2}$ is constant at -0.530 ± 0.001 volts (S.C.E.) when the concentration of excess fluoride (based on the vanadium mono-complex species) is greater than 0.045 M. With smaller concentrations of fluoride, it is shifted to a more positive value as C_{F^-} decreases. This effect is shown more clearly by the plot of these data in figure 8. Three

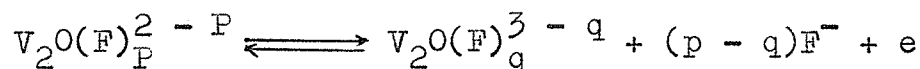
different slopes of 0.035, 0.0775 and 0 are obtained from the corresponding three dotted lines a, b and c. The 0 slope is agreeable to the theoretical slope predicted by equation (22) for $p = q$. The values $p - q$ corresponding to slopes 0.035 and 0.0775 are 0.59 and 1.31 respectively. These are not integral numbers owing to the mixture of different coordination numbers of complex ions present in the solution, and only the average of these values is significant.

The data from table (IV) combined with the data from table (II) can be used to evaluate the ratio of formation constant of vanadium (II) and (III) complexes.

For the reaction



and for complex ion reaction:



the $(E_{1/2})_c = -0.530$ volt vs S.C.E. and $p = q$ when fluoride concentration is higher than 0.045 M. Hence from equation

(22), we have

$$0.059 \log \left(\frac{K_{\text{V}_2\text{O}(\text{F})_P^{2-P}}}{K_{\text{V}_2\text{O}(\text{F})_P^{3-P}}} \right) = -0.530 - (-0.449) = -0.081 \text{ volt.}$$

and therefore

$$\frac{K_{\text{V}_2\text{O}(\text{F})_P^{3-P}}}{K_{\text{V}_2\text{O}(\text{F})_P^{2-P}}} = 13.70$$

where

$$K_{\text{V}_2\text{O}(\text{F})_P^{3-P}} = \frac{[\text{V}_2\text{O}(\text{F})_P^{3-P}]}{[\text{V}_2\text{O}^{+++}][\text{F}^-]^P}$$

and

$$K_{\text{V}_2\text{O}(\text{F})_P^{2-P}} = \frac{[\text{V}_2\text{O}(\text{F})_P^{2-P}]}{[\text{V}_2\text{O}^{++}][\text{F}^-]^P}$$

Table IV. Half-Wave Potential Of Vanadium (II) Fluoride Complex Ion As A Function Of The Fluoride Concentration. Concentration Of Vanadium (II) Sulfate Was 0.005 To 0.0045 M.

Na F in excess $\times 10^2$ M	Log C_{F^-}	$-E_{1/2}$ vs. S.C.E. volts
3.3	-2.48	0.476
6.6	-2.18	0.489
9.8	-2.01	0.492
13.0	-1.89	0.497
16.1	-1.79	0.501
23.7	-1.63	0.514
31.3	-1.50	0.518
45.5	-1.44	0.529
59.0	-1.23	0.530
71.8	-1.14	0.529
89.6	-1.05	0.532
100.4	-0.99	0.528

