ELECTRODEPOSITION OF NICKEL

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ELECTRODEPOSITION OF NICKEL

THESIS

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By

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INTRODUCTION

Most of the inorganic and a great number of the organic compounds are decomposed when subjected to the action of an electric current. This decomposition is called "electrolysis." The substance decomposed is termed an "electrolyte." The products of the decomposition are the anions and cations. The "anions" are those products which separate at the anode, the positive electrode or pole, and "cations" are those products which separate at the cathode, the negative electrode or pole.

This behavior of compounds has become of great service to the chemical industry in the protective or ornamental plating of metals and alloys, and to the analyst in as much as it has enabled him to effect the isolation of metals from their solutions. By carefully studying the electrolytic behavior of salts, it has been possible for the analyst to bring about quantitative determinations and separations of various substances. This method of analysis has been designated "electro-chemical analysis," or better, "electroanalysis." It is especially inviting, since it permits clean, accurate and rapid determination.

The purpose of this research is to investigate the varying conditions in types of solutions, concentrations of solutions, hydrogen-ion concentration, current densities and potentials in the electro deposition of nickel, as well as to
determine and clarify some of the general principles underlying the electro analysis and electro plating of the metal. The equipment at hand limited the research to small quantities of solution and small electrodes, thereby rendering some of the results inapplicable to large scale production.
CHAPTER I
HISTORY

The history of electrochemistry dates\(^1\) to the early part of the last century. In these early years, the activities in electrical studies were mainly directed to the solution of the physical side of electrolysis.

Chrinthshank\(^2\) (1801) observed the readiness with which the metal copper was deposited by the current, and first suggested electricity as a possible agent in the detection of metals. Fisher (1812) detected arsenic by electrolysis. Michael Faraday\(^3\) (1833) laid the foundation of the general principles of electro-metallurgy and introduced the present nomenclature, that is, such terms as electrolyte, electrode, cathode, anion; and he gave us the fundamental quantitative laws on which both scientific and industrial electrolytic processes are founded.

The concentration of certain electrolytes increases at one electrode and decreases at the other when subjected to electrolysis. Hittorf\(^4\) (1853) was the first to notice that the concentration of the solute in the solvent altered during electrolysis. By a series of experiments he was able to cal-

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\(^1\)Edgar F. Smith, *Electro-Analysis*, p. 18.
\(^2\)Ibid.
\(^4\)Ibid.
culate the transport number.

C. Desperts\(^5\) (1857) described the decomposition of certain salts by means of the electric current, and remarked that, while operating with solutions of the acetates of copper and of lead, he expected both metals would be deposited upon the negative pole, and was much surprised to find that the copper was deposited upon the cathode while lead formed the oxide at the anode. He also found manganese was deposited on the anode as the black oxide, antimony as a yellow-red coating and bismuth as a reddish-brown deposit. Desperts concludes his paper by stating that although the facts were few in number, yet they were new in so far as they concerned lead, antimony, and manganese; and, furthermore, that the separation of copper from lead by current was almost complete.

The first notice of the quantitative estimation of metals electrolytically was that of Walcott Gibbs (1864), when he published the results he had obtained with copper and nickel. Luckow, in alluding to this work a year later (1865), says: "I take the liberty to observe that so far as the determination of copper is concerned, I estimated that metal in this manner more than twenty years ago, and as early as 1860 employed the electric current for the deposition of copper quantitatively in various analysis." It was Luckow who proposed the name "Elektro-Metals Analyse" for this new method of quantitative analysis. According to this writer the current may be applied as follows:

1. To dissolve metals and alloys in acids by which they would not be affected unaided by the

\(^5\)Edgar F. Smith, op. cit., p. 19.
electric current.

2. To detect metals like manganese and lead (silver, nickel, cobalt); separating them in form of peroxides; also manganese as permanganic acid.

3. To separate various metals, e.g., copper and manganese, from zinc, iron, cobalt, and nickel.

4. To deposit and estimate metal quantitatively in acid, alkaline, and neutral solutions.

5. For various reductions, e.g., silver chloride, basic bismuth chloride, and lead sulphate, in order that the metals in them may be determined. To reduce chromic acid to oxide, e.g., potassium bichromate acidulated with dilute sulphuric acid.6

By an elaborate investigation on the molecular conductivities of dilute solution, Kohlrausch7 (1869) was able to determine the velocities of the ions under a definite potential gradient. From the figures of Hittorf and Kohlrausch it was possible to calculate the actual ionic velocities in centimeters per hour under a potential gradient of one volt per centimeter in dilute solutions.

