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ELECTROMETRIC TITRATION
OF
OXIDIZING AND REDUCING SUBSTANCES
Thesis for Degree of M. S.
Charles Henry Spurway
1926

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ELECTROMETRIC TITRATION
OF
OXIDIZING AND REDUCING SUBSTANCES

A Thesis Submitted to the Faculty of the
Michigan State College of Agriculture and
Applied Science in Partial Fulfillment of
the Requirements for the Degree of Master
of Science

By
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1926

CHEMISTRY DEPT.

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Associate Professor of Chemistry
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TABLE OF CONTENTS

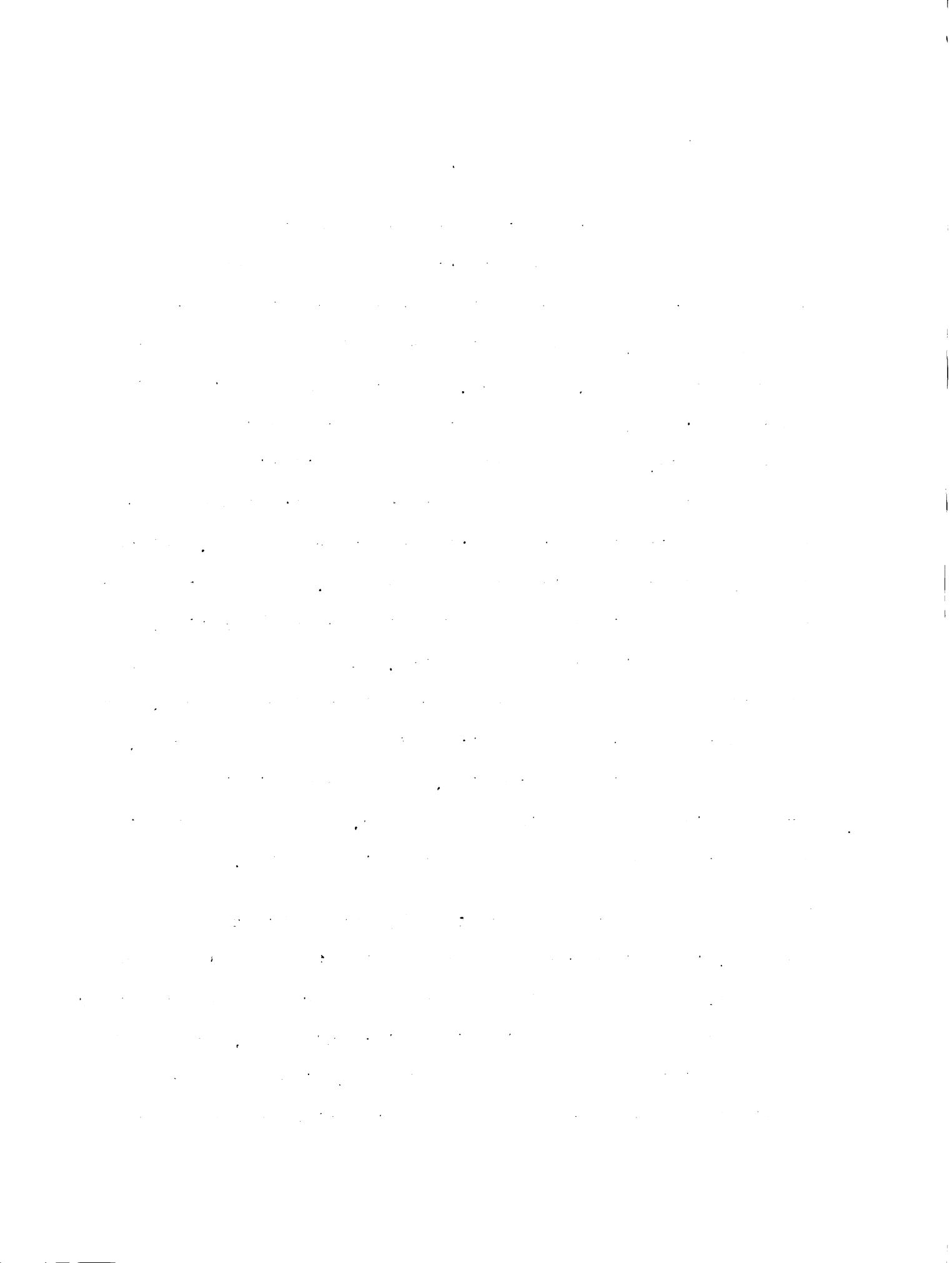
- I. Introduction
- II. General Theory
- III. Methods and Apparatus
- IV. Special Points Taken from the Literature of
the Subject Concerning the Electrometric
Titration of Several Chemical Substances
- V. Electrometric Titration Curves
- VI. Curve Data and Discussion
- VII. Bibliography

I

Introduction

Electrometric titration methods of chemical analysis, particularly for the determination of small quantities of several of the elements combined in some oxidizable or reduceable form, are coming into general use in laboratories devoted to teaching, research, and the process control of many industries. In addition to the work already done on these methods, there are still many possibilities and some opportunities for applying them to the qualitative and also to the quantitative determination of other elements, and to the control of other industrial processes. These methods are valuable to chemists because of their ease of operation, accuracy, and time saving qualities. Not only are electrometric titration methods serviceable for analytical procedures, but because they deal with quantity and movement of electrons, or charges of negative electricity, they are applicable to problems involving chemical hypotheses, and theories relating to the state or properties of matter in solution.

As is the case with practically any division of a general science, the literature dealing with the theory and the problems of electrometric titration is scattered through a large number of scientific and industrial journals; and hence, is buried from the sight of the average student and investigator in chemical science largely because of the time and labor found



necessary to assemble, arrange, and mentally digest the contents of the many papers extant on the subject. Collecting and cataloging the knowledge on any subject, interesting in itself, and also applicable to the study of various scientific problems is considered advisable, because by this means such knowledge is placed within easy reach of students and other interested persons; and in addition, complete bibliographies of the subject may be maintained.

This thesis has for its object, then, four main divisions of effort: (1) An exposition of the general theoretical and practical principles upon which electrometric titration methods are based, more particularly with respect to oxidation and reduction effects; (2) A description of the several analytical methods now in use; (3) A search for possible new correlations that might be exposed by a study of the titration curves found in the literature; and, (4) A complete, up-to-date bibliography of the subject.

1. The first part of the document discusses the importance of maintaining accurate records of all transactions. It emphasizes that proper record-keeping is essential for the integrity and transparency of the financial system. This includes not only recording the amount and date of transactions but also identifying the parties involved and the nature of the exchange.

2. The second part of the document outlines the various methods used to collect and process data. It details the steps from data entry to final reporting, highlighting the need for consistency and accuracy throughout the process. The document also addresses the challenges of data collection, such as incomplete information and the potential for human error, and offers strategies to minimize these risks.

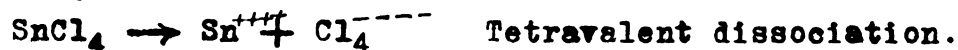
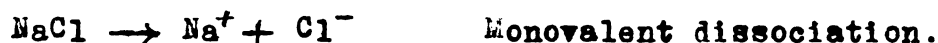
3. The third part of the document focuses on the analysis and interpretation of the collected data. It describes the techniques used to identify trends, patterns, and anomalies within the data set. This analysis is crucial for understanding the underlying causes of financial fluctuations and for making informed decisions based on the findings.

4. The final part of the document provides a summary of the key findings and conclusions. It reiterates the importance of ongoing monitoring and evaluation of the financial system, as well as the need for continuous improvement in data collection and analysis practices. The document concludes by emphasizing the role of all stakeholders in ensuring the accuracy and reliability of the financial information.

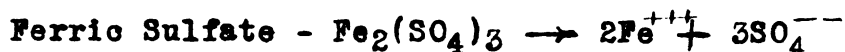
II

General Theory

The theoretical basis for electrometric methods dealing with oxidation and reduction phenomena lies chiefly in the work of the Swedish physicist Arrhenius in establishing the electrolytic dissociation theory of substances in solution (177); and lies also in the second law of Faraday which states that the valence of an ion is a function of the number of electrical charges it carries (177). Acids, bases, and salts when in water solution are dissociated into ions (electrically charged particles) and the number of these electrical charges are proportional to the valence of the elements involved. This phenomenon may be graphically illustrated as follows:



Some of the chemical elements may exist in combination in more than one state of valence, and dissociate electrolytically in accord with this valence state, thus, —



We can change the valence of iron and some of the other chemical elements by adding or subtracting electrical charges - electrons. The valence of iron from two in the ferrous state

1. The first part of the document discusses the importance of maintaining accurate records of all transactions. It emphasizes that proper record-keeping is essential for the integrity of the financial system and for the ability to detect and prevent fraud.

2. The second part of the document outlines the various methods used to collect and analyze data. It describes the use of statistical techniques to identify trends and anomalies in the data, and the importance of using reliable sources of information.

3. The third part of the document discusses the role of the auditor in the financial system. It explains that the auditor's primary responsibility is to provide an independent and objective assessment of the financial statements, and to ensure that they are prepared in accordance with the applicable accounting standards.

4. The fourth part of the document discusses the importance of transparency and accountability in the financial system. It explains that transparency is essential for the confidence of investors and other stakeholders, and that accountability is necessary to ensure that the system is operating in the best interests of the public.

5. The fifth part of the document discusses the role of the government in the financial system. It explains that the government has a responsibility to regulate the system and to ensure that it is operating in a fair and efficient manner. It also discusses the importance of the government's role in providing a stable and secure environment for the financial system.

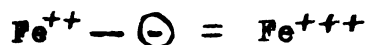
6. The sixth part of the document discusses the importance of international cooperation in the financial system. It explains that the financial system is a global system, and that international cooperation is essential for the stability and integrity of the system. It also discusses the importance of the government's role in promoting international cooperation.

7. The seventh part of the document discusses the importance of the financial system in the economy. It explains that the financial system is a key component of the economy, and that it plays a vital role in the allocation of resources and the promotion of economic growth. It also discusses the importance of the government's role in supporting the financial system.

8. The eighth part of the document discusses the importance of the financial system in the lives of individuals. It explains that the financial system is a key component of the lives of individuals, and that it plays a vital role in the accumulation of wealth and the provision of financial services. It also discusses the importance of the government's role in protecting the interests of individuals in the financial system.

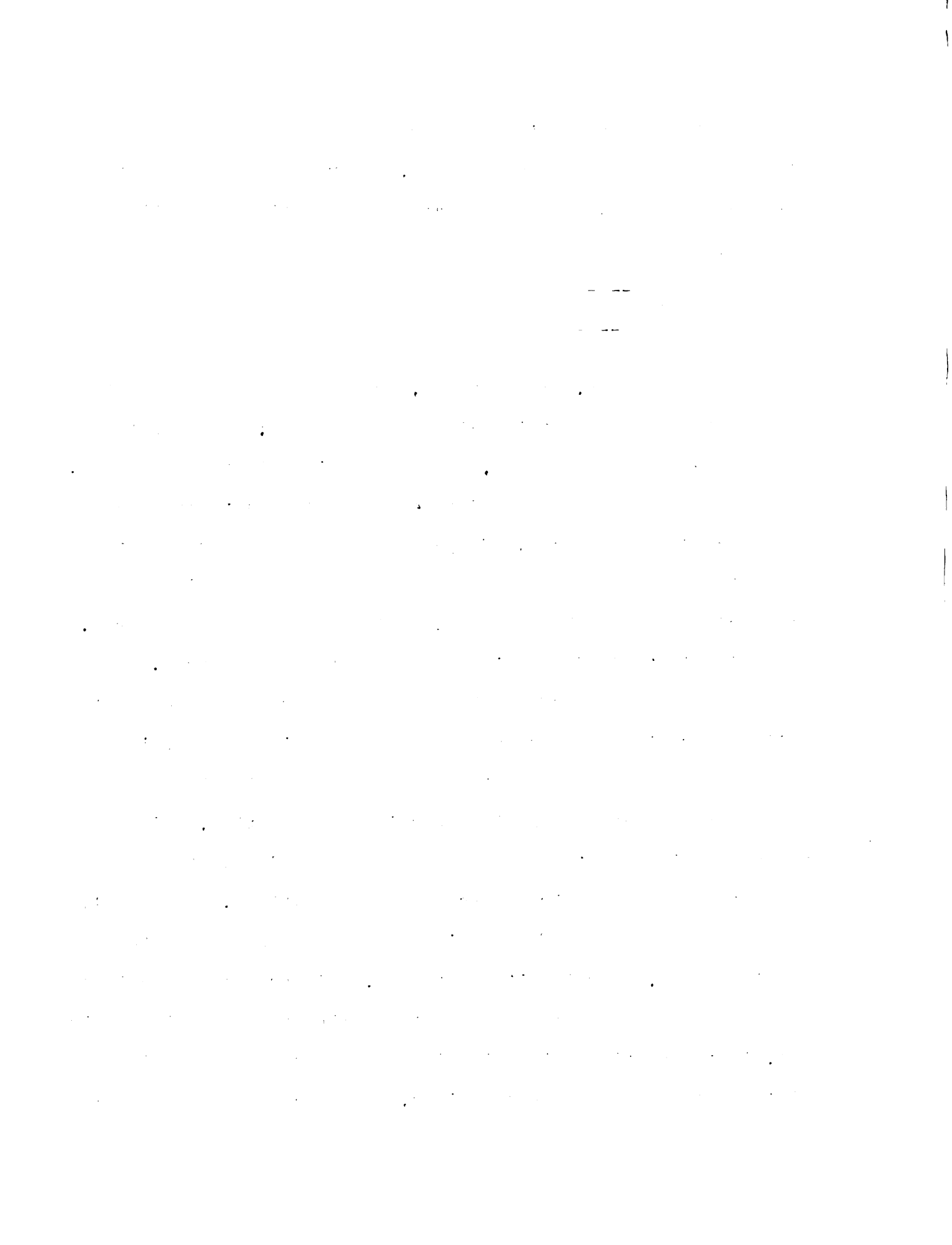
9. The ninth part of the document discusses the importance of the financial system in the future. It explains that the financial system is a dynamic system, and that it is constantly evolving. It also discusses the importance of the government's role in ensuring that the financial system is able to meet the needs of the future.

can be raised to three in the ferric state by subtracting one electron(adding a positive charge), or from the ferric to the ferrous state by adding one electron(subtracting a positive charge).



When an electron, or electrons, are taken from an element in solution the element is said to be oxidized; and when the opposite change takes place, the element is said to be reduced. These changes are accompanied by electrical effects which can be observed and measured. The common method of measuring these electrical effects is by comparing them with a normal or a standard electrode which gives a definite electromotive force. The calomel standard cell is the one most commonly used.

If an electrode of a noble metal such as a piece of platinum foil or wire is placed separately into solutions of ferric and ferrous ions, a definite potential difference will be set up between the electrode and the ions in each solution, and the value of this potential difference will depend upon the concentration of the iron ions of these solutions. There will be a tendency for the ferrous ions to give up electrons to the platinum wire, charging it negatively, and for the ferric ions to take up electrons from the platinum wire charging it positively. But, if the platinum wire dips into one solution containing a mixture of ferric and ferrous ions, and is connected externally



with a normal calomel electrode which in turn makes contact with the ferrous-ferric solution by means of a salt arm making a liquid-liquid junction, a potential difference is established which is determined by the ratio of the ferrous to the ferric ions in the solution. In the measuring process this potential difference is compared to that of the normal calomel cell. The relationship is expressed by Peter's equation (6).

$$E = C - \frac{RT}{nF} \ln \frac{\text{(reduction product)}}{\text{(oxidation product)}}$$

Where:

E = observed potential difference

C = a constant applying to this particular case
and is equal to E when $\frac{\text{(reduction product)}}{\text{(oxidation product)}} = 1$

R = the gas constant = volts x coulombs

T = absolute temperature

n = valence of the metal

F = Faraday = 96,540 coulombs

When applied to the case under consideration, the formula becomes,-

$$E = C - \frac{RT}{nF} \ln \frac{(\text{Fe}^{++})}{(\text{Fe}^{+++})}$$

Subtracting numerical values and changing to common logarithms, we have,-

$$E = 0.46 + 0.058 \log \frac{(\text{Fe}^{++})}{(\text{Fe}^{+++})}$$

E, or the potential difference, then becomes a measure of

1. $\frac{1}{2} \times \frac{1}{2} = \frac{1}{4}$

2. $\frac{1}{2} \times \frac{1}{3} = \frac{1}{6}$

3. $\frac{1}{3} \times \frac{1}{3} = \frac{1}{9}$

4. $\frac{1}{4} \times \frac{1}{4} = \frac{1}{16}$

5. $\frac{1}{5} \times \frac{1}{5} = \frac{1}{25}$

6. $\frac{1}{6} \times \frac{1}{6} = \frac{1}{36}$

7. $\frac{1}{7} \times \frac{1}{7} = \frac{1}{49}$

8. $\frac{1}{8} \times \frac{1}{8} = \frac{1}{64}$

9. $\frac{1}{9} \times \frac{1}{9} = \frac{1}{81}$

10. $\frac{1}{10} \times \frac{1}{10} = \frac{1}{100}$

11. $\frac{1}{11} \times \frac{1}{11} = \frac{1}{121}$

12. $\frac{1}{12} \times \frac{1}{12} = \frac{1}{144}$

13. $\frac{1}{13} \times \frac{1}{13} = \frac{1}{169}$

14. $\frac{1}{14} \times \frac{1}{14} = \frac{1}{196}$

15. $\frac{1}{15} \times \frac{1}{15} = \frac{1}{225}$

16. $\frac{1}{16} \times \frac{1}{16} = \frac{1}{256}$

17. $\frac{1}{17} \times \frac{1}{17} = \frac{1}{289}$

18. $\frac{1}{18} \times \frac{1}{18} = \frac{1}{324}$

19. $\frac{1}{19} \times \frac{1}{19} = \frac{1}{361}$

20. $\frac{1}{20} \times \frac{1}{20} = \frac{1}{400}$

21. $\frac{1}{21} \times \frac{1}{21} = \frac{1}{441}$

22. $\frac{1}{22} \times \frac{1}{22} = \frac{1}{484}$

23. $\frac{1}{23} \times \frac{1}{23} = \frac{1}{529}$

24. $\frac{1}{24} \times \frac{1}{24} = \frac{1}{576}$

25. $\frac{1}{25} \times \frac{1}{25} = \frac{1}{625}$

26. $\frac{1}{26} \times \frac{1}{26} = \frac{1}{676}$

27. $\frac{1}{27} \times \frac{1}{27} = \frac{1}{729}$

28. $\frac{1}{28} \times \frac{1}{28} = \frac{1}{784}$

29. $\frac{1}{29} \times \frac{1}{29} = \frac{1}{841}$

30. $\frac{1}{30} \times \frac{1}{30} = \frac{1}{900}$

the relative concentration of the ferric and ferrous ions. As the ratio of these ionic concentrations gradually changes, due to the addition of oxidizing or reducing reagents, E will also show a gradual and corresponding change in value until one of the ionic concentrations becomes vanishingly small as compared with the other, when E will show an abrupt change of comparatively great magnitude which may be taken as the end-point of the reaction. The theory may be applied to all oxidation and reduction reactions, but the constant, C , is different in value for the different chemical elements that may be oxidized or reduced. Some of these constants are given by LeBlanc (177).