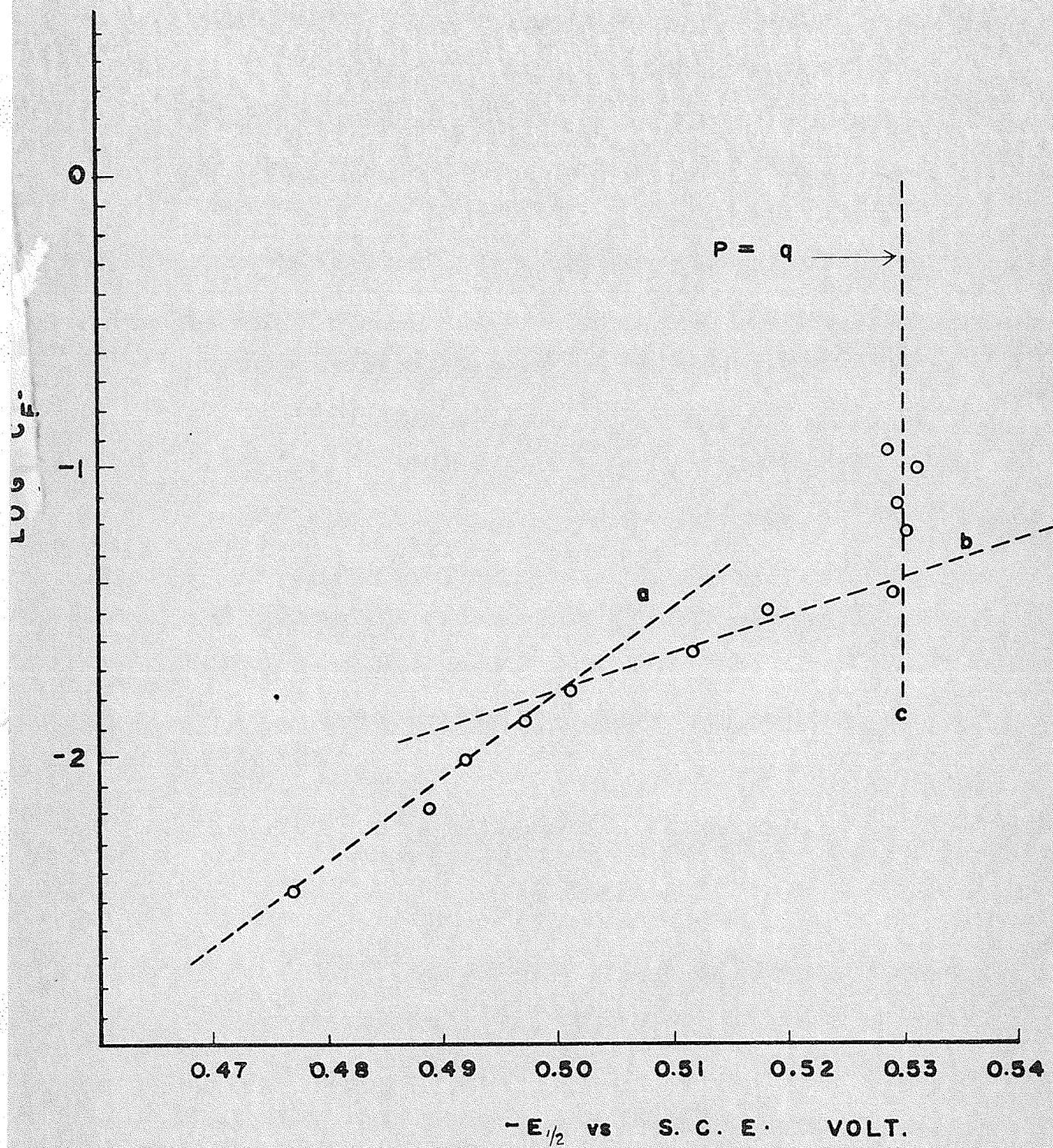


FIG. 8 HALF WAVE POTENTIAL OF VANADIUM (II) FLUORIDE COMPLEX ION AS FUNCTION OF THE EXCESS FLUORIDE CONCENTRATION

ii) Thiocyanate complex: Data are shown in table (V) and also a plot of the half-wave potential vs logarithm concentration of free thiocyanate ion as Fig. 9. Values of $p - q$; 0.525, 2 and 0 were obtained from the corresponding slopes of 0.031, 0.018 and 0 of the dotted line a, b and c. When the concentration of excess thiocyanate is smaller than 0.03 M, the value of 0.525 indicates that a mixture of complex ions different coordination numbers was present in the solution. The value 2, obtained when the free thiocyanate ion concentration ranged from 0.03 to 0.043 M, is in agreement with the theoretical slope predicted by equation (22) for $p - q = 2$. This means that the coordination number of vanadium (II) complex is larger than vanadium (III) complex by 2 in this concentration range. Above 0.045 M, $p - q = 0$ indicates that the same coordination number in both oxidized and reduced form.

Treating the same procedure as previous section, we got :

$$\frac{K_{V_2O(CNS)}^2 - p}{K_{V_2O(CNS)}^3 - q} = 23.45 \text{ for } p = q$$

iii) The results on the chloride, bromide and iodide showed that the half-wave potentials were independent of those ions present and always kept at -0.449 volts vs S.C.E. This fact indicates the complex formation of vanadium (II) with those anions are very weak.

Table V. Half-Wave Potential Of Vanadium (II) Thiocyanate Complex Ion As A Function Of The Thiocyanate Conc. Concentration Of Vanadium (II) Sulfate Was 0.005 To 0.0045 M.

NH_4CNS in excess $\times 10^3 \text{M}$	$\text{Log } C_{\text{CNS}^-}$	$-E_{1/2}$ vs. S.C.E. volts.
3.15	-2.50	0.467
7.81	-2.11	0.478
15.39	-1.81	0.489
22.74	-1.64	0.494
29.88	-1.53	0.498
36.80	-1.43	0.503
43.54	-1.36	0.514
56.43	-1.25	0.516
68.64	-1.16	0.516
91.11	-1.04	0.517
120.93	-0.92	0.515