The first quantitative determination of nickel by electrolysis was described by Heinrich Fresenius and Bergmann8 (1860) who found that it was best to carry out the determination in an excess of free ammonia and ammonium sulphate.

At this stage in the development of the principles of electro-chemistry, no hypothesis as to the state of the solute in the solvent had been made. Arrhenius and Van't Hoff9 (1887) described their dissociation theory of electro-

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6Edgar F. Smith, op. cit., p. 22.
7Eric K. Rideal, op. cit., p. 2.
8Edgar F. Smith, op. cit., p. 25.
lytes. Their conclusion showed that an electrolyte contained two kinds of solute particles; these were supposed to be active particles responsible for electrical conductance, and inactive molecules. Further, it was suggested that in very dilute solutions that all the inactive molecules were converted into active particles. The assumption was made that when an acid, base or salt was dissolved in water, a considerable portion became dissociated into positively and negatively charged particles, or ions. These ions are free to move independently, and they are simply guided towards the electrode of opposite sign under the influence of the electric field. The ratio of the ions to the total number of particles, or the degree of dissociation, was believed to vary with the concentration of the electrolyte, and to be equal to unity in dilute solutions.

Suppose each molecule when it dissociates yields v ions, then if a solution contains a total of m molecules in a given volume and a is the fraction of these molecules that are dissociated, there will be present m(1-a) undissociated molecules and vma ions; that is, a total of m-ma+vma particles. The osmotic pressure, like the gas pressure, may be taken as proportional to the number of individual molecular particles in a given volume; therefore the Van't Hoff factor may be written as equal to:

\[ \frac{\text{number of particles actually present}}{\text{number of particles which would have been present had there been no dissociation}} \]
that is,

\[ i = \frac{m - ma + mva}{m}. \]

It is clear therefore that the factor \( i \) can be calculated either from the freezing point, boiling point or osmotic pressure measurements, or from a knowledge of the degree of dissociation of an electrolyte; Arrhenius suggested a method for calculating the latter from conductance measurements, and hence was able to calculate \( i \) on the basis of his theory, without reference to osmotic pressure or allied effects.

Two years after the ionic theory was advanced, Nernst in 1889\(^\text{10}\) advanced the hypothesis of electrode "solution pressure". On this hypothesis all metals possess a solution pressure or a tendency to give up ions to the solution. When these positively charged ions go into solution, it leaves the electrons, or negatively charged particles, on the metal. These positively charged ions pass into solution until the potential difference between the metal and layer of solution in contact with the metal is great enough to prevent the further discharge of metallic ions.

A. A. Noyes\(^\text{11}\) (1908) postulated that strong electrolytes were, at least potentially, completely dissociated.

\(^{10}\) Eric K. Rideal, op. cit., p. 3.

\(^{11}\) Frederick W. Miller, Jr., Elementary Theory of Qualitative Analysis, p. 91.
X-ray work on crystals indicated that a crystal of solid sodium chloride contained no molecules at all, but that the elements, even in the solid form, were present as ions. As a result Debye and Huckel\textsuperscript{12} in 1923 developed the interionic attraction theory or the theory of complete ionization. Debye and Huckel assume complete dissociation at all concentrations, and the divergencies from the mass-action principles are due to electric forces between the ions. In electrolysis as each negative ion moves to the anode it attracts a sphere of positive ions which pile up behind it and retards its motion, and each positive ion is dragged back in a like manner. As the dilution is increased, the ions become farther and farther apart and the interionic attraction becomes less and less. At great dilutions the interionic attraction is negligible and the ions have their maximum velocities, and are uninfluenced by further dilution. Although this theory has overcome several of the shortcomings of the older theories, it cannot yet be regarded as complete since it does not hold for concentrated solutions of strong electrolytes.