The potential at the beginning and end of the reaction depends upon the nature and concentrations of other ions which may be present as well as the concentrations of the ferrous or ferric ions, but the changes in potential due to the addition of reagents are always slight in magnitude until the end-point of the reaction is reached when a great change takes place.

It is possible to determine quantitatively two or more substances present in the one solution providing they can be oxidized or reduced by the same reagent, and that their oxidation or reduction potentials are far enough apart in values to give separate end-points within the voltage range obtainable.

The oxidation or reduction reaction must progress quite rapidly for the electrometric method to be of value.

UNITED STATES DISTRICT COURT
SOUTHERN DISTRICT OF NEW YORK

MEMORANDUM OF DECISION AND ORDER
ON THE DEFENDANT'S MOTION TO DISMISS
THE COMPLAINT

On July 16, 1998, Defendant [Name] filed a motion to dismiss the Complaint filed herein on July 1, 1998. The motion is supported by the following grounds:

- 1. The Complaint fails to state a claim for which relief may be granted.
- 2. The Complaint is barred by the statute of limitations.
- 3. The Complaint is barred by the doctrine of res judicata.
- 4. The Complaint is barred by the doctrine of estoppel.
- 5. The Complaint is barred by the doctrine of laches.

The Court has reviewed the Complaint and the Defendant's motion. The Court notes that the Complaint alleges that Defendant [Name] committed certain acts which allegedly caused Plaintiff [Name] to suffer certain damages. The Court notes that the Complaint fails to state a claim for which relief may be granted.

The Court notes that the Complaint is barred by the statute of limitations. The Court notes that the Complaint is barred by the doctrine of res judicata. The Court notes that the Complaint is barred by the doctrine of estoppel. The Court notes that the Complaint is barred by the doctrine of laches.

WHEREFORE, Defendant [Name] requests that the Court grant its motion to dismiss the Complaint. Defendant [Name] respectfully requests that the Court grant its motion to dismiss the Complaint.

III METHODS

A classification of the different systems used in the methods of electrometric titration has been made by Kolthoff (Chem. Weekblad 50,659(1920)). Three systems are given by Kolthoff, to which a fourth may be added. 1. The common system, consisting of a stable electrode, unattacked in an acid solution, used with a constant half-cell such as the calomel cell or a similar electrode. 2. The Pinkhof system (Chem. Weekblad 16,1163-7,1919) in which a compensating electrode replaces the calomel half-cell, the potential of the compensating electrode being equal to the stable electrode at the end of the titration. A reversal of polarity marks the end-point in this case. The common disadvantages of this system is that each titration requires a different compensating electrode, and the concentration of substances foreign to the titration may interfere with the compensating effects. 3. The Treadwell system (Helv. Chim. Acta 2,680,1919) is composed of a half-cell replacing the standard electrode which contains an electrolyte having the same composition at the titrated solution at the end-point of the reaction. This system has the same disadvantages as the Pinkhof system being specific for each titration. 4. The bimetallic system of Willard and Fenwick (J.A.C.S. 44,2504,1922) may be mentioned as a fourth system of electrometric titration. In this system the standard half-cell is replaced with an inactive metal or a

The first part of the document discusses the importance of maintaining accurate records of all transactions and activities. It emphasizes the need for transparency and accountability, particularly in financial reporting. The text outlines various methods for data collection and analysis, including the use of spreadsheets and specialized software. It also mentions the importance of regular audits and the role of external auditors in ensuring the integrity of the data.

In the second section, the author discusses the challenges of data management and the need for effective data storage and retrieval systems. It highlights the importance of data security and the implementation of robust backup and recovery procedures. The text also touches upon the legal and ethical considerations surrounding data handling and the need for compliance with relevant regulations.

The third part of the document focuses on the application of data analysis in decision-making. It discusses the use of statistical methods and data visualization techniques to identify trends and patterns in the data. The author emphasizes the importance of interpreting the results of data analysis in the context of the organization's goals and objectives. It also mentions the role of data in identifying areas for improvement and the need for continuous monitoring and evaluation.

Finally, the document concludes by discussing the future of data management and analysis. It mentions the emergence of big data and the need for advanced analytical tools and techniques. It also highlights the importance of data literacy and the need for organizations to invest in training and development programs to ensure their workforce is equipped to handle the challenges of the data-driven era.

metal-alloy electrode which shows no great change in potential at the end-point of the reaction. Some of the metals used are tungsten, and alloys of the platinum group of metals. Another form of this system consists of two inactive metallic electrodes, one of platinum, upon which is imposed an e.m.f. equal to the hydrogen overvoltage of the platinum electrode.

Some data regarding the specific use of these systems are discussed in connection with the methods used for the several elements that may be determined quantitatively by means of electrometric titration.

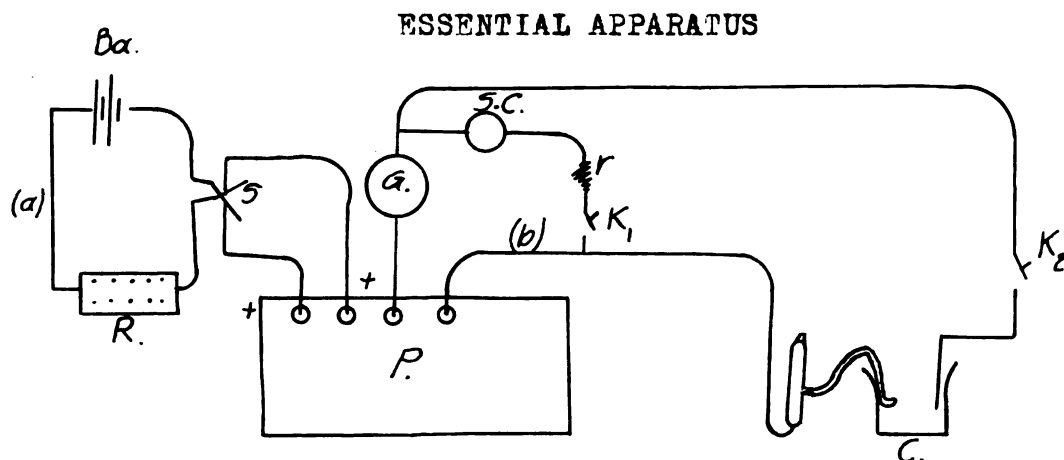
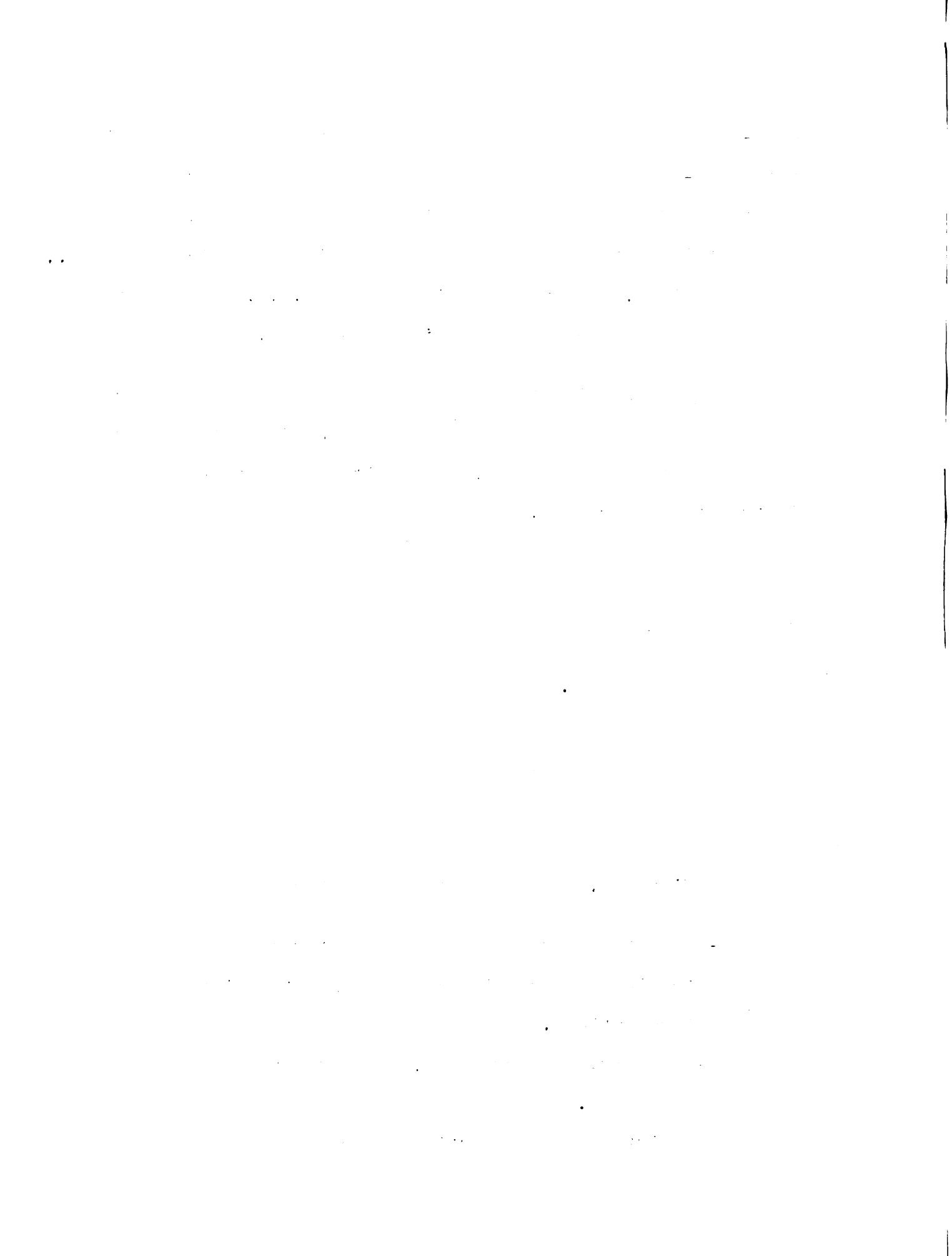


Figure 1. Diagram of the apparatus.

P - Potentiometer. ▲ Leeds and Northrup Students' potentiometer is suitable for a great variety of determinations.

Ba - Battery. Two dry cells, or a four volt accumulator may be used.

R - Resistance for adjusting the electric current in



in the (a) circuit. A plug resistance of 11, 110 ohms capacity works well with two dry cells.

S - A current reversing, double pole, double throw switch. The reversing feature of this switch aids in making voltage readings if the voltage should become negative during a titration. By reversing the (a) circuit current, the potentiometer may be read directly.

G - Galvanometer. A sensitive, dead beat, galvanometer is very good for the purpose, although a too sensitive galvanometer is not to be desired for some work.

S.C. - A standard cell, used for calibrating the potentiometer as a direct reading voltmeter.

r - A high resistance used to protect the standard cell. This high resistance may also be used in the titrating cell circuit to prevent drawing a current from it.

C - Titrating cell. These titrating cells may be of a variety of forms depending upon the nature of the work to be done.

K₁ and K₂ - are key-switches used to momentarily close their respective circuits when calibrating or reading the potentiometer.

The apparatus illustrated and described belongs to the commonly used compensating system devised by Poggendorf for the measurement of voltages. It consists, essentially, of two electrical circuits, one of which (a) may be set at a

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known value through the potentiometer, and the value of the other unknown circuit (b) measured by comparison with the circuit (a).

Titrating Cells.- Various forms of titrating cells are in general use. If in any particular case it is unnecessary to protect the solutions being titrated from oxidation by the oxygen of the air, or from possible contamination by carbon dioxide gas, or any other laboratory gas or fume; an open beaker, or other open dish of suitable size and shape is all that will be required. On the other hand, a closed container, or cell, is necessary for the titrating of solutions that oxidize readily in the air, or that require elimination of the adsorbed oxygen by eleutration with an inert gas passed through the solution preliminary to the titration, or that need to be protected from gas injury by maintaining constantly an atmosphere of an inert gas over them during the titration procedure. Two common forms of closed containers for electro-titration work are; 1. the titrating head described by Hostetter and Roberts (45), and 2. the closed container used by Ewing and Eldridge (75). Burette tips, electrodes, stirrers, or the delivery points of other pieces of apparatus, or gas inlets and outlets are sealed into the cells in some suitable manner.

In the earlier electrometric titration work, a capillary electrometer was used in place of the galvanometer; and for



end-point determination only, a common sliding resistance, of the proper value, took the place of the potentiometer. In this case, the end-point readings were taken by constantly adjusting the resistance to hold the electrometer at zero as the titration progressed, and the end-point was shown by a marked deflection of the electrometer. This arrangement is now used sometimes in laboratories where rapid work is required, but the galvanometer has practically replaced the capillary electrometer as a null-point instrument in the electrometric titration work. Titration curves may be plotted from the readings taken in the above manner when the resistance is first calibrated and provided with a scale for interpreting the results.

Calibration of the potentiometer.- In calibrating the potentiometer to read as a voltmeter, the potentiometer is first set at its voltage reading corresponding to the exact voltage of the standard cell. The resistance R is then adjusted until by slight tapping of the key K_2 the galvanometer shows no deflection. Practically no current should be taken from the standard cell, hence, for accurate work, a rough standard cell should first be used while the preliminary resistance adjustments are being made, and the final adjustment then made with the accurate standard cell. For accurate work this calibrating of the potentiometer should precede each titration, especially if titration curves are to be plotted from the voltage readings.

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Special kinds of electrometric titrating apparatus made in compact, portable forms and adapted to different types of analytical work are now on the market.

The vacuum tube generally used in radio sets has also been used in place of the potentiometer for making electrometric titrations. For references see Geode(93), Calhane & Cushing(134b), Treadwell(168), and Gardner(176).

Method of making electrometric titrations.- The actual method of operation used will depend somewhat upon the nature of the work; certain precautions being necessary in most cases. It is the plan of the writer to give only a general outline of the methods used at the present time.

The common technic adapted by investigators for making electrometric titrations is to place a known quantity of a certain oxidizable or reducible solution into the titrating vessel, usually in an acid solution, although some titrations require an alkaline solution, and then titrating this solution with a reducing or oxidizing reagent, as the case may require, and the voltage readings taken in a manner that allows for the plotting of a curve with the voltage readings plotted against cubic centimeters of the reagent used. This procedure is known as direct titration. An indirect method of titration is used in cases where a sharp end-point can not be obtained by means of the direct method. The indirect method consists of adding an excess of reagent to the solution to be titrated and then

1. The first step in the process of identifying a problem is to define the problem. This involves identifying the symptoms and the underlying causes of the problem.

2. The second step is to gather information about the problem. This involves collecting data and identifying the stakeholders who are affected by the problem.

3. The third step is to analyze the information. This involves identifying the key issues and the potential causes of the problem.

4. The fourth step is to develop a plan of action. This involves identifying the goals and objectives of the plan and the resources needed to implement it.

5. The fifth step is to implement the plan. This involves putting the plan into action and monitoring progress.

6. The sixth step is to evaluate the results. This involves assessing the effectiveness of the plan and identifying any areas for improvement.

7. The seventh step is to communicate the results. This involves sharing the findings of the evaluation with the stakeholders and the public.

8. The eighth step is to review the process. This involves reflecting on the experience and identifying lessons learned.

titrating this excess with a reagent that does give a sharp end-point with the first solution used in excess. In making a first study of a reaction, known solutions are used in order to prove the accuracy or advantage of the method before the method is applied to unknown solutions. As stated before, if the end-point alone is desired in a titration it is only necessary to determine the point in the titration where the greatest deflection of the galvanometer takes place. It is advisable to know just about the quantity of titrating reagent that will be required for a determination, and as the end-point is approached, to add the reagent, drop by drop, until the end-point is exactly reached.

It must be remembered that in making titrations by the electrometric method the voltage changes are caused by the changing concentrations of the ions in the solutions, and that any ionic concentration change will cause a corresponding change in voltage. This being the case, the operator must know, in order to do accurate work, that the only concentration changes taking place are due to the additions of the reagent used, and not due to changes at the electrodes, or to oxidation or reduction effects not due to the reagent added, or to side reactions that may take place under the conditions of the titration. This means that the electrodes should not be attacked by the original solutions, or by the products formed during the reaction; and that the oxygen of the air must be excluded when easily oxidizable solutions are being used; and

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also, that possible side reactions do not interfere with the main determination. It is also necessary to know that the reaction is completed when the end-point deflection occurs.

The common method of protecting a titration against air oxidation is to bubble an inert gas through the solution preliminary to the titration operation in order to remove absorbed oxygen, and then during the titration to maintain an atmosphere of the gas over the solution in the titrating cell. Carbon dioxide, hydrogen and nitrogen are the inert gases ordinarily used. However, bubbles of the gas should not be allowed to adhere to the metallic electrode, as this tends to form a gas electrode and causes a change in e.m.f. of the cell; hence, the adsorbed oxygen, or other gas, should be removed before the metallic electrode is inserted into the solution.

The metallic electrode generally used is platinum. Some workers prefer platinum foil of a certain size for the metallic electrode, while others have found platinum wire best, at least for certain determinations. The shape and size of the platinum electrode is probably specific for some titrations, but this point seems to have been little investigated. These platinum electrodes must be kept clean and bright by washing in acids, cleaning solutions, ignition, scouring, or by electrolyzing deposited substances from them; the most



suitable method in any case depends upon the nature of the deposit on the electrode.

Mechanical stirring of the solution during the titration process is practically always used.

Temperature control is unimportant for reduction or oxidation reactions that take place rapidly at room temperature. Where heating is required to hasten the reaction, the usual method is to heat the solution to the required temperature and then titrate rapidly for the end-point. Some workers have found, however, that by cooling the solutions to a low temperature, better results could be obtained. The proper temperature for a reaction, at least within a certain range, is important for reactions that require heating in order to increase the speed at which they take place.

The advantage of using the electrometric end-point in a titration method is its high degree of accuracy, and to make the fullest use of the delicacy of these methods, all standard solutions used for making electrometric titrations should be standardized by the most accurate methods possible for each particular solution. When a high degree of accuracy can be attained in the standardization of the titrating reagents, the electrometric titration method is exceedingly accurate, and very small quantities of a substance may be determined by means of it if sharp end-points may be obtained.