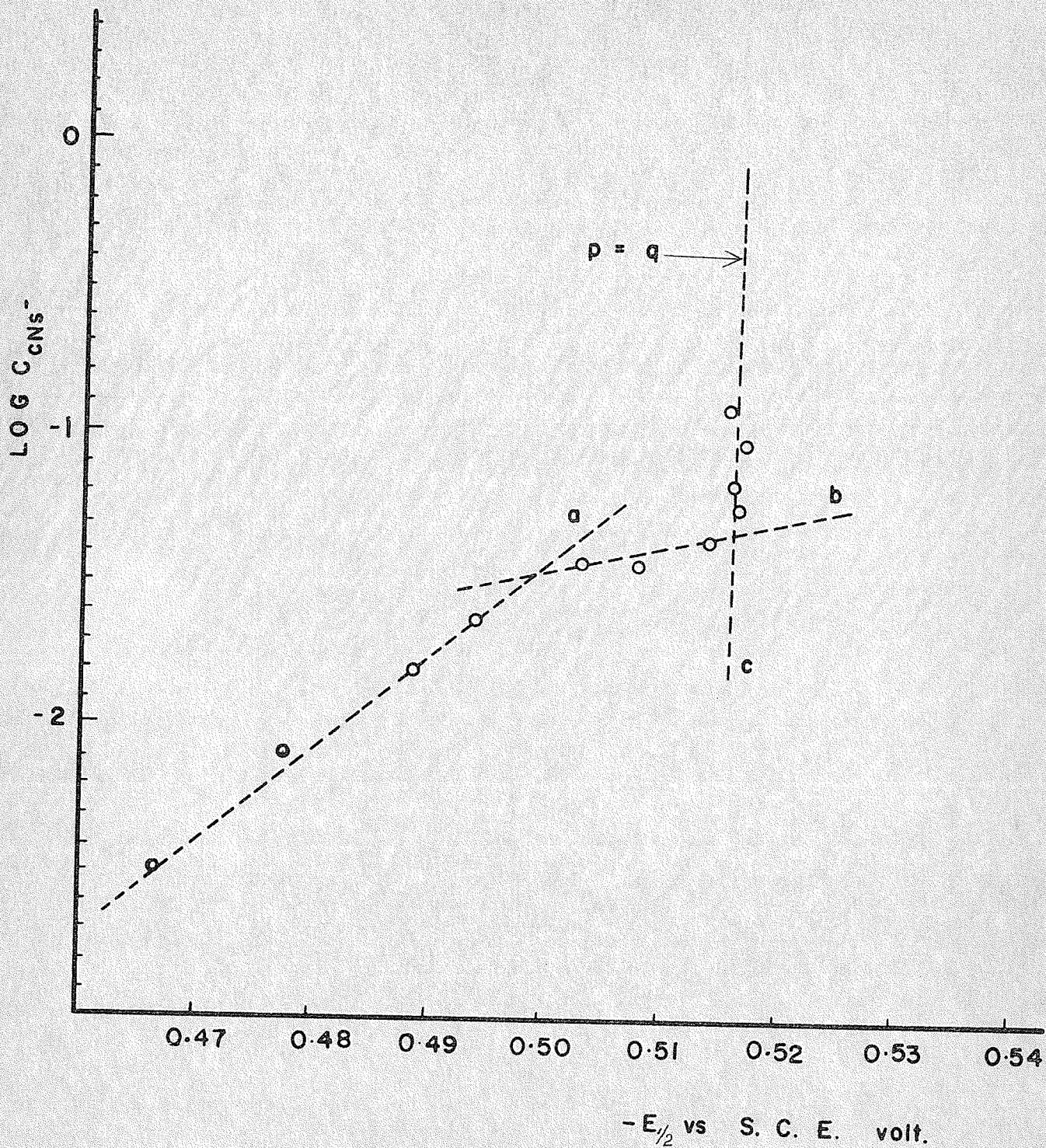
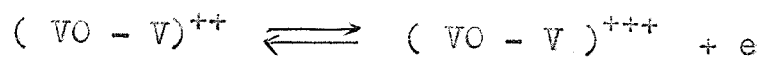


FIG. 9 HALF WAVE POTENTIAL OF VANADIUM(II) THIOCYANATE COMPLEX ION AS A FUNCTION OF THE EXCESS THIOCYANATE CONCENTRATION.

CONCLUSION

The anodic diffusion currents are proportional to the concentration of vanadium (II) ions with the diffusion current coefficient $2.02 \pm 0.03 \mu\text{A}/\text{millimole per liter m}^{2/3} \text{ t}^{1/6}$.

In 0.1 M perchloric acid solution, the dropping mercury electrode reaction of vanadium (II) and (III) couple is shown to be



This is confirmed by potassium permanganate titration.

Due to its high reducing power and instability in complex formation, it is hard for us to determine directly the vanadium (II) complex formation constants. The ratio of formation constants of vanadium (II) and (III), 13.70 and 23.45 corresponding to fluoride and thiocyanate complexes, obtained in our investigations will enable us to evaluate the vanadium (II) complex formation constants as the corresponding vanadium (III) complexes formation constants become available.

The complexes formed by vanadium (II) with chloride, bromide and iodide are indicated to be very weak by analysis of the half-wave potentials.

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