Most of the electroplating before the World War was carried on more as an art than as a science, many of the processes were kept secret, and many were protected by

\textsuperscript{12}Frederick W. Miller, Jr., op. cit., p. 3.
The many applications of electroplating in the production of military supplies during the World War, and the difficulties encountered both in meeting new problems and in standardizing well-known processes were noted by the producers; and stress was laid upon the relation of electroplating technique to the appearance and durability of their products. In consequence, chemists connected with large manufacturing plants were often called upon for the first time to assist in the solution of electroplaters' problems. During the last few years a movement in the United States has been to employ scientific methods. The American Electroplaters' Society and the International Association of Electrotypers have led the field to a better knowledge through publication, classes conducted under their auspices and at regular meetings.

CHAPTER II
GENERAL PRINCIPLES OF ELECTRODEPOSITION

Current Density. A limiting relation between the current strength and the area of the electrodes must be maintained. The ratio of the current strength in amperes to the area of the electrodes of an electrolytic cell expressed in square decimeters (or square feet) is known as the "current density." The terms "cathodic" and "anodic" current density are used to express the intensity of current per unit area of the cathode or anode surface, respectively, in an electrolytic cell. The ratio of the current strength to the number of cubic centimeters of electrolyte is termed the "current concentration."

These factors determine to a large extent the form in which the metals are deposited upon the cathode, through the course of electrolysis, and the quality and quantity of the products of electrolysis. In this paper current density will always be referred to as amperes per square decimeter.

Current Efficiency. In practice it is found that a gram-equivalent is not deposited by 96,500 coulombs or 26.8 amp. hr., the theoretical amount of electricity necessary, but that a greater quantity is necessary. The fact that this actual quantity exceeds the theoretical does not mean that Faraday's law breaks down but it is found to be due to
other causes, such as the following: the separation of several substances at either electrode and not taken into account; mechanical losses of the products of electrolysis; secondary reactions which take place at the electrodes; current leaks; short circuits; and losses in the form of heat. The ratio of the theoretical to the actual quantity of current used is termed the current efficiency, which is expressed thus:

\[
\frac{\text{Theoretical quantity of electricity}}{\text{Actual quantity of electricity}} = \frac{\text{Actual amount of the product formed}}{\text{Theoretical amount}}
\]

In commercial practice, current efficiencies vary from 25 or 30 per cent in the decomposition of certain fused salts to 95 per cent in copper refining, and even 100 per cent in the electrolytic oxidation of anthracene to anthroquinone.\(^1\)

The current divided by the volume upon which the current acts is called "current concentration." If a high concentration is to be produced of some compound subject to electrolytic decomposition, a high value of this quantity is desirable.

Energy Efficiency. If it were possible to carry out electrolysis in a reversible manner at 100 per cent effi-

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\(^1\)C. L. Mantell, *Industrial Electrochemistry*, p. 15.
ciency, the electrical energy required to produce a definite quantity of substance electrolytically would be the product of the corresponding number of coulombs and the theoretical decomposition voltage. The percentage ratio between the theoretical quantity of energy necessary for the production of a given amount of a substance and the actual quantity of energy, the latter always being the larger, is termed the "energy efficiency" of the process, and is expressed thus:

\[
\frac{\text{Theoretical quantity of energy}}{\text{Actual quantity of energy employed}}
\]

The energy efficiency may also be described as the product of the current efficiency and the percentage ratio of the theoretical to the actual voltage.

Obviously the energy efficiency is of great importance in technical work, and is of greater significance than current efficiency.

**Current Measurement.** The determination of current efficiency involves the weight or volume of a product produced as a result of electrolysis, and the quantity of electricity used. The current may be measured with an ammeter at frequent intervals; then the average value multiplied by the time will give the number of ampere-hours expended. Galvanometers are used for the detection of the current and occasionally for the measurement of the small ones. Ammeters are generally employed for the measurement of elec-
tric current. Coulometers are used for the measurement of the quantity of electricity in small-scale experimental work. With these instruments, measurement is made of the passage of the current. From this amount, by the assumption of Faraday's law, the quantity of electricity passed through can be readily calculated. In a good coulometer there must be no disturbing or secondary side reactions, since the operation of the instrument depends upon 100 per cent current efficiency, or as close to this as it is possible to approach.