So great is the accuracy attainable as compared with the common volumetric analysis, by means of these methods that many workers in this field recommend that the standard reagents be made up by weight instead of by volume, and that the titrating additions of reagents be made by weight also instead of being measured from a buret. The degree of accuracy required or desired will probably be a determining factor in this connection with many operators of the electrometric titration methods.

Another important factor in electrometric titration is the kind of acid used to acidify the solution being titrated, and the degree or quantity of this acidity necessary for best results. This factor is specific for each titration, within certain limits, and when not known, or can not be determined from the literature on the subject, it must be experimentally determined.

Breaking the circuit while taking the voltage readings is sometimes done in order to prevent deposition of metals on the electrodes.

The magnitude of the end-point voltage deflection depends upon the intensity of the reduction or oxidation processes and may be used as a measure of them.

1. The first step in the process of identifying a problem is to recognize that a problem exists. This is often done by comparing current performance with a desired state or goal. For example, a manager might notice that sales are declining or that customer satisfaction is low. Once a problem is identified, the next step is to define it more precisely. This involves determining the scope of the problem, its causes, and its effects. For instance, a manager might define a sales decline as a 10% drop in revenue over the last quarter, caused by a decrease in the number of new customers and a loss of existing customers. The third step is to analyze the problem. This involves gathering data, identifying patterns, and testing hypotheses. For example, a manager might analyze sales data to see if there is a seasonal trend or if the decline is more pronounced in certain regions. The fourth step is to generate solutions. This involves brainstorming ideas, evaluating them, and selecting the most promising ones. For instance, a manager might generate ideas such as increasing advertising, improving customer service, or offering discounts. The fifth step is to implement the solution. This involves developing a plan, allocating resources, and putting the plan into action. For example, a manager might develop a plan to increase advertising by 20% and allocate the necessary budget. The final step is to evaluate the results. This involves monitoring performance, comparing it to the desired state, and making adjustments as needed. For instance, a manager might monitor sales data to see if the advertising increase has led to an improvement in sales.

IV

SPECIAL POINTS TAKEN FROM THE LITERATURE OF THE
SUBJECT CONCERNING THE ELECTROMETRIC TITRATION OF
SEVERAL CHEMICAL ELEMENTS

In the following discussion the several elements and substances that have been investigated by means of the electrometric titration methods are listed alphabetically. The numbers in parentheses given in connection with the subjects and paragraphs refer to the numbers of the references in the bibliography appended to this thesis. The references marked with a "*" were not found in the Michigan State College library (December 31, 1925.) This list of subjects with the reference numbers will serve as a cross reference to the bibliography.

Antimony.- (107), (147)

Antimonous sulphate may be titrated with potassium bromate in various concentrations of hydrochloric acid, 3-20 percent. (107) (C.A. 17, 1604)

Antimony in the form of antimonous chloride may be titrated with potassium dichromate in the presence of hydrochloric acid, 100 cc. of the solution containing 15 cc. of hydrochloric acid (d. 1.18), at room temperature, and with constant stirring. Antimonous chloride and stannous chloride may be titrated together in one sample, but mercuric chloride should be present in the solution in excess when antimony is titrated in the presence of tin. (147) (C.A. 19, 451)



Arsenic.- (107), (151)

Arsenic may also be titrated by means of potassium bromate in a 5-20 percent hydrochloric acid solution. (107)

(C.A. 17, 1604)

A sodium arsenite solution, 0.0222N, was prepared as recommended by the American Society of Testing Materials for steel analysis, and titrated against an iodide solution which had been standardized against potassium bromate. The sodium arsenite was titrated electrometrically with a potassium permanganate solution, 0.113N, standardized by means of sodium oxalate. 25 cc. of the permanganate solution was titrated in 100 cc. of nitric acid (d. 1.13) with the arsenite solution.

A tungsten electrode was used in place of the calomel electrode, as in the presence of potassium chloride in the solution, the theoretical end-point was not obtained. The potassium chloride causes a more complete reduction of the manganese.

This reaction was also carried out in a 2.5N sulfuric acid solution with 0.0964N sodium arsenite.

In the nitric acid solution the manganese is reduced from a valence of 7 to an average valence of 3.3. $-6\text{MnO}_4^- + 11\text{H}_2\text{AsO}_3^- + 15\text{H}_2^+ \rightarrow 2\overset{+++}{\text{Mn}} + 4\overset{+++}{\text{Mn}} + 11\text{HAsO}_4^-$. But in the sulfuric acid solution, the valence is reduced to an average of 2.5; $-4\text{MnO}_4^- + 9\text{HAsO}_3^- + 14\text{H}_2^+ \rightarrow 2\overset{+++}{\text{Mn}} + 2\overset{+++}{\text{Mn}} + 9\text{HAsO}_4^-$.

In the electrometric titration of arsenic attention should be paid to details especially acid concentration,

temperature, presence of halide or manganous salt, and to standardize the solutions used under the same conditions as they are to be used in the method of analysis. (131)

(C.A. 17, 2687)

Azo dyes.- (94)

The azo dyes were reduced by means of a 0.25N titanous chloride solution in excess and the excess titrated with a 0.05N ferric alum solution. The titrations were carried out in an atmosphere of carbon dioxide. Thiocyanate was not satisfactory as an outside indicator, because of the presence of carbon dioxide, and because the solutions themselves were sometimes either pink, blue, or green in color. The reaction flask consisted of a 250 cc. Pyrex extraction flask with a 3-hole stopper to accommodate a platinum electrode, the salt-arm of the calomel half-cell, and a buret.

Procedure.- 0.5 to 1.0 gram of the finely powdered dye, sufficient in quantity to require 30 to 40 cc. of the titanous chloride solution for reduction, was placed into the reaction flask; and 25 cc. of distilled water was then added, the flask covered loosely, and placed on a steam bath for about 10 minutes to dissolve or soften the particles. Next, 25 cc. of 40 percent sulphuric acid was added, the flask stoppered, and a current of carbon dioxide was passed through for five minutes. Then the required amount of the titanous chloride solution was added, at least five cc. more than was required for reduction. The liquid was then boiled for five minutes and then cooled to 30° C. in a water bath, and titrated. (94)

(C.A. 16, 1155)

Bromine.- (11)*, (61), (105), (116), (120)*

A known weight of potassium iodide solution was titrated with a potassium bromate solution in the presence of enough sulfuric acid to make the solution about 2N at the end of the experiment, and until about 10 percent of the iodide remained undecomposed. Then the voltage became constant, the titration was completed with potassium permanganate. Experiments indicated that in this titration the presence of small amounts of chlorate had no influence. The iodide solution was also successfully titrated with the bromate solution. The last drops of the bromate solution were added very slowly to avoid running by the end-point, and the whole titration required at least 15 minutes for end-point, and much longer to acquire the data for plotting a curve. Hydrochloric acid may not be present in quantities in excess of 0.2N. (61)

(C.A. 15, 3799)

Dutoit and von Weisse used the electrometric method for the titration and separation of the halides, and recommended precipitation with a silver salt or some other suitable precipitant. They call attention to the suitability of the method for determining the halides in very dilute concentrations as 10-20 milligrams of chloride per liter, or smaller quantities of bromide or iodide. Two end-points are obtained in a mixture of the three halides, the first one is the iodide precipitation, and the second one occurs when all the halides are precipitated. These authors claim that

iodide may be determined in this way in the presence of a great excess of bromide or chloride. (11)

(C.A. 6, 722)

Bromate may also be titrated with titanous chloride at a concentration of $0.05N \times 1.4663$, and protecting the solution by means of carbon dioxide gas. 50 cc. of a solution of potassium bromate, $0.05N$, in 200 cc. of boiled water, and 10 cc. of $10N$ sulfuric acid were used for the titration. Hydrochloric acid may be used in place of the sulphuric acid, but should not exceed a concentration of $0.5N$ at the end of the titration. The change of bromide in hydrocyanic acid solution to bromine cyanide by titrating with potassium permanganate is too slow for the bimetallic electrode system to be used; but the end-point in this reaction may be determined by means of the usual monometallic system if the titration curve is plotted. This oxidation requires the theoretical equivalent of oxygen, and the exalate factor of the permanganate may be used. (105), (116), (C.A. 17, 1397)

(C.A. 17, 3306)

By means of the mercury electrode, chlorides and bromides may be titrated electrometrically with mercurous nitrate, but not in the presence of each other. (126)

(C.A. 18, 1799)

Copper.- (10)*, (88)*, (120)*, (157)*

Dutict and von Weisse made a detailed study of the principles of concentration cells as applicable to volumetric analysis by precipitation. They produced polarization in

the cell by means of a feeble, imposed current and used revolving electrodes to prevent this current from setting up concentration differences. The several points studied are: (1) Speed of stirring. (2) Effect of foreign substances. (3) Effect of dilution. (4) Influence of the auxiliary current. (5) Duration of the titration. Copper was titrated with a solution of potassium ferrocyanide, and also with a solution of sulfide. Sodium or potassium sulfide was found to be the most satisfactory precipitant. Copper could be determined with an accuracy of 0.1-0.2 milligram per liter. (10)

(C.A. 6, 722)

Copper may be accurately determined by electrometric titration by means of reduction with titanous chloride in excess in hydrochloric acid solution, and titrating the excess of titanous chloride with potassium bromate or potassium chromate in an atmosphere of carbon dioxide. The reaction is slow at room temperature, but instantaneous at 80° C. 4-8 percent of hydrochloric acid should be present in the solution. If iron is present, it is determined with the copper. (88)

(C.A. 17, 702)

Copper may be titrated simultaneously with silver. The silver is first titrated with potassium cyanide, and the silver cyanide removed from the solution by filtration, and the copper titrated with the potassium cyanide solution. This is a convenient method for the separation of copper and silver. (120)

(C.A. 18, 640)

Cupric salts alone, or when mixed with ferric salts, or both in the presence of antimony, may be titrated by means of titanous chloride. (157), (C.A. 19, 450)

Cyanides.- (12)*, (36), (40)*, (76)*, (77)*, (78)*, (116), (126)*, (143)*

Treadwell titrated potassium cyanide in the presence of potassium ferrocyanide with silver nitrate by first adding to the titrated solution 0.1 gram of potassium iodide in a 0.1N solution. The solution was slightly alkaline. Addition of ammonia is not necessary. Increasing the amount of potassium iodide overcame the disturbing influence of sodium hyposulfite. The influence of an excess of ammonia, sodium hyposulfite, or potassium ferrocyanide was found to be due to the formation of complex ions and the lowering of the concentration of the silver ion below that required for the precipitation of the silver cyanide. (12) (C.A. 5, 3391)

Muller states that all cations can be electrometrically determined by means of a solution having an ion which will produce a constant insoluble compound. Potassium ferrocyanide may be used to determine zinc or lead. All ferrocyanide solutions contain some ferricyanide. The low solubility of zinc ferrocyanide makes the value ferro ion-ferric ion large so a small, constant amount of potassium ferricyanide is added to the solution to make the ferric ion portion independent of the other. The temperature used was 75°. Several metals in the same solution could not be determined by the

method because of the variation in the composition of most ferrocyanides. Cadmium did not interfere with this titration. A calculated table in which a cc. of potassium ferrocyanide, b number of ohms required for compensation in the determination of the potential against a normal calomel electrode with a capillary electrometer used as a null-point instrument; and taking the number of cc. of titrating solution corresponding to the highest value of da/db , was found to be more convenient and more accurate than the graphic method of plotting the titration curve. (40) (C.A. 14, 3205)

Two end-points are obtained when cyanogen ion is titrated with silver ion; the first corresponds to the addition of one-half silver ion for each cyanogen ion present, and the second for equal amounts and when silver cyanide is precipitated. It is possible to titrate cyanogen ion in a halide mixture and determine each constituent. With iodine and cyanogen three end-points are obtained; the first when one-half silver has been added for each cyanogen ion, the next when silver iodide is precipitated, and the third when both cyanogen and iodide are precipitated. Two end-points were found in the presence of chlorine or bromine. The first corresponds to one-half the silver as above, the second to the precipitation of silver cyanide and silver chloride or silver bromide as the case may be. With a mixture of iodine, bromine and cyanogen, three end-points were obtained. The first one on one-half the cyanogen, second on the precipitation

of silver iodide, and the third on the precipitation of all the ions. With bromine, chlorine, and cyanogen, only two end-points are obtained so that only the cyanogen and total halogen content may be determined. (76) (C.A. 16, 2818)

Kulthoff titrated potassium ferrocyanide with potassium permanganate in concentrations of more than 0.02 mol in the presence of sufficient sulfuric or hydrochloric acid to prevent the precipitation of potassium or manganese ferricyanide, and by comparing the color of the solution at the end-point with a potassium ferricyanide solution. (77) (C.A. 16, 3281)

The titration of ferrocyanide with potassium permanganate gives better results when the end-point is determined electrometrically than when it is obtained by the change in color of the solution. (78) (C.A. 16, 3601)

Cyanide can be titrated by means of mercuric chloride. (126) (C.A. 18, 1799)

Ferricyanide can be directly titrated with potassium iodide. If the ferricyanide solution is run into a known quantity of potassium iodide and enough zinc is added to form the double compound, zinc-potassium ferrocyanide, the end-point is obtained more promptly. (143) (C.A. 18, 3020)

About one gram of potassium ferrocyanide in 250 cc. of water and 2.5 to 5 cc. of sulfuric acid (sp. gr. 1.58), may be titrated with 0.05N potassium permanganate. The potassium permanganate should be accurately standardized with sodium oxalate. Ferricyanide does not interfere with this titration.

The permanganate should be added to the ferrocyanide with constant stirring. As the end-point is approached, the permanganate should be added drop-by-drop, and sufficient time allowed for the completion of the reaction. Chloride in amount equivalent to one gram of sodium chloride does not interfere with the reaction. Any salts, which under the conditions of the reaction, produce a precipitate with either ferro- or ferricyanide do interfere with the reaction. (36)

(C.A. 14, 30)

Hendrixson titrated a solution of pure potassium ferricyanide of a concentration of $0.05N \times 0.72$, standardized by means of the iodine method, with titanous chloride, and he claims a high degree of accuracy for this determination. (116)

(C.A. 17, 3506)

Chromium.- (14), (17), (20), (25), (49)*, (61), (63)*, (64)*, (66)*, (79), (144)*

Dichromate ion was successfully titrated by means of ferrous ion using a platinum electrode and a calomel half-cell. The author used a plunger consisting of a glass rod which passed through a rubber stopper inserted in the top of the calomel electrode cell to force the potassium chloride through the salt arm of the cell and flush it out before each potentiometer reading. A wheatstone bridge potentiometer and a capillary electrometer were used to make the voltage readings. The dichromate solution was titrated with

the ferrous solution. In titrating a dichromate solution, the ferrous iron solution was found to be more accurate than than a ferricyanide solution. The presence of chlorides was found to interfere with the proper end-point. (14)(C.A. 7, 3938)

Tiegel titrated a potassium dichromate solution with ferrous sulfate using the Ostwald-Luther, electrically controlled automatic buret. The results obtained were not of a high degree of accuracy. (17) (C.A. 9, 898)

Kelley and Conant used the electrometric method to determine the amount of chromium in steel. They used the method and apparatus of Forbes and Bartlett. The chromium was first oxidized to chromate and then titrated. Large amounts of ferric iron in the solution affect the accuracy of the endpoint. Temperature had little effect on the reaction or delicacy of the end-point. The acid concentration should be quite high, particularly in the presence of chlorides. Cold solutions containing high concentrations of hydrochloric acid gave good results. (20) (C.A. 10, 2179)

Kelly, Adams, and Wiley combined the several pieces of electrometric titration apparatus into a portable unit for use in industrial laboratories. Using this portable apparatus to determine chromium in steels, they claim an accuracy of nearly 0.001 percent. The titrating reagent used was ferrous sulfate which was standardized electrometrically by means of potassium permanganate; but the permanganate was standardized with sodium oxalate in the usual way. The

chromate may be titrated with ferrous sulfate, or the ferrous sulfate added to the chromate in excess, and the titration completed with permanganate and ferrous sulfate. (25)

(C.A. 11, 2567)

A method for determining chromium in steel in furnace tests, while the steel is held in a molten condition, has been devised. The chromium is oxidized by means of the bismutate method and then titrated electrometrically with ferrous ammonium sulfate and potassium dichromate. The method is not applicable to forged steels or those that have been heat-treated, or when chromium carbide is set free in more than small amounts while obtaining the solution. (49)

(C.A. 13, 1802)

Pendrixson titrated a potassium iodide solution with a potassium dichromate solution in a solution of sulfuric acid of at least 2N, by allowing sufficient time near the end-point for the reaction to reach completion. At least half an hour was required. One gram of the dichromate solution set free 0.006356 grams of iodine from the iodine solution, and the proportion of iodide to permanganate was one to 0.999; one gram of permanganate required 0.003366 grams of sodium oxalate. (61)

(C.A. 15, 5799)

In the determination of chromium and vanadium in ferrovanadium, these elements are oxidized by means of ammonium persulfate, and then titrated with ferrous sulfate in a hydrochloric acid solution. In a separate portion of the

solution, vanadium is oxidized to the quinquivalent condition by means of nitric acid which does not affect the chromium, and is then reduced by titrating with ferrous sulfate. (63)

(C.A. 15, 3955)

In the determination of chromium in ferrochromium, the sample is fused in an alkaline oxidizing flux, the excess of oxidizer is removed, and the solution acidified and titrated with ferrous sulfate. (64)

(C.A. 16, 37)

Owing to the hydrolysis of potassium chromate, it is not possible to neutralize chromous or chromic acid directly towards phenolphthalein; hence, potassium dichromate is not to be recommended as a standard for acidimetry (Compare with the electrometric methods). (65)

(C.A. 16, 1056)

Eppley and Vasburgh titrated potassium dichromate with ferrous sulfate and studied the effects of concentration of salts and acids on the reaction and end-point. The reverse titration of ferrous sulfate with potassium dichromate was also studied by them. These authors found that electrolyzing the platinum electrode a few minutes in sulfuric or hydrochloric acid, as anode, was an efficient method for cleaning it. The direct and reverse titrations, as stated before, agreed with each other. Dissolved air was found to have a negligible effect on this titration. (79)(C.A.16,3831)

Working with pure ammonium vanadate and potassium dichromate these authors titrated mixtures of solutions of these salts using standardized ferrous ammonium sulfate, and pro-

tecting the solutions with an atmosphere of carbon dioxide gas. In the mixture only one break occurs in the curve which corresponds to the known composition of the mixture. These elements may be determined in the presence of large amounts of iron. Vanadium is determined by a special method (see vanadium) and the chromium estimated by difference. (see also the abstract for the use of this method in steel analysis. (144) (C.A. 18, 3872)

Chlorine.- (11)*, (81), (69)*, (105), (116), (126)*, (129)*, (132)*, (136)*, (160), (163)*, (164)*

The electrometric method may be applied to the determination of chlorine by precipitation with silver or some other suitable reagent by means of which an insoluble chloride may be formed. The method is of importance for determining chlorine in low concentrations, or in the presence of a large excess of bromide or iodide. Chloride may be determined in concentrations as low as 10-20 milligrams of chloride per liter. (11) (C.A. 6, 722)

For the determination of chlorine, a known solution of silver, and solutions of iodide and potassium permanganate were used. In carrying out the determination, an excess of silver solution was added to a known weight of chloride solution, with stirring. The precipitate was then filtered through asbestos on a Gooch crucible into the titrating vessel. Sulfuric acid was then added to the solution, and also an excess of iodide solution of known concentration, and this excess of iodide was titrated with the permanganate

solution. The silver chloride must be filtered off as it would change largely to iodide upon the addition of the iodide solution; but the silver iodide does not interfere with the titration of excess silver solution by the permanganate. The results were satisfactory. (61) (C.A. 15, 3799)

In the determination of the available chlorine in bleaching powder two difficulties may be encountered. (1) Some chlorate may be reduced and estimated as hypochlorite. (2) Some chlorate may be formed from hypochlorite during the analysis. These difficulties may be overcome by using the electrometric method of analysis. As a comparison electrode an eight centimeter long glass tube was taken, the end of which was drawn out into a capillary and turned upward. The end of the capillary was stoppered with filter paper or with gelatin containing potassium sulfate. The tube was filled with potassium sulfate solution to which a little titrated hypochlorite solution was added or a drop of very dilute potassium iodate solution. Two platinum wires were used for the electrodes, one was placed into the hypochlorite solution to be titrated, and the other in the comparison electrode. The electrodes were connected through a millivoltmeter with high resistance, or through a galvanometer with suitable ballast resistance. The end-point was shown by a sudden drop of the galvanometer to zero. Excellent results were obtained with two methods: (1) The Penot method of titrating hypochlorite with an arsenite solution containing an excess of sodium bicarbonate, and (2) by the Pontius method of titrating

in alkaline solution with potassium iodide. (69)(C.A.15, 3052)

Willard and Fenwick titrated sodium chloride with silver nitrate by means of the bimetallic electrode system, cleaning the electrodes between each titration. The silver nitrate solution was prepared from pure silver and nitric acid. Two fine platinum thermocouple wires wound in loose spirals, and polarized with a 0.5 volt potential through a resistance of 100,000 ohms, comprised the electrode system. The theoretical figures of the reaction were obtained regardless of the direction of approach to the end-point. (105) (C.A. 17, 1397)

Willard and Fenwick also titrated chlorate ion with titanous sulfate, in a titrating vessel sealed with mercury, and the solution protected by an atmosphere of carbonic acid gas. The solutions affected by light were stored in bottles covered with black enamel paint, and provided with a siphon for removing the needed portions of the solutions. Either sulfuric or hydrochloric acid may be used to acidify the titrated solution. (116) (C.A. 17, 3306)

Chlorides may be titrated with mercuric nitrate using the mercury electrode, but not in the presence of bromides. (126)

(C.A. 18, 1799)

In the titration of bleaching powder solutions, with arsenious acid, good agreement was found between the electrometric and the ordinary titration method with iodo-starch paper as indicator. Evidence that chlorate vapors were not formed during the titration was found, which is contrary to the findings by Clareus. (129) (C.A. 17, 2545)

Silver chloride is more soluble in the presence of a protective colloid like gelatin, but this phenomenon has little effect on the titration of silver with a sodium chloride solution. Some medicinal silver preparations cannot be titrated with sodium chloride until the organic matter is destroyed by fusing with sodium peroxide; but they may be titrated with sodium sulfide. (132) (C.A. 17, 3003)

Sodium chloride was titrated electrometrically in the presence of 0.5 percent soluble starch, egg albumin, Witte peptone, boiled and raw milk, and ashes from the same for comparison. Dilute albumin and 5 percent peptone gave curves with no flat portion. With milk the curve was better, but showed an error of 1:30 as compared with the ash. (136)

(C.A. 18, 1960)

Muller worked out a method for titrating chloride ion, in sodium chloride, with silver nitrate using metallic electrodes of palladium, platinum, gold, mercury, silver, and carbon. Carbon and the metals forming easily soluble chlorides do not serve this purpose well. The mercury electrode gave the sharpest end-point. In case of the reaction between sodium chloride and mercurous nitrate, either platinum or mercury will serve as a metallic electrode. This author also makes use of the compensating electrode system in these titrations. (160) (C.A. 19, 1236)

For the titration of chlorous ion with sodium arsenite, W. D. Treadwell used a platinum electrode and a comparison electrode containing potassium sulfate and a titrated solution

of chlorous ion in a capillary tube. The salts, sodium sulfate, sodium bicarbonate, ammonium acetate, sodium chloride, ammonium chloride, sodium nitrate, or potassium nitrate in 0.2 M solutions can be used in place of the titrated solution in the comparison electrode. A reducing reagent gives readings above the normal, and an oxidizing reagent below the normal; but a 0.2 volt displacement does not seriously affect the results. The compensating method of A. Fischer may also be used to titrate chlorous ion. (163) (C.A. 19, 1829)

Iodium hyposulfite may be used to titrate solutions of soluble chlorites after adding an excess of potassium iodide to the sulfuric acid solution. Hypochlorous acid may be titrated with sodium arsenate solution with and without the addition of sodium bicarbonate. In a mixture, the chlorous ion may be titrated first with arsenate and the hypochlorous ion afterwards as indicated above. (164) (C.A. 19, 1829)

Cobalt.- (127)*, (140)*

This method of determining cobalt by electrometric titration depends upon addition of an excess of potassium cyanide and the titration of the excess cyanide with silver nitrate. With an excess of cyanide cobalt is supposed to form a quadri-valent anion. The ratio of cobalt to cyanide was found to be 1:5 both in the presence and absence of air. The titrations were made with a silver electrode. In the absence of ammonia the results were low, and the sudden change in potential was at -0.290V.; but in the presence of ammonia the results were

accurate and the potential change was greatest at $-0.320V$.

(127)

(C.A. 17, 942)

Cobalt can be titrated successfully with potassium cyanide when silver electrodes are used and the solution protected from the air. The potassium cyanide solution should be standardized against a known cobalt solution, and the unknown cobalt solution should be added to the standardized potassium cyanide solution. (140)

(C.A. 18, 2662)

Cadmium.- (114)*

It was found possible to titrate cadmium with sodium ferrocyanide to form cadmium ferrocyanide. In titrating cadmium with potassium ferrocyanide the ratio of cadmium to ferrocyanide was found greater than 1:1. When cadmium and zinc are both to be determined in the same solution, it is advisable to titrate the zinc with potassium ferrocyanide, and then use the empirical factor recommended by Hedrich (Muller, Die Uectrometrische Massanalyse) for computing the cadmium content in the next titration. (114)(C.A.17,2689)

Cerium.- (175)*

To the cerium solution to be titrated, add about three-quarters of the necessary amount of potassium ferricyanide, and expell the air from the solution with carbon dioxide gas. Then add 50 percent of potassium carbonate solution, with stirring, until the solution contains about 30 percent of carbonate ion. The titration is conducted in the usual way with a platinum electrode.

The inflection of the titration curve depends upon the concentration of the potassium carbonate, being shifted towards the negative side as the concentration increases. The titration was conducted in an alkaline medium in order to avoid the precipitation of cerium salts. The method gave exact results with several specimens of cerium metal and alloys. (175) (C.A. 19, 2922)

Formaldehyde.- (148)*

Silver nitrate solution reacts with aldehyde to form silver and formic acid quantitatively, if at least three times as much sodium carbonate is present than required to neutralize the three molecules of acid from one molecule of aldehyde. An approximate determination may be made by adding 25 cc. of saturated soda solution to one cc. of aldehyde, and titrating with 0.1N silver solution, using a platinum electrode, until the e.m.f. against the calomel electrode is 0.2 plus volts. Then mix five cc. more of the standard silver nitrate solution than was required for the preliminary determination with one cc. of aldehyde and 25 cc. of the saturated soda solution. After five minutes add dilute sulfuric acid until the solution is acid to methyl orange, and titrate the excess silver with 0.1N potassium chloride using a silver electrode. Satisfactory results can be obtained. (148)

(C.A. 19, 452)

Gastric Juices.- (24)*

A special electrode is used consisting of a tube ending

in a glass bell. A side tube is fused to the glass bell, which contains mercury, and has a platinum wire fused into the lower end which dips under the liquid to be titrated. Hydrogen is passed into the former tube and a connection is made between the liquid to be titrated and the other half-cell through an inverted test tube containing a gel of saturated potassium chloride and 3 percent agar, connected with a saturated potassium chloride solution, and then with a calomel half-cell. The electrometric measurement of hydrogen ion concentration is recommended for determining free acid in gastric juice. Combined hydrochloric acid is determined by titrating to pH 6.5. (24) (C.A. 11, 2213)

Indigo.- (99)*

"If a sample of indigo is dissolved in concentrated sulfuric acid and the resulting indigosulfonic acid diluted so that it is 0.05 - 0.01N with respect to indigo and 0.2 - 0.5N with respect to sulfuric acid, passage through a cadmium reductor will result in the formation of indigo white which can be titrated electrometrically with ferric chloride solution" (99) (C.A. 17, 39)

Iodine.- (11)*, (44)*, (53)*, (59), (62)*, (67), (105), (116), (126)*

The electrometric method may be applied to precipitation analysis and hence to the determination of the halides by precipitation with silver compounds. Determination may be made on solutions as dilute as 10 - 20 milligrams of chloride per

liter, or smaller quantities of bromide or iodide. Iodide may be titrated in the presence of large quantities of bromide or chloride. The method may be applied to the determination of iodide in urine. (11) (C.A. 6, 722)

Twenty-five cc. of 0.1N potassium iodide and 5 cc. of 3 percent potassium iodate may be titrated with 1N hydrochloric acid added to 0.5 cc. at a time. The theoretical quantities were obtained. The presence of bromide up to four times the iodide does not interfere, although longer time is required to make the readings. Chlorides interfere with this determination. A solution of 0.01N potassium iodide may be titrated but about 30 seconds time should be allowed for each reading. (44) (C.A. 13, 2167)

The oxidizing power of the halides stands in the order iodine, bromine, chlorine, and in the presence of a strong oxidizing agent they are liberated from their salts in the order given, and there is a sharp change in potential between iodine and bromine. Potassium dichromate, potassium bromate, and potassium iodate may be used. Hence, iodide may be determined in the presence of considerable amounts of bromide, and in the presence of large quantities of chloride by the oxidopotentiometric method in the presence of hydrochloric acid. (53) (C.A. 14, 3204)

In place of the ordinary potentiometer, Hendrixon used a rheostat coil of 169.45 ohms resistance having a graduated contact beam. 229 additional ohms resistance were added to

the end of the coil not traversed by the contact slide. This made the scale one meter long in effect, and each millimeter equaled a potential of two millivolts. This improvised potentiometer was used in connection with a galvanometer having a sensitivity of 106 megohms. A three necked Woulff bottle served as a titrating flask, the necks holding the calomel cell, platinum electrode, and carbon dioxide tube, respectively, with an extra hole bored in the flask, or cork, to admit the tip of a buret. Weighing burets were used in some cases. Carefully prepared iodine was titrated with potassium permanganate solution, standardized with sodium oxalate, in about 1N solution of sulfuric acid. Chloride and bromide in the titrating solution prevents accurate determinations; but it was found that chloride equivalent to the iodide, and bromide equivalent to 25 percent of the iodide, could be present in the titrating solution and not interfere with the accuracy of the results. This reaction was also carried out by adding an excess of potassium dichromate and titrating the excess with potassium permanganate. (59) (C.A. 15, 639)

Kolthoff made some observations on the titration of iodides by means of potassium permanganate, and found that if this reagent is added drop by drop near the point of equivalence, and E determined for each addition, this point is made known by the relative variation of the potential. The maximum potential corresponds to the point of equivalence. The method is exact when the determinations are made in a sulfuric acid medium of at least 0.12N. Iodide may be determined in the

presence of twice as much bromide and five times as much chloride although the fall of potential at the equivalent point is lowered by their presence. (62) (C.A. 15, 3799)

Hendrixon titrated potassium biniodate with potassium iodide in excess and determined the excess of iodide with potassium permanganate. This investigator also studied the effects of hydrochloric acid and sulfuric acid on the reaction. The iodide solution was standardized by means of thiosulfate solution which had first been standardized by resublimed iodine. The permanganate solution was standardized by means of sodium oxalate. The strength of the iodide solutions was 0.05N and also 0.02N.

Iodide, in sulfuric acid, may be determined in the presence of chloride up to a concentration of 0.1N in the titrated solution by means of permanganate; but hydrochloric acid can not be substituted for sulfuric acid, except in low concentrations and within narrow limits of concentration.

Iodide, in sulfuric acid, may be titrated directly with iodate. (67) (C.A. 15, 1668)

Willard and Fenwick showed that iodide could be determined by oxidizing it to iodine cyanide with potassium permanganate in hydrocyanic acid solution. The titration was made in 100 cc. volume of solution which contained 15-20 cc. of hydrochloric acid and five cc. of a 10 percent potassium cyanide solution. This method was applicable in various concentrations of chloride ion, and in moderate concentrations of bromide ion. The authors claim, however, as a more accur-

ate method, the oxidation of iodide to iodate by excess of alkaline hypobromite, and titrating the excess of hypobromite with arsenite. Bromide or chloride does not interfere with this last reaction, and either the bimetallic electrode system or the monometallic electrode system may be used. The hypobromite solution was made by pouring 40-50 grams of bromine, slowly, into a solution of about 30 grams of potassium hydroxide in 250 cc. of water at about zero temperature, then diluting to five liters. This solution was standardized with a 0.1N solution of sodium arsenite prepared by weight from pure arsenous oxide dissolved in sodium carbonate. The actual operation of the method was as follows: A weighed portion of a standard potassium iodide solution was made alkaline with one gram of potassium hydroxide, an excess of the standardized hypobromite solution was added, the whole diluted to 100 cc., allowed to stand for five minutes and the excess of hypobromite titrated with the standard arsenite solution. (105)

(C.A. 17, 1397)

Hendrixson also titrated iodate with titanous sulfate solution. The 0.05N iodate solution was standardized with iodide and thiosulfate, and the titanous sulfate solution with permanganate and dichromate. The volume of the titrated solution was about 300 cc. and the acidity between 1.0N and 2.0N sulfuric acid. Hydrochloric acid was found to be unsatisfactory. The correct end-point was found by multiplying the volume of titanous solution at the first fall in voltage by the factor 1.2 which is in accord with the theory.

the strength of the titanous sulfate solution was 0.05N x
1.727. (116) (C.A. 17, 5006)

Iodides, at very great dilutions, can be titrated accurately with mercuric chloride and the mercury electrode. Large amounts of bromide interfere with this titration. (126)
(C.A. 18, 1799)

Iron (Ferrous and ferric).- (6), (14), (17), (28), (59)*, (45), (49)*, (87), (89)*, (119)*, (124)*, (125)*, (144)*, (153), (157)*, (165)*

As shown by the large number of references, considerable work has been done on the determination of iron by electro-metric methods. Iron salts are also extensively used as titrating reagents.

Peters was one of the first investigators to work with oxidizing and reducing cells from the standpoint of quantitative determination of ions; and his work was concerned chiefly with the ions of ferrous and ferric compounds. He developed the formula commonly used as the theoretical basis for oxidizing and reducing reactions, and established the relationship between ferrous and ferric ions in solution. (See the part of this thesis dealing with the theory of electro-metric titrations). The electrodes used by Peters were the Weston electrical element and metallic electrodes of platinum, gold plated platinum, and platinized platinum. Peters also studied the effects of chlorides and fluorides on the oxidation potential of ferrous and ferric ion, and came to the conclusion that the changes in potential observed by him

were due to the formation of complex ions by the interaction of the substances present in the titrated solutions. (6)

Forbes and Bartlett titrated dichromate ion with ferrous ion. (See under chromium, 14)

Tiegel titrated potassium dichromate solution with ferrous sulfate using an automatic, electrically controlled buret. (17) (C.A. 9, 898)

The electrometric method was used by Ferguson for determining small quantities of iron in glass sand. The sand was first decomposed in platinum by means of sulfuric acid and hydrofluoric acid, and the residue ignited with iron-free potassium pyrosulfate, and the cake dissolved in dilute sulfuric acid. The iron was then reduced with stannous chloride and the excess of stannous chloride titrated with dichromate in a platinum-calomel electrode cell. The purity of the reagents, and of the platinum were of great importance in this determination. (28)

Ferrous sulfate was titrated with potassium dichromate in both hydrochloric and sulfuric acid solutions; with potassium bromate in hydrochloric acid solution; and with potassium permanganate in both hydrochloric and sulfuric acid solutions. Potassium dichromate and potassium bromate gave satisfactory results. Potassium permanganate was more satisfactory in hydrochloric acid solution than in solutions of sulfuric acid. A platinum electrode and the calomel half-cell were used in this work. (39) (C.A. 14, 3204)

The work of Hastetter and Roberts on the electrometric determination of ferrous and ferric ion has been widely quoted. They studied the effects of different metallic electrodes used with the calomel half-cell; also the effect of varying the concentrations of the titrating reagents, and of the acid solutions; and they combined the various necessary pieces of titrating apparatus into one unit which they called the titrating head.

The titrating head.- This apparatus consists of a closed glass tube of suitable size, through the bottom of which is passed the salt arm of the calomel cell, the delivery tube of a buret, and the platinum electrode which passed through a jacket tube with a side arm to admit carbon dioxide gas to the flask. This titrating head was made to fit over an Erlenmeyer flask, the salt arm of the calomel cell and the platinum electrode being long enough to reach the bottom of the flask. By means of this form of titrating head, the solutions under investigation could be heated to the desired temperature, and also protected against oxidation by the oxygen of the air by an atmosphere of an inert gas placed over the solution in the flask.

The end-points were checked in two ways, (1) by balancing known quantities of two reagents, and (2) by checking against the pink color of a permanganate solution as used in the common method of volumetric analysis.

Electrodes.- The kind of electrodes used, and the inverse

order of their suitability to the purpose was as follows: Palladium, 60 percent gold-40 percent palladium, gold, platinumized platinum, bright platinum. The palladium electrode did not show a noticeable change in voltage at the end-point. A small, bright platinum electrode of small surface area was found to be the best kind of electrode. The electrodes must be carefully cleaned, and the inert gas used to protect the solutions against oxidation, must not come in contact with them. A calomel half-cell was used with these electrodes.

Temperature.- Temperature is specific for certain reactions, and sudden changes in temperature should always be avoided.

Acidity of the titrated solution.- Sharp end-point voltage deflections were obtained over a wide range of acidity with sulfuric acid (17 to 67 percent). Nitric acid cannot be used because of its oxidizing power. Hydrofluoric acid, in the presence of hydrochloric acid and sulfuric acid, was not detrimental to the titrations. In using 0.001N dichromate, the acidity and volume of the solution became important factors. It was found that small volume of solution with 25 percent concentrated sulfuric acid, and 0.001N or 0.0005N dichromate also in 25 percent sulfuric acid gave sharp end-points.

The titration of ferrous iron in the presence of various amounts of ferric iron gave definite end-points, but the range of the difference of potential at the end-points was shortened. The method can be used to determine ferrous iron in ferric

compounds. Ten grams of the ferric salt was dissolved in water in an atmosphere of carbon dioxide, and an equal volume of concentrated hydrochloric acid added to the solution; after which the titrating head was put into place and the solution titrated with 0.01N potassium dichromate. This method is also applicable to determining small quantities of ferrous iron in other substances.

Ferric iron was also successfully titrated with stannous chloride and the method adapted to the determination of small amounts of ferric iron in ferrous salts.

Since stannous chloride can be titrated with dichromate solution, a method for determining the total iron in a solution is as follows: The iron solution was first completely reduced with stannous chloride solution in slight excess, as shown by the voltage; and then titrated with dichromate. The first end-point shows the end of the oxidation of the stannous chloride, and the second one, the end of the oxidation of the reduced iron. The volume of the solution used between these two points was taken as a measure of the iron present. The method has been used on glass sand, sodium and potassium salts, barium carbonate, zinc oxide, borax and boric acid, and the oxides of lead; and can be used for determining iron in any substance not reduced by stannous chloride.

This method for iron may also be used to determine blanks, to make corrections necessary to be applied to these reactions when carried out with permanganate or color indicators under different conditions, and for various purposes. (45)(C.A.13,2319)

Ammonium ferrous sulfate was used to titrate chromium in steel analysis. This reagent was added in excess to the prepared sample, and the excess titrated by means of potassium dichromate in a cooled, sulfuric acid solution. (49) (C.A. 13, 1802)

Gustavson and Knudsen titrated iron in the presence of uranium and vanadium. Ten cc. of a solution containing 41.1 milligrams of iron as ferrous sulfate, 18.7 milligrams of vanadium as vanadyl sulfate, and 121.0 milligrams of uranium as uranyl acetate was diluted to 250 cc. and five grams of zinc added. Sulfuric acid was then added and the whole boiled for 30 minutes, filtered through cotton, and titrated while hot with permanganate solution in an atmosphere of carbon dioxide gas. Four cc. of sulfuric acid was added at the start, and after the titration has proceeded to the point of the second voltage deflection, four cc. more were added. This method of adding the acid proved highly successful, as it provided for a sharper inflection at the end-points. It was possible by this method to calculate the quantities of iron, vanadium and uranium present in a mixture of salts of these metals. (87) (C.A. 17, 507)

The reducing power of ferrous solutions is greater than that of vanadyl solutions. A mixture of these solutions may be analyzed by means of potassium permanganate. The ferrous iron is oxidized first and the second potential deflection is due to the oxidation of the vanadium. The temperature should be raised to 70° for the vanadium end-point. (89)

(C.A. 17, 1401)

If potassium permanganate is added to a ferrous iron solution in the presence of dilute sulfuric acid, the iron is oxidized to the ferric state and the manganese reduced. If potassium fluoride is then added to the solution and the titration continued, a second end-point is obtained when the manganese is in the tervalent condition. In case the original solution contained no manganese, the volume of the permanganate used in the second step of the titration will be 1.2 times as large as that used in the first step. About 125 cc. of solution was used, about 0.5N in sulfuric acid, and seven grams of potassium fluoride with five cc. of 2N sulfuric acid were added for the second part of the determination. Fluoride cannot be present at the start of the titration. (119) (C.A. 18, 363)

Ferric chloride equivalent to a 3 M solution was titrated with N sodium hydroxide by means of the oxygen electrode and saturated calomel cell. The curve was continuous, showing that iron oxychloride does not exist. (124)

(C.A. 18, 1099)

This method is an improvement over one previously given (119). A mixture of ferrous and manganous solution is first titrated, in a platinum dish with potassium dichromate until the potential against a normal electrode is 0.57 volts, which corresponds to the complete oxidation of the iron. Then heat the solution to 80°C, add seven grams of potassium fluoride, and continue the titration with permanganate until the manganese is oxidized. A possibility is indicated of titrating

iron, vanadium, uranium, and manganese in a single operation.
(125) (C.A. 18, 1628)

Several references to the subject are cited in this article. Vanadium can be oxidized by means of permanganate to three states of oxidation. Vanadic acid can be determined in the presence of iron but not in the presence of chromic acid. Ferrous ammonium sulfate is a good reagent for determining vanadium. (144) (C.A. 18, 3571)

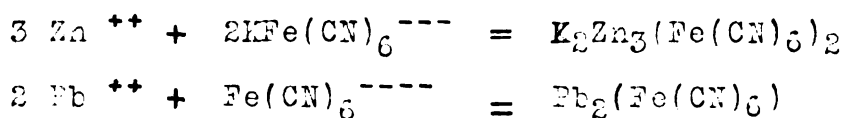
The oxidation potentials of ferrous and ferric salts were studied by Carter and Cleaves using both concentrated hydrochloric and phosphoric acid. Platinum foil electrodes and electrodes made from glass coated with platinum gave concordant results. The logarithmic relationship of Peters was substantiated. The oxidation potential decreases with increasing concentration of hydrochloric acid. This decrease is linear with the normality of the acid between 1N and 10N. The variation in the diffusion potential does not account for this change in voltage. Results were nearly the same with the phosphoric acid. (155) (C.A. 19, 945)

Ferric salts may be titrated at room temperature with titanous chloride, but too much reagent is used unless sufficient time is given for the reaction when near the endpoint. Ferric ions can be titrated in the presence of cupric ions and also quinquivalent antimony ions, with titanous chloride. When copper is present, meconic acid is used as an external indicator. (157) (C.A. 19, 450)

Ferrous iron may be titrated with potassium dichromate in a strongly acid hydrochloric solution. Magnetites not decomposed by sulfuric-hydrofluoric acid treatment are decomposed by hydrochloric acid. Adding excess of stannous chloride to a ferric iron solution and titrating back with dichromate or iodine is better than the direct titration. Titanium in the solution does not interfere with the reduction of ferric iron by means of stannous chloride. (165) (C.A. 19, 1832)

Lead.- (128)*

The platinum-calomel cell system was used in this research. Lead and zinc, in the presence of one another, may be determined electrometrically by two titrations; one for total lead and zinc, and one for zinc alone. For the sum of both metals, to every 100 cc. of solution one cc. of potassium ferricyanide was added and the titration made with potassium ferrocyanide at 75°. The reactions are:

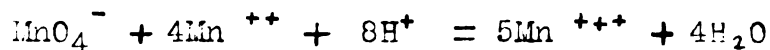


The zinc is precipitated first. There are two breaks in the titration curve, the first at 0.54 plus volts, and the second at 0.19 plus volts. Three to five minutes time should be allowed near the first break for the potential to become constant. If the lead is first precipitated with dilute sulfuric acid, then the zinc may be determined alone, and the lead quantitatively estimated by difference in the titrating solution used for each titration. (128)(C.A.17, 943)

Manganese.- (30), (68)*, (117)*, (119)*, (125)*

Kelley, Spencer, Illingworth, and Gray studied the electro-metric method for manganese in connection with the determination of this element in steels, and claim that the presence of chromium and vanadium is not detrimental to the titration. Mercurous nitrate was used as the reducing reagent and this solution was standardized by means of permanganate. The oxidation of the manganese may be done by either of two methods; (1) Solution of the steel in nitric acid and oxidizing with ammonium persulfate and silver nitrate; or (2), the oxidation may be carried on by means of sodium bismuthate. 200 cc. volumes were used for titrating, containing 50 cc. of sulfuric acid (sp. gr. 1.58). The temperature should not be above 40°. Nitrous acid interferes with the titration, but nitric acid does not. (30) (C.A. 12, 458)

A reaction which may be taken as the basis for an electro-metric oxidation method for manganese is as follows:



In the presence of F^- this reaction proceeds with the quantitative formation of a complex ion MnF_5^{--} . The neutral or slightly acid manganese solution, containing not more than 0.2 grams of manganese, is diluted to 300 cc. and 5-10 cc. of sulfuric acid (1:7), and 5 grams of ammonium fluoride added. The titration is carried out with 0.1N potassium permanganate in the cold. The presence of ferric iron, chlorine, or nitrates do not interfere with the quantitative nature of this reaction. (68) (C.A. 15, 2800)

The Volhard titration method for manganese was carried out electrometrically, in which the manganese is oxidized by means of permanganate. About seven minutes time was required to establish the end-point. Best results were obtained in a volume of 100 cc. 0.4N with sulfuric acid, and containing eight grams of potassium fluoride. (117) (C.A. 17, 3306)

According to Muller and Wahle the method described in the preceding reference may be applied to the determination of iron and manganese together. These investigators used 125 cc. of solution 0.5N in sulfuric acid and titrated with permanganate to the iron end-point, then they added seven grams of potassium fluoride, and five cc. of 2N sulfuric acid for the second part of the titration. If fluoride is present at the start, there will be some atmospheric oxidation of the iron. (119) (C.A. 18, 363)

This reference is supplementary to the preceding one. The change in the method is as follows: Place the reduced iron and manganese in a platinum dish, and titrate with potassium dichromate until 0.57 volts are obtained. This potential corresponds to the complete oxidation of the iron. Then heat to 80°, add seven grams of potassium fluoride, and finish the titration with potassium permanganate. (125)

(C.A. 18, 1628)

Molybdenum.- (108)

Willard and Fenwick used their polarized, bimetallic electrode system composed of platinum electrodes to determine

the end-point in the reduction of molybdic acid to a salt of the pentavalent molybdenum. The reaction was found to be rather slow for ideal results. A 5 - 10 percent solution, by volume, of hydrochloric acid was found to be the best for this determination. Sulfuric acid was found to be unsatisfactory. The reduction was carried out by means of titanous sulfate standardized with ferric sulfate prepared from electrolytic iron; and the strength of the titanous solution was 0.05N. A solution of sodium molybdate of approximately 0.017N was titrated with the titanous sulfate solution. The authors state that the titanous solution should be standardized against a molybdate solution. The method is not highly accurate.

Ammonium phosphomolybdate was dissolved in ammonia, filtered, acidified and titrated with standard titanous sulfate. Phosphoric acid may be used provided the solution is titrated hot. The method is highly recommended. Tungsten does not interfere with this method. (108) (C.A. 17, 1766)

Mercury.- (135)*, (161)*

Mercuric ions in a nitric acid solution react with ammonium cyanide to form the insoluble mercury cyanide, and a slight excess of cyanide gives a red color with ferric iron. This reaction can be used for the titration of mercury in the absence of halides or mercurous salt. The mercury can be dissolved in nitric acid, treated with an excess of potassium permanganate, and the excess of permanganate removed with ferrous iron, after which the solution may be titrated electro-

metrically with standard ammonium cyanide. The mercury electrode-calomel electrode system was used in these experiments. (155) (C.A. 18, 1959)

This reference contains a review of the literature on the use of mercuric salts in electrometric titration methods. The difficulty experienced in the use of mercury salts with the mercury electrode is the reduction of metallic mercury on the electrode. Mercurous chlorate is considered the best titrating mercury reagent. The salt is prepared by heating a weighed amount of oxide of mercury with the equivalent amount of concentrated perchloric acid, free from chlorine if possible, and excess of mercury in a flask under a condenser until in a test portion, after the addition of excess chlorine, no mercury can be detected in the filtrate. Chlorine and bromine may be determined accurately with this reagent. In titrating iodides, cyanides and thiocyanates, solutions of these compounds should be run into the mercury chlorate solution. Chlorine may also be determined with mercuric chlorate as well as with mercurous chlorate. The determination of mercuric and mercurous ions simultaneously with chloride was not successful. (161) (C.A. 19, 1387)

Nitrates.- (137)*

If a nitrate, in the presence of hydrochloric acid, is treated with a ferrous salt solution, ferric iron will be formed which can be titrated with a standard titanous chloride solution in an atmosphere of carbon dioxide gas. The method

is rapid and accurate. The sign of the potential changes at the end-point. (137) (C.A. 18, 1960)

Nitrites.-

Hendrixson determined nitrous acid by adding to it a 5 - 10 percent excess of a standard potassium permanganate solution, and then an excess of a standard potassium iodide solution, and titrating the excess of iodide with the permanganate solution. The titrations were made in a 1.5N sulfuric acid solution. The method was found to be highly accurate. (61) (C.A. 15, 3799)

Nickel.- (85)*, (140)*

Muller and Lauterbach determined nickel with potassium cyanide and silver nitrate. The 0.1N silver nitrate solution was standardized electrometrically with potassium cyanide. The standard cyanide solution was added to 10 - 20 cc. of the nickel solution in excess, and this excess titrated with the silver nitrate solution. (85) (C.A. 17, 249)

Nickel and cobalt may be titrated together with a solution of potassium cyanide and with the use of silver electrodes. The unknown nickel and cobalt solution should be added to the cyanide solution after standardizing the cyanide solution by means of a known nickel-cobalt solution. (140) (C.A. 18, 2662)

Reducing Sugars.- (113)

This reference describes the use of the potentiometer

method for determining reducing sugars quantitatively by means of reduction with Fehling's solution. The Fehling's solution was standardized against pure dextrose. The "B" part of the Fehling's solution was made up with only one-half of the quantity of sodium hydroxide as recommended in order to get a more distinct end-point. In the actual titrating procedure, equal portions of the "A" and "B" solutions (10 cc. of each) were mixed and 50 cc. of distilled water added. The mixture was then brought to the boiling point, and the sugar solution added until the end-point of the reaction was reached. The results were considered as being satisfactory. (113) (C.A. 17, 2545)

Silver.- (10)*, (67), (120)*, (132)*

Dutoit and VonWeisse used a silver electrode in their studies on the practical application of the properties of concentration cells to analysis by precipitation. They also called attention to the value of silver salts as precipitants in volumetric analysis. (10) (C.A. 6, 722)

Silver nitrate solution is commonly used as a reagent to determine the halides quantitatively by the potentiometric method. The process can be reversed and silver ion may be determined by means of potassium iodide solution; or in some cases, potassium cyanide is preferred as a reagent for silver. Hendrixson determined silver by means of an excess of potassium iodide and titrating this excess with permanganate. A solution of silver sulfate containing 0.0021573 grams of silver per gram

of solution was used. The permanganate solution was standardized with sodium oxalate and the potassium iodide solution with the permanganate solution. Nitric acid may be used on concentrations up to 2N. A solution of silver nitrate prepared from pure silver and nitric acid contained 0.004714 grams of silver per gram of solution, was also used, and titrated by the method without filtering off the precipitate. The results were satisfactory. The author also calls attention to the value of pure metallic silver for use as a standard to make up known solutions of iodide and permanganate. (67)

(C.A. 15, 1668)

Silver can be titrated accurately with potassium cyanide. Silver and copper can be determined simultaneously with potassium cyanide provided that the silver cyanide first formed is filtered off when its end-point has been determined; then by adding sodium bisulfate the copper can be determined at 70° with the same reagent. (120)

(C.A. 18, 640)

The presence of gelatin as a protective colloid has little effect upon the electrometric titration of silver with sodium chloride solution, although the solubility of the silver is increased. Some medicinal silver preparations cannot be titrated until the organic matter has been destroyed by fusing with sodium peroxide, or by titrating directly with sodium sulfide. (132)

(C.A. 17, 3003)

Sulfur.- (84), (95)*, (106), (126)*, (155)*

Hendrixson and Verbeck attempted to titrate sulfuric

acid with permanganate and found that only about 90 percent of the sulfurous acid was oxidized to sulfuric acid. A weighed quantity of standard permanganate solution was titrated with a sodium sulfite solution in an acid concentration of about 1N sulfuric acid at the end of the titration. The solution was protected from oxidation by means of carbon dioxide gas. Permanganate solution was used with large excess, slight excess, and to the end-point; and the excess of permanganate titrated with potassium iodide. The large excess of permanganate was the most efficient, oxidizing 93 percent of the sulfite to sulfate. (84) (C.A. 17, 39)

Free sodium sulfite in a sulfur black dye bath may be determined to an accuracy of 0.5 percent by titrating with iodine and sodium thiosulfate. By a pipet method the iodine is allowed to react with the dye solution for one minute, and then the thiosulfate is added in excess and back-titrated with more iodine. (95) (C.A. 16, 3208)

Willard and Fenwick titrated sodium sulfide solution with an ammonical silver solution. The change of e.m.f. at the end-point was great. The sodium sulfide solution was made by dissolving 9 to 10 grams of hydrogen sulfide in a solution of 96 grams of sodium hydroxide and diluting to six liters. A 0.05N silver nitrate solution containing an excess of about 30 cc. of 28 percent ammonium hydroxide per liter, and standardized gravimetrically by precipitation of chloride, was used as the titrating solution. The addition of more sodium or ammonium hydroxide was without effect in the end-point.

presence of sulfite, thiosulfate, and sulfate was practically without effect, but slightly decreased the quantity of silver required for the titration. The presence of chloride reduces the quantity of silver required somewhat more than does the presence of sulfite or sulfate. The method is applicable to the determination of sulfur in steel by first converting it to hydrogen sulfide and then titrating with ammonical silver solution. (106) (C.A. 17, 1398)

Sulfides can be determined in dilute solution with mercuric chloride, by means of the mercury electrode, and in the presence of sodium hydroxide. The effectiveness of this method is diminished slightly in the presence of salts of divalent ions. Silver nitrate is a better reagent for determining sulfides in concentrated solutions, but in dilute solutions the results are too low. The complex ion mercury thiosulfate is formed at the potential break in the titration of thiosulfate solutions. Sulfide and thiosulfate can be titrated in the same solution with mercuric chloride, and at the neutral point. (126) (C.A. 18, 1799)

A solution of a soluble sulfate may be treated by means of a solution of a lead salt in excess and the excess determined by electrometric titration with 0.1N potassium ferrocyanide. (135a) (C.A. 18, 1626)

Selenium.- (109)

Willard and Fenwick determined selenium quantitatively in selenious acid by titrating with titanous sulfate in a cold hydrochloric acid solution saturated with sodium chloride,

and using the bimetallic electrode system. Moderate amounts of sulfuric acid had no harmful effects, and the reduction is independent of the presence of iron. The reduction of copper and selenium by titanous sulfate is selective and both may be determined in the same solution. (109) (C.A. 17, 1766)

Tin.- (147)

Fleysher titrated stannous chloride alone, and in mixtures with potassium dichromate in hydrochloric acid solution; and he also titrated antimonous and stannous chlorides together with dichromate solution, after first adding an excess of mercuric chloride. A platinum foil-calomel electrode cell was used. The titrating solutions were protected by means of an atmosphere of carbon dioxide gas. The reducing solutions were prepared by dissolving pure tin and antimonous oxide in dilute hydrochloric acid. Mohr's salt was used to standardize the dichromate solution. The values for the solutions are as follows: stannous chloride, 0.2020N; dichromate, 0.1N; antimonous chloride, 0.09893N. The titrations were made at room temperature and with constant stirring. (147)(C.A.19,451)

Titanium.- (72)*, (83), (99)*, (146)*

By means of cadmium powder used in a Jones' reductor, titanium was satisfactorily reduced in titanium sulfate solutions. This reduced titanium was titrated with potassium permanganate with good results in sulfuric acid solutions containing 0.9 to 18.8 grams of sulfuric acid to 10 cc. of

a 1 to 10 titanium sulfate solution. There was less neutralization of the acid than when zinc was used in the Jones' reductor. Iron and titanium was reduced together in the cadmium reductor and titrated electrometrically with permanganate solution. (72) (C.A. 15, 5041)

Hendrixson and Verbeck used the electrometric method to investigate methods of accurately standardizing titanous solutions. The titrations were carried on with titanous sulfate in sulfuric acid solution protected by an atmosphere of hydrogen. 50 cc. of about 0.1N ferric alum made up to 150 cc. with dilute sulfuric acid was washed first with carbon dioxide gas; the electrodes (platinum calomel) were then inserted and the titanous sulfate solution added to a liberal excess of the ferric alum solution, and this excess of ferric alum titrated with 0.05165N permanganate solution. The permanganate solution was also replaced with a 0.05N dichromate solution. Titanous sulfate solutions may be accurately standardized by titrating them into standard permanganate or dichromate solutions. Both methods were found to be accurate. (83)

(C.A. 17, 38)

Titanium may be titrated in the presence of iron by first reducing with cadmium powder in a Jones' reductor tube, and then titrating with permanganate or ferric chloride solution. It is a good plan to add some sodium fluoride to the solutions being titrated. When the titanium content is low as compared to the iron, reduce the iron with sulfurous acid, add ammonia, and filter off the precipitate of titanic acid

which will be contaminated with some ferric hydroxide, reduce the titanium with cadmium and titrate with ferric chloride.

(99)

(C.A. 17, 59)

Zotthoff made quite a complete study of the reducing action of titanous solutions, and found that the equation $C_H = 0.05 + 0.058 \log. (Ti^{IV})(H^+) / (Ti^{III})$ holds at 18°. In this paper are given methods for preparing pure titanium chloride crystals; for detecting iron as an impurity in titanium solutions; for standardizing the solutions; and for the estimation of dichromate, vanadate, molybdate and iodate. Directions are also given for estimating some oxidizing agents when present together. Details of these methods are not given in the abstract. (146)

(C.A. 19, 449)

Uranium.- (75), (87), (99)*, (122)*

Ewing and Eldridge successfully titrated trivalent uranium to the tetravalent form and then to the hexavalent condition; both with potassium permanganate in sulfuric acid solution, and with potassium dichromate in hydrochloric acid solution. The method was also used to titrate uranium in the presence of iron where three end-points were obtained. The uranium solution was standardized by evaporation and igniting to uranium oxide (U_3O_8), one cc. containing 0.0151 gram. The permanganate solution was standardized with sodium oxalate and was 0.1011N; and the dichromate solution with iron ore and it was 0.09064N. A closed platinum-calomel electrode cell was used which admitted the electrodes, buret, stirrer, and a Jones' reductor tube used for reducing the uranium

solutions by means of zinc directly before titrating them.

A new form of platinum electrode was used by the authors which was made by sealing a large platinum wire into the end of a glass capillary tube and grinding the exposed end flush with the end of the glass tube. This electrode was kept bright by rubbing it across carborundum paper before each determination.

The solution proportions used for making the titrations were 10 cc. of the uranium solution and 40 cc. of a sulfuric acid solution containing two cc. of concentrated sulfuric acid per 90 cc. of solution. After warming to 80-90°, the air was removed by carbon dioxide gas, and the solution poured slowly through the reductor tube which was then rinsed with 50 cc. of the sulfuric acid solution, and the reduced uranium solution was titrated with permanganate. The iron-oxidation end-point is last in the series when iron is present. The titration may be made with dichromate in hydrochloric acid solution. The sulfuric acid concentration should be less than two cc. per 100 cc. (75) (C.A. 16, 2459)

Gustavson and Knudson used the electrometric method to determine uranium in the presence of vanadium and iron. The common form of apparatus was used, and the solutions were protected by means of carbon dioxide gas. When compared with platinum foil, a platinum wire electrode was found more suitable for this titration. The elements were reduced with zinc and titrated in a sulfuric acid solution with potassium permanganate. For titrating uranium in the presence of iron,

the optimum concentration of sulfuric acid was found to be five cc. of concentrated acid in 250 cc. of solution. When uranium, vanadium, and iron were determined together, it was found best to add the acid in two portions of four cc. each to the 250 cc. of solution. (87) (C. A. 17, 507)

Uranium may be reduced in a cadmium reductor and titrated with potassium permanganate on the basis of the equation:

$$5\text{U}^{++++} + 2\text{MnO}_4^- + 2\text{H}_2\text{O} = 5\text{UO}_2^{++} + 2\text{Mn}^{++} + 4\text{H}^+$$
 The results are better than when the uranium is reduced with zinc, and also when the reduced solution is caught in an open beaker. (99) (C.A. 17, 39)

Uranium and iron can be titrated electrometrically in the same solution, the first break in the titration curve shows the oxidation of uranium from a valence of four to one of six, and the second break shows the oxidation of the iron. These titrations are all carried out with potassium permanganate. When uranium and vanadium are together reduced with zinc, three end-points are obtained with permanganate, and best at 80°. The first end-point represents in this series the oxidation of the vanadium from two to three valence; the second, oxidation of vanadium from three to four valence and of uranium from four to six; the third end-point represents the oxidation of vanadium from four to five valence. Iron, vanadium and uranium may be determined all together by reduction with zinc and titrating while hot in an acid solution with permanganate. (122) (C.A. 18, 643)

Vanadium.- (20), (21), (43), (63), (87), (89)*, (99)*, (103), (122)*, (144)*

Kelly and Conant were probably the first investigators to determine vanadium by means of electrometric titration methods. They used the method particularly to determine vanadium in the presence of chromium in steel. The steel was dissolved in sulfuric acid and heated to 80° C. After adding five grams of sodium phosphate to the solution, 0.1N potassium permanganate was added to the "gray" color. The solution was then cooled in ice to 10 to 20° C., and more sulfuric acid added. This solution was then titrated with ferrous sulfate for vanadium. A portion of the solution representing one gram of steel was then taken for the chromium determination. (See under chromium). (20), (21)

(C.A. 10, 2179)
(C.A. 10, 729)

Kelley, Wiley, Bohn and Wright developed a method for the determination of vanadium in steel in the presence of chromium based on the selective oxidation of vanadyl salts by nitric acid. After this oxidation, the vanadium was titrated with ferrous sulfate. The authors tried several oxidizing agents but nitric acid proved to be the most efficient.

The method was carried out by dissolving a 2-gram sample of steel in 100 cc. of sulfuric acid (Sp. Gr. 1.20). Two cc. of nitric acid was then added, drop by drop, and the solution boiled to free from oxides of nitrogen. The solution was then diluted to 100 to 120 cc. with hot water, 40 cc. of

concentrated nitric acid added, and boiled for one hour keeping the solution volume above 100 cc. After cooling to 20° C, or lower, the solution was titrated with ferrous sulfate and potassium dichromate, 0.9609 grams per liter. These same authors further improved the method to include the determination of vanadium in ferrovandium. (43), (63)

(C.A. 13, 1985)

(C.A. 15, 3955)

A method for the determination of vanadium in the presence of iron and uranium was worked out by Gustavson and Knudson. They determined vanadium in a vanadyl sulfate solution. 20 cc. of solution containing 18.7 milligrams of vanadium, together with ferrous sulfate and uranyl acetate was diluted to 250 cc. with water and five grams of zinc added, and two portions of four cc. each of sulfuric acid were added during the titration, one at the start of the titration, and the other at the end of the first end-point. The solution was titrated directly with permanganate. The oxidation is selective, and the three elements may be determined in the same solution. (87)

(C.A. 17, 597)

Willard and Fenwick used the polarized bimetallic electrode system for the determination of vanadium in the presence of iron and chromium, and claim for the method a more sensitive means of determining the end-point when ferrous sulfate is the titrating agent. The chromium was reduced, selectively, with hydrogen peroxide in the presence of acetic acid in 20-30 percent solution. 25 to 50 cc. of concentrated

hydrochloric acid was then added and the titration made with ferrous sulfate. The authors have adapted the method for determining vanadium in special alloy steels. (103)(C.A.17, 507)

Ferrous solutions are more vigorous in their reducing power than are vanadyl solutions. When these solutions are titrated together with permanganate two sudden changes in e.m.f. are observed. The first change representing the oxidation of the iron, and the second one to the oxidation of the vanadium. The last part of the titration should be made at 70°. (89) (C.A. 17, 1401)

Vanadic acid is reduced by cadmium in a Jones' reductor. The reduced solution can be titrated with permanganate if protected by carbon dioxide gas. The equation $5V^{++} + 3MnO_4^- + 3H_2O = 5HVO_3 + 3Mn^{++} + H^+$. (99) (C.A. 17, 39)

Vanadium can be reduced to the bivalent condition in a zinc reductor, and can be oxidized back to the quinquivalent condition by means of permanganate. The titration is best conducted at 80° temperature. Vanadium and iron can be titrated together; first hot until two stages are completed -- oxidation of the vanadium; then cold for oxidation of the iron, and hot again until vanadium oxidation is complete. (122) (C.A. 18, 645)

This reference contains a review of the literature on electrometric titration of vanadium. Vanadium and chromium may be determined together by titrating with ferrous ammonium sulfate, protecting with carbon dioxide. Only one end-point is obtained which corresponds to the known composition of the

mixture. After this determination has been made, the vanadium is determined by titrating with permanganate until the iron is oxidized, heating to 70-80°, and finishing the titration with permanganate. The reagent used between the first and second break corresponds to the vanadium. Manganese does not interfere in this titration. A complete method for the determination of vanadium and chromium in steel is given. (144) (C.A. 18, 5571)

Zinc.- (27), (72)*, (77)*, (112)*, (114)*, (128)*, (134c)*, (138)*

Bichowsky used the platinum-calomel electrode system for the determination of zinc, by titrating with ferrocyanide. Zinc ore was put into solution with a minimum quantity of strong hydrochloric acid, and a small quantity of potassium chlorate added. The solution was then made alkaline with ammonia, an aliquot portion filtered off and acidified with 10 percent excess of hydrochloric acid. Sulfur dioxide gas was then added to saturation, and the excess of this gas dispelled by boiling. Test lead may be employed to free the solution of copper. The solution was then heated to 70°, and titrated with ferrocyanide solution. If cadmium is present in considerable quantities, it should be separated by some suitable method. 10 to 20 percent of hydrochloric acid should be present in the solution for best results. (27)(C.A. 11, 2312)
(C.A. 11, 1800)

Zinc can be titrated electrometrically by means of potassium ferrocyanide, the zinc being precipitated as the double ferrocyanide of potassium and zinc. A 1/40 molar solution of potassium ferrocyanide, and a titrating temperature of 70° degrees is recommended. In a faintly acid solution two milligrams of zinc can be determined with an accuracy of one percent. Sulfates in large amounts interfere with the titration. This titration can be reversed with accurate results. (77)

(C.A. 16, 3281)

Muller and Adam determine zinc by adding to a zinc solution an excess of cyanide with silver nitrate using a silver electrode. Cadmium, lead, and copper can not be determined by this method. (112)

(C.A. 17, 2093)

Zinc can be determined electrometrically with potassium ferrocyanide even in the presence of cadmium. (114)

(C.A. 17, 2689)

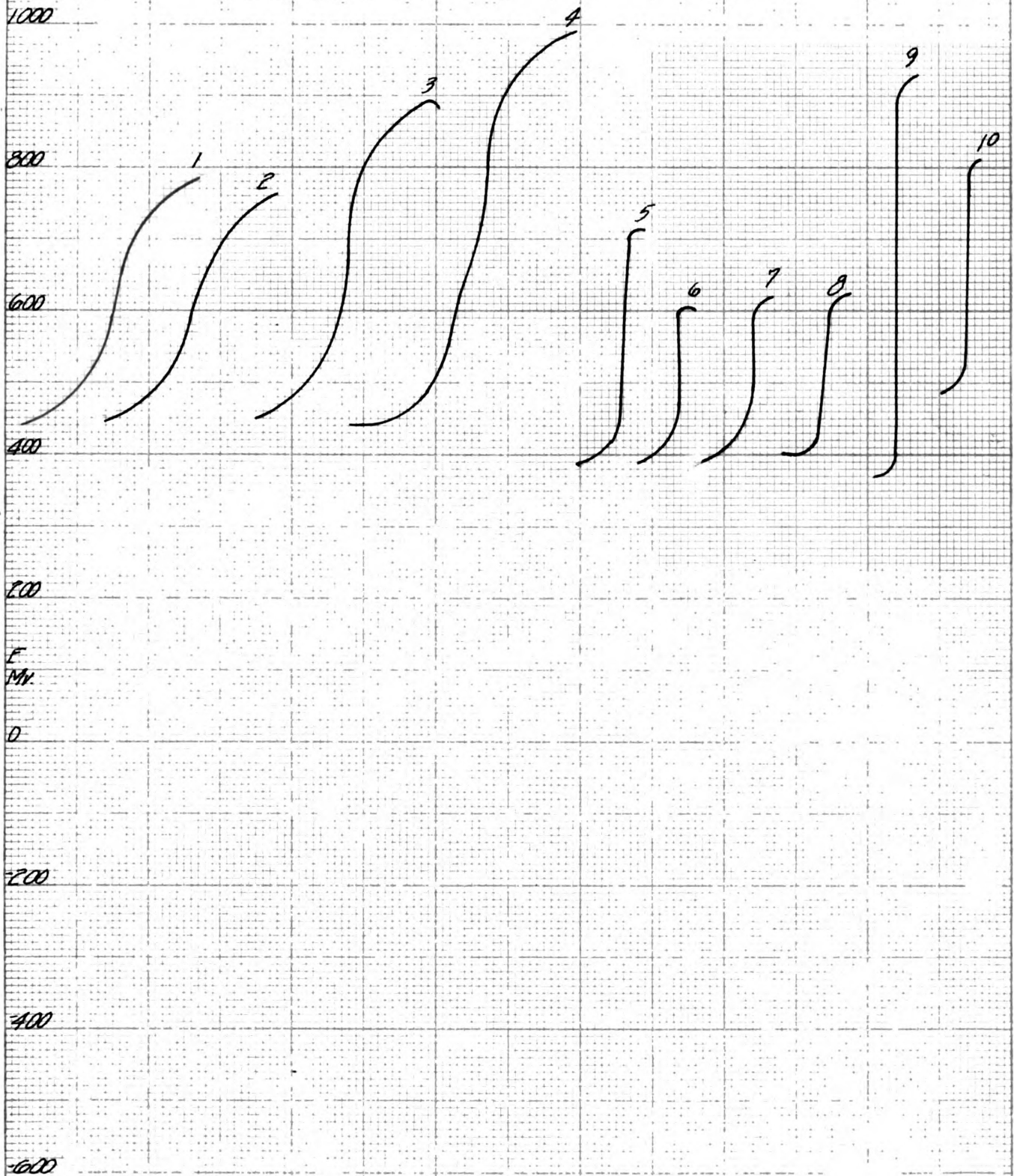
Zinc and lead may be determined electrometrically with potassium ferrocyanide. To every 100 cc. of solution one cc. of M potassium ferricyanide is added and the titration made with 0.1 M potassium ferrocyanide at 75°. Near the first break in potential, a wait of three to five minutes is necessary in order for the potential to become constant. A first break occurs at - 0.54 volts and a second one at - 0.19 volts. The results are exact for the sum of both metals, but not for zinc alone, and attempts made at higher temperatures failed to produce good results. The lead, however, can be precipitated with a slight excess of dilute sulfuric acid and the zinc

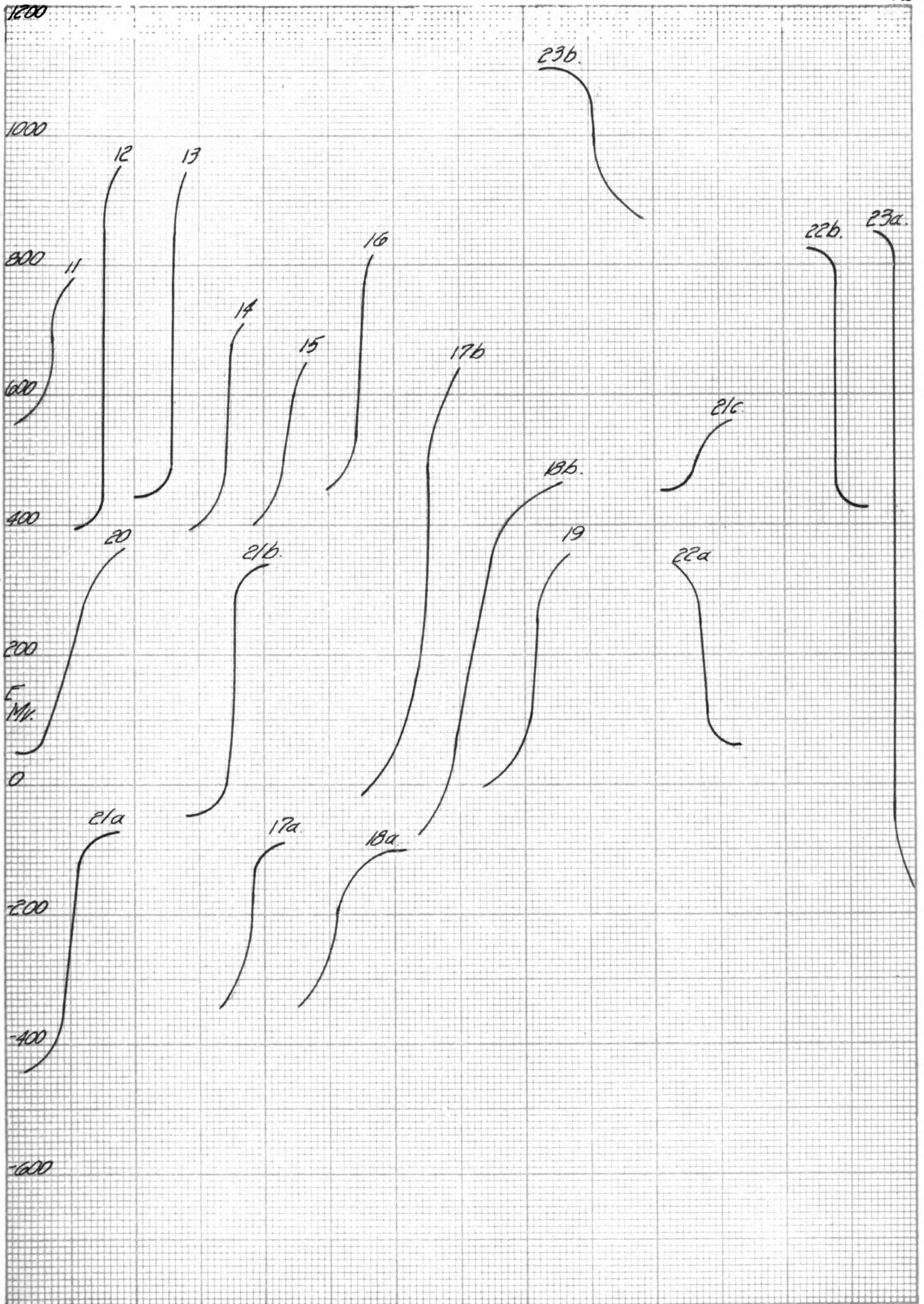
determined with ease. Therefore, two titrations are necessary in order to successfully determine zinc and lead in solution together. (128) (C.A. 17, 943)

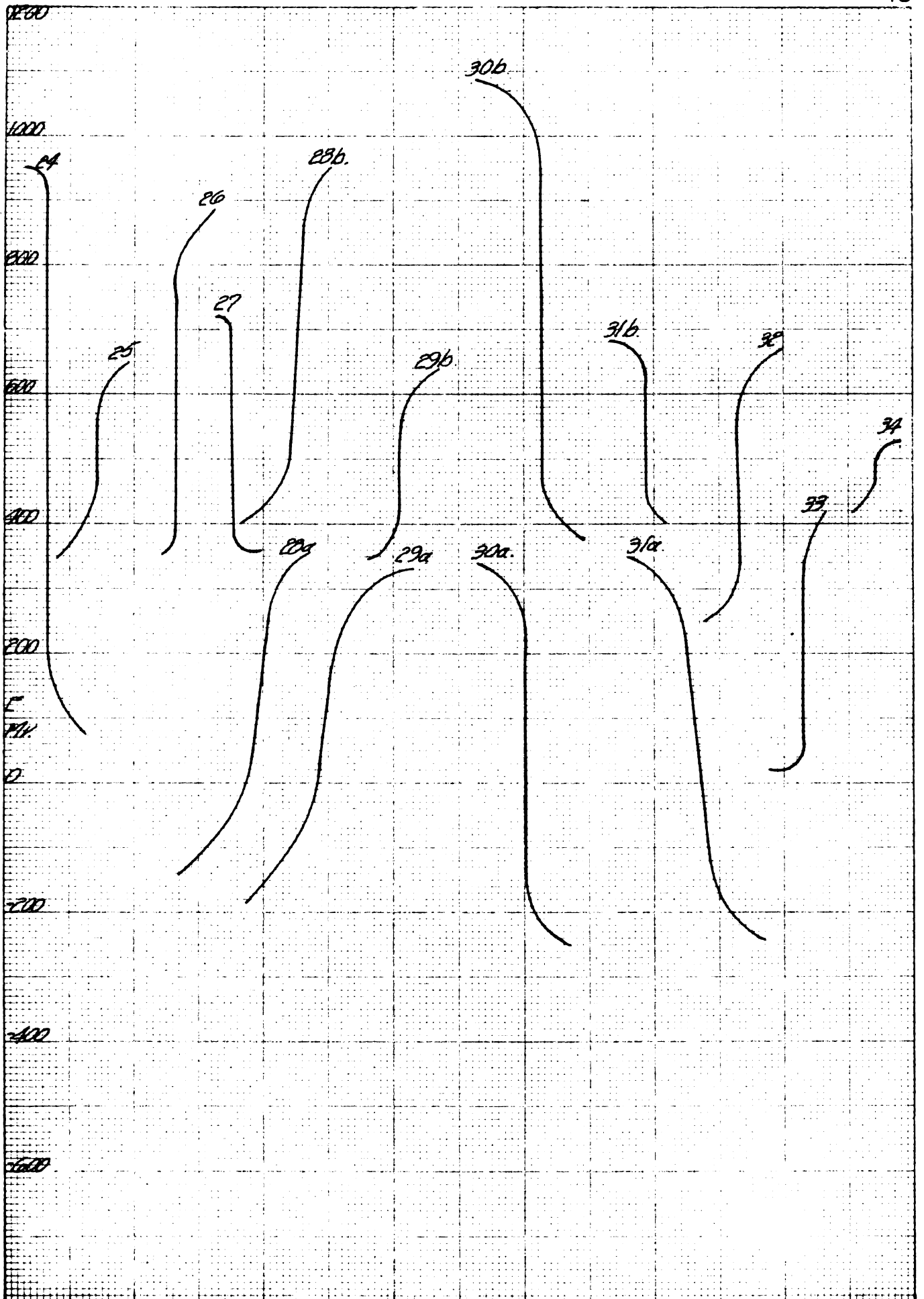
In titrating zinc sulfate solutions with potassium ferrocyanide solutions, Kolthoff and Verzyl showed that 15° and 65° about one percent too little of the reagent is used when the sudden potential change is observed. The addition of three cc. of 0.25N sulfuric acid to 100 cc. of a solution containing 1.08 grams of zinc sulfate changed the error to 0.72 percent, and the further addition of 3 grams of potassium sulfate reduced it to 0.48 percent. (134)(C.A. 18, 1627)

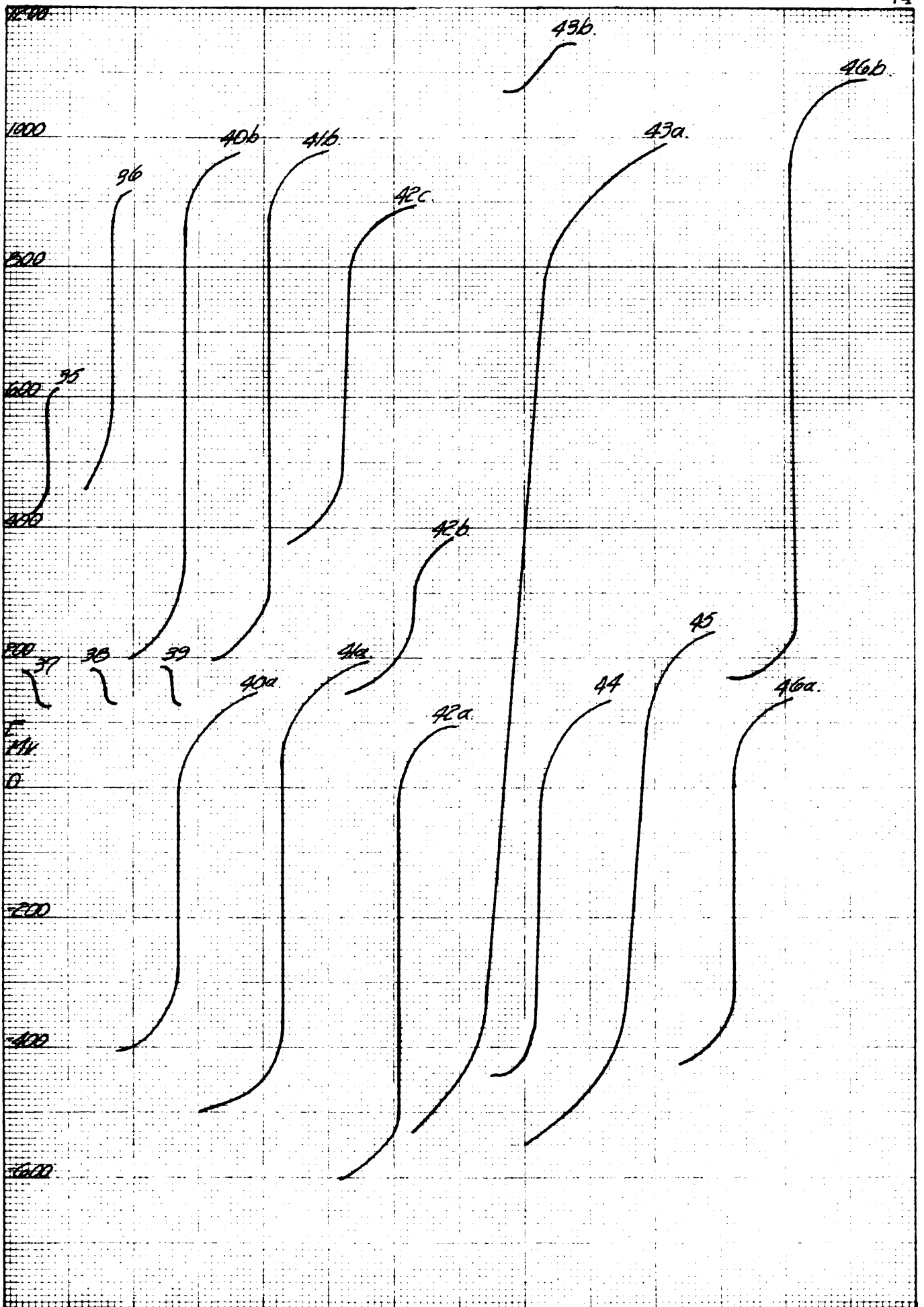
Good results are obtained with a few grams of ammonium sulfate in titrating zinc with ferrocyanide. (see preceding abstract). The presence of large amounts of sodium, aluminum, magnesium, and calcium salts lowers the results. Magnesium, cadmium, and copper interfere with the method and should be removed from the solution. Ferric compounds are made harmless by adding ammonium fluoride and sulfuric acid. (138) (C.A. 18, 2482)

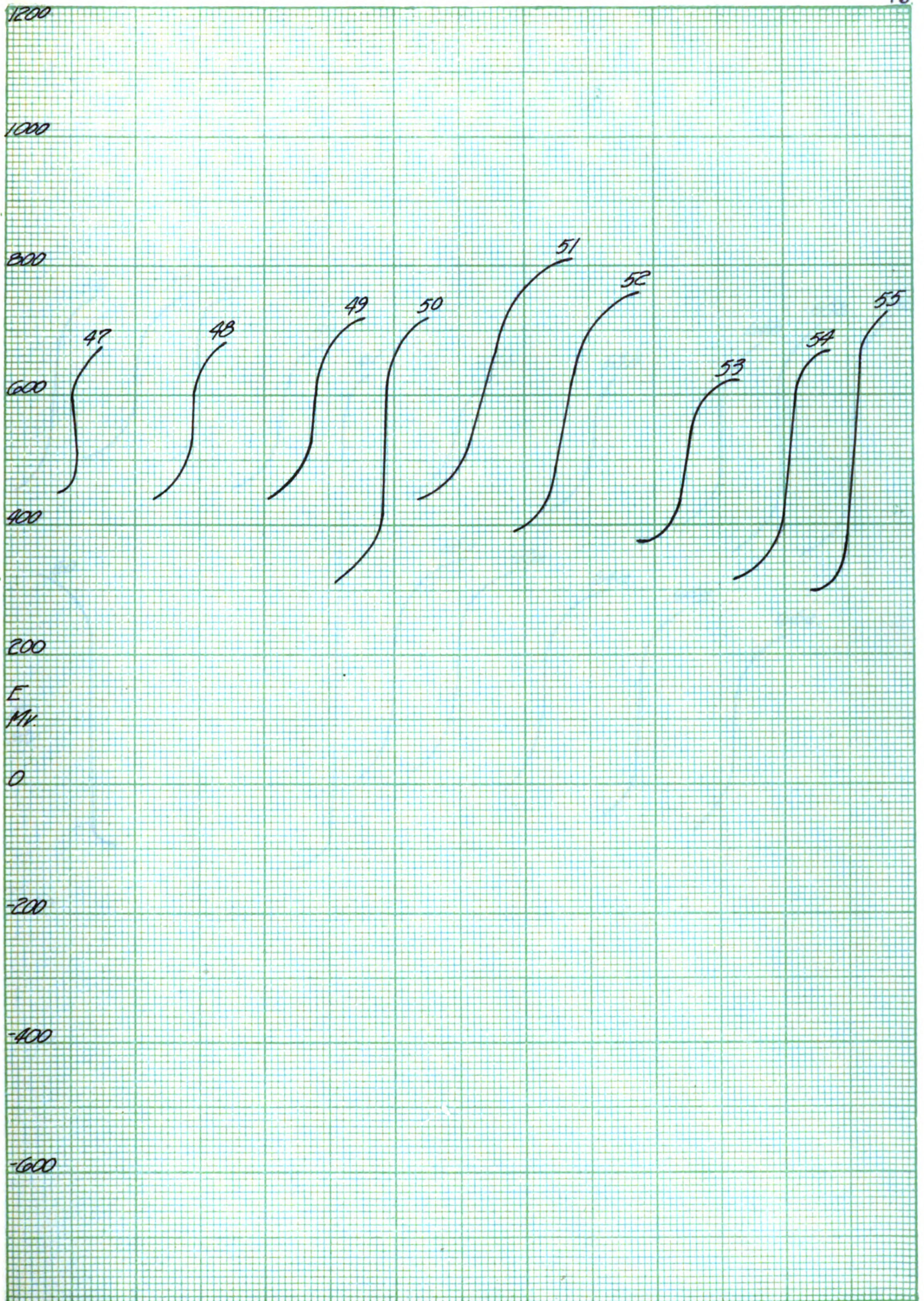
V
ELECTROMETRIC TITRATION CURVES

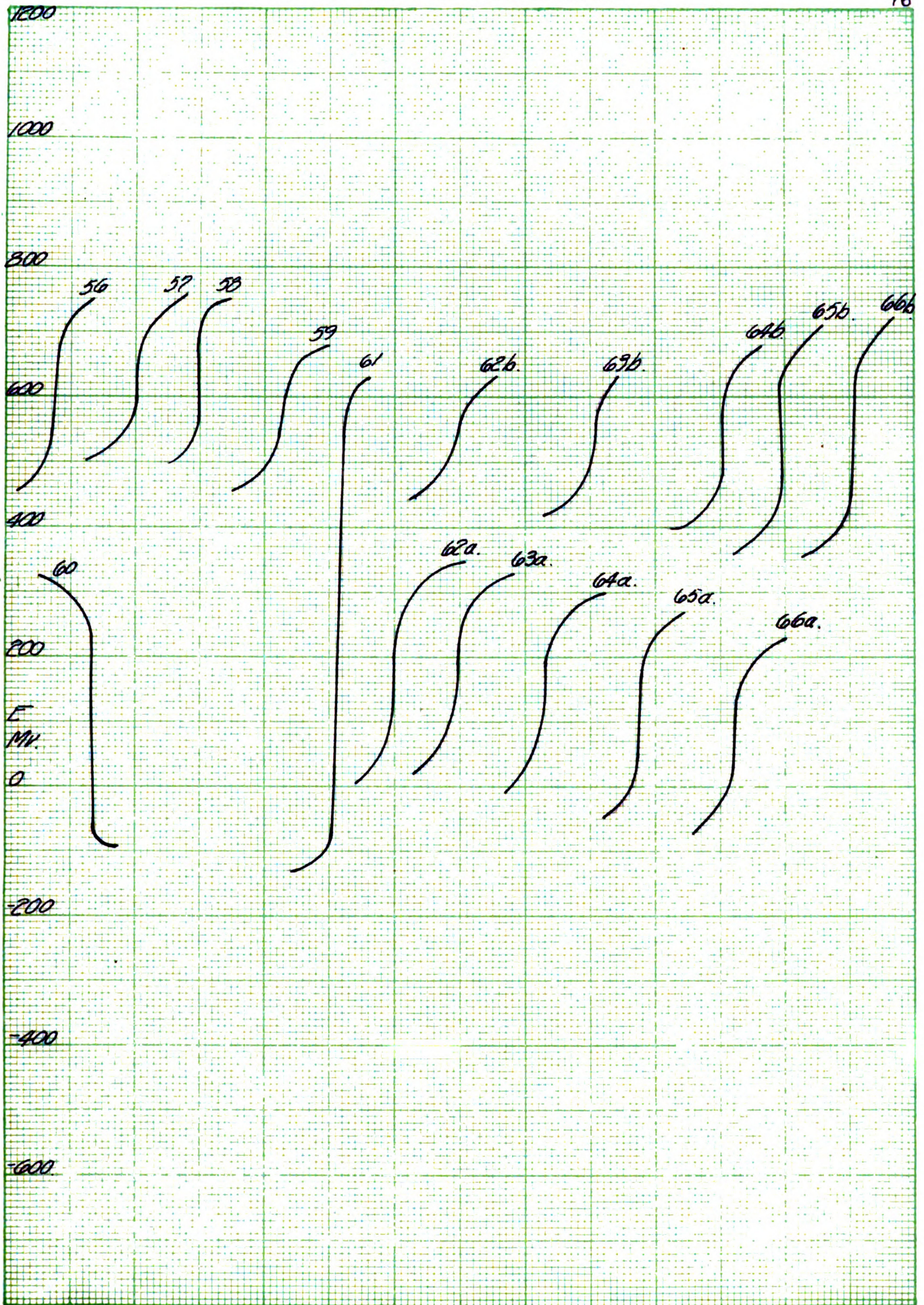


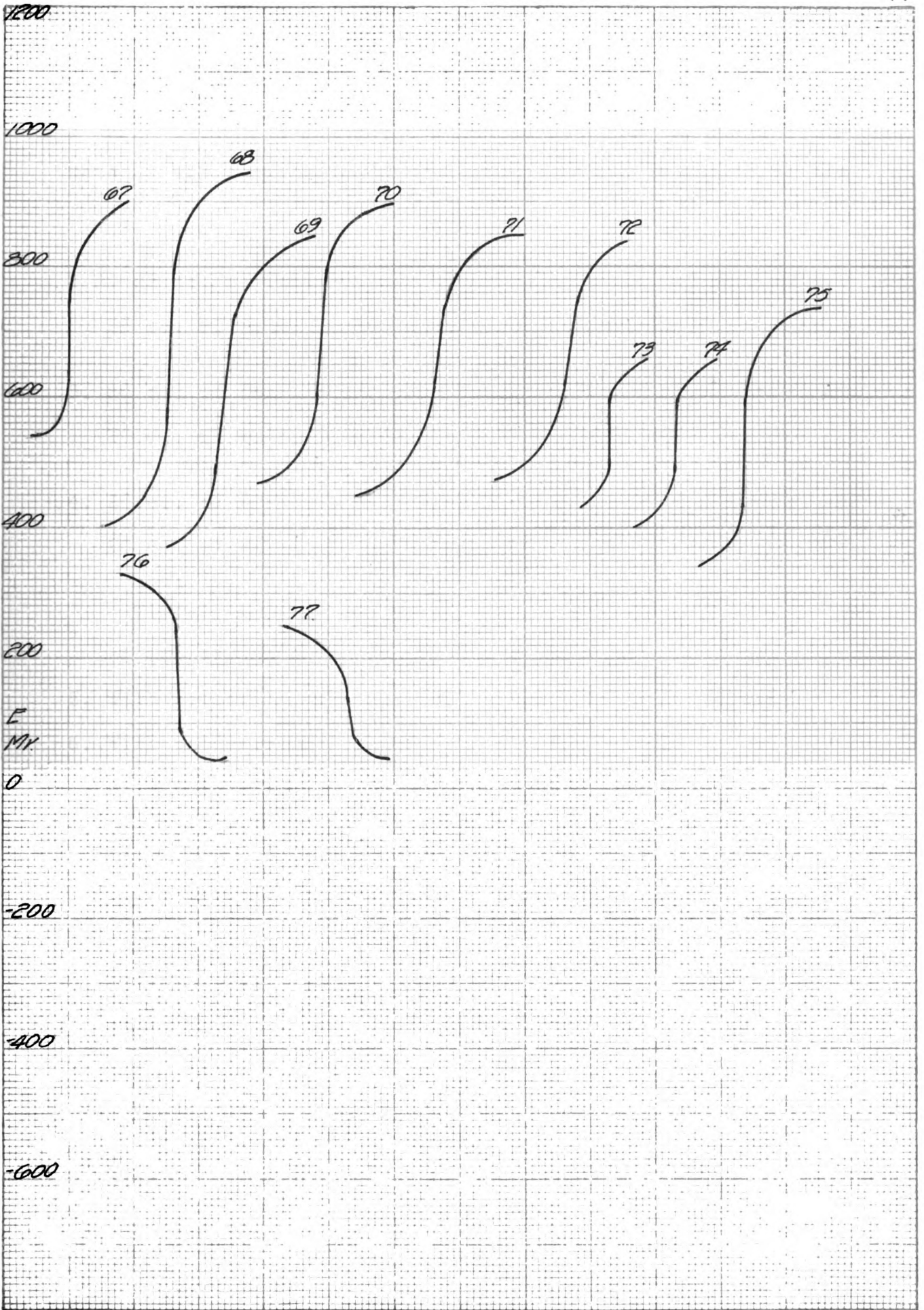












VI

Curve Data and Conclusions

Note:- The marginal numbers correspond to the curves on the graphs.

- 1,2. 25 cc. of ferrous sulfate, 30 cc. of 4N sulfuric acid, 25 cc. of water titrated with 0.1N potassium dichromate.
3. 25 cc. of ferrous sulfate, 20 cc. of 4N sulfuric acid, and 30 cc. of water titrated with 0.1N potassium bromate.
4. 25 cc. of ferrous sulfate, 20 cc. of 4N sulfuric acid, and 20 cc. of water titrated with 0.1N potassium permanganate.

Titration of potassium iodide -- 0.25384 grams in 100 cc. of 10 percent sulfuric acid solution. --

5. With potassium permanganate -- 3.161 grams per liter.
6. With potassium dichromate -- 4.903 " " "
7. With potassium bromate -- 2.783 " " "
8. With potassium iodate -- 3.567 " " "

Titration of potassium ferrocyanide -- 0.8448 grams in 100 cc. of 10 percent sulfuric acid solution. --

9. With potassium permanganate -- 3.161 grams per liter.
10. With potassium bromate -- 2.783 " " "
11. With potassium dichromate -- 4.903 " " "

Titration with potassium permanganate -- 3.161 grams per liter.--

12. Of potassium ferrocyanide -- 0.8448 grams in 100 cc. of 10 percent sulfuric acid solution.

13. Of ferrous sulfate -- 0.556 grams in 100 cc. of 10 percent sulfuric acid solution.

14. Of potassium iodide -- 0.25384 grams in 100 cc. of 10 percent sulfuric acid solution.

Titration with potassium bromate -- 2.783 grams per liter.

15. Of potassium ferrocyanide -- 0.8448 grams in 100 cc. of 10 percent sulfuric acid solution.

16. Of potassium iodide -- 0.25384 grams in 100 cc. of 10 percent sulfuric acid solution.

Titration with potassium permanganate. --

17a,17b. Of vanadium and iron.

18a,18b. Of vanadium and uranium.

19. Of iron.

20. Of iron, vanadium, and uranium in 7cc. sulfuric acid.

21a,21b,21c. Of iron, vanadium, and uranium in two additions of sulfuric acid of 4 cc. each during the titration.

Titration with potassium dichromate. --

22a,22b. Of iodate in sulfuric acid.

23a,23b. Of bromate in sulfuric acid.

24. Of chlorate in hydrochloric acid.

Titration with potassium permanganate. --

25. Of iodide and bromide in the presence of chloride.

26. Of iodide in the presence of chloride.

27. 0.021 grams of chromium titrated with ferrous sulfate.
- 28a, 28b. Ferrous and titanous ion titrated with potassium permanganate.
- 29a, 29b. Ferrous and titanous ion titrated with potassium dichromate.
- 30a, 30b. Reverse of curves 28a and 28b. Ferric ion and permanganate titrated with titanous ion.
- 31a, 31b. Reverse of curves 29a and 29b. Ferric ion and dichromate titrated with titanous ion.
32. 75 cc. of 0.033 ferrous sulfate in a high concentration of hydrochloric acid titrated with 0.1N potassium dichromate. Electrodes -- platinum; 0.1N potassium chloride calomel electrode.
33. 25 cc. of 0.1N ferrous sulfate, 20 percent sulfuric acid, titrated with 0.1N potassium permanganate. Electrodes -- platinum; tungsten.
34. Ferrous sulfate in 33 percent hydrochloric acid solution titrated with 0.1N potassium dichromate. Electrodes -- platinum; standard silver chloride half-cell.
35. Ferrous sulfate in 33 percent hydrochloric acid solution titrated with 0.1N potassium dichromate. Electrodes -- platinum; silver chloride platinum.

36. Ferrous sulfate in 20 percent sulfuric acid titrated with 0.1N potassium permanganate.

Electrodes -- platinum; silver chloride platinum.

250 cc. of solution containing 75 cc. of a 0.03N potassium dichromate solution titrated with 0.1N ferrous sulfate in different concentrations of hydrochloric acid.

37. 0.4M hydrochloric acid.

38. 0.8M hydrochloric acid.

39. 2.0M hydrochloric acid.

Titration with potassium permanganate --

(a) Uranium solution -- 1 cc. equals 0.0131 grams.

(b) Permanganate solution -- 0.1011N.

(c) Ferrous solution -- 0.1001N.

10 cc. of uranium solution, 40 cc. of 2 cc. concentrated sulfuric acid in 90 of solution, 80-90° -- reduced.

40a,40b. Uranium titrated with permanganate.

41a,41b. " " " "

42a,42b,42c. Uranium plus 1 cc. of ferrous sulfate solution titrated with permanganate.

Uranium titrated with permanganate in various concentrations of sulfuric acid. --

43a,43b. 20 cc. sulfuric acid in 100 cc. total volume.

44. 10 " " " " " " " "

45. 5 " " " " " " " "

46a,46b. 2 " " " " " " " "

- Potassium biniodate treated with excess iodide and
the excess iodide titrated with potassium permanganate -
47. 0.02N iodate in 150 cc. with sulfuric acid.
 48. 0.05N " " 250 " " " "
 49. Iodate titrated with permanganate in sulfuric acid.
 50. 4.1 mg. ferrous iron in 70 percent hydrochloric acid
titrated with 0.01 potassium dichromate.
 - 4.24 mg. ferrous iron titrated with 0.01N potassium
dichromate.
 51. In 67 percent sulfuric acid.
 52. " 33 " " "
 53. " 17 " " "
 54. " 50 " hydrochloric acid.

Effect of adding ferric iron --

55. No ferric iron.
56. 500 ppm. of ferric iron.
57. 1500 ppm. of ferric iron.
58. 2500 ppm. of ferric iron.
59. 0.558 mg. ferrous iron and 1680 mg. ferric iron.
60. Ferric iron titrated with 0.005N stannous chloride.
61. Stannous chloride titrated with 0.01N potassium
dichromate.

Ferric iron reduced with stannous chloride in excess
and both titrated with 0.01 potassium dichromate.--

62a,62b. In 40 percent hydrochloric acid.

63a,63b. " 50 " " "

64a,64b. " 60 " " "

65a,65b. " 70 " " "

66a,66b. " 90 " " "

Ferrous iron titrated with 0.01N potassium permanganate -

67. 2.87 mg. ferrous iron in 17 percent sulfuric acid.

68. 2.87 mg. ferrous iron in 10 percent sulfuric acid with
28.7 mg. of ferric sulfate.

69. 2.87 mg. ferrous iron in 2.5 percent of 85 percent phos-
phoric acid with 57.3 mg. of ferric sulfate.

70. 2.87 mg. ferrous iron in 2.5 percent of 85 percent phos-
phoric acid with 57.3 mg. of ferric sulfate and 5 percent
sulfuric acid.

71. 2.87 mg. ferrous iron and 6 percent of the phosphoric-
sulfuric acid mixture with 250 mg. of iron as ferric
chloride.

72. 2.87 mg. ferrous iron and 6 percent of the phosphoric-
sulfuric acid mixture with 250 mg. of iron as ferric
chloride, and 5 percent of hydrochloric acid.

Ferrous iron titrated with potassium dichromate in
various concentrations of hydrochloric acid. --

73. 50 cc. concentrated hydrochloric acid, 100 cc. water,
1.4 gm. ferrous ammonium sulfate.

74. 50 cc. concentrated hydrochloric acid, 100 cc. water,
1.05 gm. ferrous ammonium sulfate.

75. 100 cc. concentrated hydrochloric acid, 50 cc. water,
1.05 gm. ferrous ammonium sulfate.
76. 10 cc. 0.1N potassium bromide titrated with approximately
0.1N mercurous nitrate.
77. 10 cc. 0.1N potassium chloride titrated with approximately
0.1N mercurous nitrate.

A general consideration of these electrometric titration curves shows that it is quite impossible to obtain from them distinct theoretical correlations of first importance. Nearly all of the investigational work pertaining to them has been done from the standpoint of analytical chemistry alone; and the chief aim of the investigators seems to have been, to discover suitable reagents for the titrations, to obtain well-marked end-points, and to determine small quantities of unknowns. In general, it may be stated that the end sought was rapidity and refinement of analytical methods. To this end, various kinds of electrodes, various concentrations of reactants and of acid solutions, and different mechanical operations have been employed; all of which is contrary in principle to the systematic research necessary in this kind of work in order to establish fundamental chemical concepts.

Some of the points taken under consideration are as follows:

1. The end-point placement on the graph with reference to the zero e.m.f. and the magnitude of the deflection of the curves.
2. Is there a "neutral point"?
3. Correlation with the Periodic Law.
4. Slope of curve deflections or speed of the reactions with reference to kind and strength of acid used.
5. Energy relationships.
6. Chemical activities.
7. Summary of rules for electrometric titration.
8. Scope and opportunities in the field of electrometric titration.

A cursory examination of the curves will suffice to show that no distinct relationship exists between the magnitude of their end-point deflections and their position on the graphs with respect to the zero e.m.f. point. However, from the standpoint of their position on the graphs alone, the curves can be classified, roughly, into three groups:

1. Those ranging from 400 millivolts up.
2. Those occupying the intermediate position of 0 to 400 millivolts.
3. Those having the e.m.f. range of 0 down to the lowest negative voltage obtained.

A list of the reactions of class 1. --
Curves 1 to 4 -- oxidation of ferrous iron.
curves 5 to 8 -- oxidation of potassium iodide.

curves 9 to 11 -- oxidation of ferrocyanide.
curves 12 to 16 -- oxidation of ferrocyanide, ferrous iron,
and potassium iodide.
Curve 21c -- oxidation of uranium.
Curves 22b to 23b -- reduction of iodate and bromate.
Curves 25 to 26 -- oxidation of iodide and bromide.
Curve 27 -- reduction of chromium.
Curves 28b and 29b -- oxidation of ferrous iron.
Curves 30b and 31b -- reduction of ferric iron.
Curves 32 to 36 -- oxidation of ferrous iron.
Curves 40b, 41b, and 42c -- oxidation of uranium and ferrous
iron.
Curves 47 to 49 -- oxidation of iodide.
Curves 50 to 59 -- oxidation of ferrous iron.
Curves 62b to 66b -- oxidation of ferrous iron.
Curves 67 to 75 -- oxidation of ferrous iron.

A list of the reactions of class 2. --

Curves 20 to 21b -- oxidation of vanadium.
Curves 17b, 18b -- oxidation of vanadium.
Curve 19 -- oxidation of ferrous iron.
Curves 28a, 29a -- oxidation of titanium.
Curves 30a, 31a -- reduction of titanium.
Curve 33 -- oxidation of ferrous iron.
Curves 37 to 39 -- reduction of dichromate.
Curve 60 -- reduction of ferric iron.

Curve 61 -- oxidation of tin.
Curves 62a, 66a -- reduction of ferric iron.
Curve 76 -- bromide and mercurous chloride.
Curve 77 -- chloride and mercurous chloride.

A list of the reactions of class 3. --
Curves 17a, 18a, 21a -- oxidation of vanadium.
Curves 40a, 41a, 42a -- oxidation of uranium.
Curves 44, 45, 46a -- oxidation of uranium.

The basis for the above classification is apparent, and can be referred to the initial and final electrode potentials of the several substances used in the titrations. The highest voltage is obtained with permanganate, and the lowest with uranium in a low state of oxidation. From these data we can conclude that permanganate is a strong oxidizer and uranium a strong reducer. Metals with two or more states of oxidation, or valences, will give end-points for these different states, and the end-point curves will occupy different positions on the graph, the lowest oxidation state corresponding to the lowest position on the graph. The electrode potential may be negative for a low state of oxidation and positive for a higher state of oxidation.

The electrode potential of a solution measures its oxidizing or reducing power. Therefore, in general, the greater the difference in electrode potential between an oxidizing solution and a solution to be oxidized, the greater the act-

ivity of the oxidizing reaction and hence the greater the speed of reaction and the sharper the end-point deflection of the measuring potentiometer. The same conditions apply to reducing reactions. In both cases, however, the strength of the acid titrating solution is an important factor, as is also the kind of acid used to acidify the titrating solution. The disturbing influences are the electrode potentials of the products of the reaction, and the kind of electrodes used in the determinations.

The titration of uranium with permanganate may be taken as illustration of the consideration. Curves 43a and 43b represent this titration in 20 percent sulfuric acid solution. In this case the change in potential is great being from about -530 to +1150 millivolts for both stages of oxidation of the uranium compound; but the endpoint deflections are not sharp. In a 2 percent solution of sulfuric acid, however, as illustrated by curves 46a and 46b, about the same change in voltage is observed while the two end-points are very distinct.

Another illustration of this same phenomenon may be found in the titration of stannous and ferrous ion with dichromate - curves 61 to 66. The influence of kind of acid is illustrated in the titration of ferrous iron with dichromate - in both sulfuric and hydrochloric acid solution - curves 51 to 54 - in which case the hydrochloric acid solution gives the best end-point.

In case certain reactions do not give suitable end-points, these end-points may be improved by reversing the reaction. Curves 28 to 31 illustrate a case of this kind. Ferrous and titanous ion titrated with permanganate or dichromate do not give suitable curves; but when ferric ion and dichromate or permanganate is titrated with titanous ion, sharp end-points are obtained in case of the ferric ion and permanganate, and for the ferric ion alone in case of the dichromate. This experiment shows, also, that titanous ion will reduce ferric ion, or that one metal ion will satisfactorily reduce or oxidize another metal ion provided that the values of electrode potentials are far enough apart.

For slow oxidation or reduction reactions, or in cases where sharp end-points may not be obtained, it is often expedient to add a known excess of the oxidizing or reducing reagent, and after sufficient time has elapsed for the reaction to be completed, this excess of reagent is titrated by means of another quickly acting reagent that does give a sharp end-point, and the unknown ion calculated from the difference between the quantity of reagent first added and the excess found by titration. Again, the oxidation process may be easier applied to a certain metal than the reduction process in titration. In this case, the metal is first reduced by some known efficient process after which it is titrated with an oxidizing reagent, or this process may be reversed.

In only one case does the end-point e.m.f. approximately coincide with 0 e.m.f.; that is in the reduction of permanganate with titanous ion in the presence of ferrous ion.

The number of elements investigated is too small to provide a means of correlation with the periodic law. Moreover, oxidizing or reducing power may be only relative; for instance, ferrous iron may reduce permanganate and oxidize a stannous salt. A metal in a low state of oxidation may be caused to reduce the same metal in a higher state of oxidation.

The formula expressing change in free energy for an electrometric reaction change is $-\Delta F = E.N.F.$ While the change in energy accompanying a change in valence for 1 gram mole is 1 Faraday, it is now known if this value can be experimentally realized. The difficulties encountered in electrometric titration processes are the unknown liquid-liquid potential values, and the unknown values of chemical activities of electrolytes in the presence of other electrolytes - acids or salts. The data at hand give no values that may be used to calculate energy changes from a theoretical standpoint. The magnitude of the curve deflections is, however, an effect of this free energy change.

From an examination of the data on electrometric titration methods, with special reference to oxidation or reduction reactions, some rules and precautions may be evolved

as follows: 1. Choose active oxidizing and reducing reagents. 2. Suitable metallic electrodes are of importance. 3. Select chemical reactions that are complete. 4. Slow reactions may be used if an excess of reagent is added and this excess back-titrated or titrated with a third substance. 5. A proper temperature is important for some reactions. 6. The interaction of components should not disturb the titration process. 7. A certain strength and kind of acid will be found necessary for sharp end-points. 8. Avoid substances that interfere with the reaction -- external oxidizing or reducing substances. 9. Weighing the solutions is more accurate than measuring them, especially for the determination of small quantities of unknowns. 10. All reagents should be accurately standardized by the best known methods, and by applying the electrometric titration method, in the same manner as the regular titration is to be conducted, when possible.

Only a limited number of elements and chemical compounds have been studied by means of the electrometric titration methods, and an opportunity exists to study those elements that have not already been employed in these methods. very little work has been done on phosphates, carbonates, sulfides, chromates, and oxalates, and the formation of colloids by means of oxidation or reduction methods. Another possible field for the use of these methods lies in a study

of the effects of catalyzers on chemical reactions and the energy changes involved. Almost no work has been done with these methods in the field of organic analyses, except on aldehydes and reducing sugars.

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