Coulometers are several classes. In the weight coulometer the gain in weight of the cathode of an electrolytic cell, due to the deposition of metal from a solution of its salt by the current, is measured. Volume coulometers are those in which the volume of a gas liberated as the result of electrolysis, or the volume of mercury set free during the electrolysis of a suitable mercury salt, is measured. In titration coulometers the change in concentration or the amount of a substance set free at one of the electrodes is determined by analytic methods.

The errors of coulometers are those inherent in the measurement of weight and volume or in titration, and also those due to imperfection in the coulometers themselves. The latter may come from a variety of causes, such as the liberation of substances other than the ones assumed, or the loss of the substance after deposition but before it is
measured. The silver weight and the iodine titration cou- 
lometers are the most accurate, partly because of the high 
equivalent weights of iodine and silver.

**Polarization.** In "gas polarization" minute gas bubbles 
gather on either anode or cathode, or both. This accumula-
tion of gases on the electrodes sets up an opposing elec-
tromotive force called the electromotive force of polar-
ization, and greatly raises the cell resistance. In general, 
gas polarization disappears when the cell is allowed to 
stand, partly through slow coalescence of the small gas 
bubbles into those large enough to escape, and partly by 
solution of the gases in the electrolyte. Polarization 
often develops slowly and cell resistance, therefore, is of-
often lower during the first few hours of running than 
later.

Another type of polarization is the so-called concen-
tration polarization. For example, in a nickel sulphate 
electrolyte the solution in contact with the cathode will 
become practically depleted of nickel ions. This applies 
to the still method, but is overcome by stirring in the 
fast method.

**Decomposition Voltage.** The decomposition potentials 
are important for two reasons; first, because they repre-
sent the minimum electromotive force that is required to 
effect the deposition of a metal, and second, because they 
show how certain metals can be separated quantitatively
from one another by varying the potential.

The smallest external electromotive force that must be applied, in order to bring about the separation of such quantities of cations and anions at insoluble electrodes that a continuous current flows through the solution, is called the decomposition voltage of the electrolyte.²

TABLE I

DECOMPOSITION POTENTIALS³
FOR MOLAR CONCENTRATION

<table>
<thead>
<tr>
<th>Salt</th>
<th>Decomposition Potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnSO₄</td>
<td>2.35</td>
</tr>
<tr>
<td>ZnBr₂</td>
<td>1.60</td>
</tr>
<tr>
<td>NISO₄</td>
<td>2.09</td>
</tr>
<tr>
<td>NiCl₂</td>
<td>1.85</td>
</tr>
<tr>
<td>Pb(NO₃)₂</td>
<td>1.52</td>
</tr>
<tr>
<td>AgNO₃</td>
<td>0.70</td>
</tr>
<tr>
<td>Ag₂SO₄</td>
<td>0.80</td>
</tr>
<tr>
<td>Cd(NO₃)₂</td>
<td>1.98</td>
</tr>
<tr>
<td>CdSO₄</td>
<td>2.30</td>
</tr>
<tr>
<td>CdCl₂</td>
<td>1.88</td>
</tr>
<tr>
<td>CoSO₄</td>
<td>1.92</td>
</tr>
<tr>
<td>CoCl₂</td>
<td>1.78</td>
</tr>
</tbody>
</table>

From Table I it will be observed that there is consid-

² H. Jermain Creighton, Principles and Applications of Electrochemistry, p. 245.
³ Frederick H. Getman, Outlines of Theoretical Chemistry, p. 491.
erable variations in the decomposition potentials of various electrolytes. Even in the different salts of the same metals a difference is noted.

**Electrolytic Separation of Metals.** As has already been

<table>
<thead>
<tr>
<th>Ion</th>
<th>Separation Potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>0.78</td>
</tr>
<tr>
<td>Cu</td>
<td>0.34</td>
</tr>
<tr>
<td>H</td>
<td>0.00</td>
</tr>
<tr>
<td>Pb</td>
<td>0.17</td>
</tr>
<tr>
<td>Cd</td>
<td>0.36</td>
</tr>
<tr>
<td>Zn</td>
<td>0.74</td>
</tr>
<tr>
<td>I</td>
<td>0.52</td>
</tr>
<tr>
<td>Br</td>
<td>0.94</td>
</tr>
<tr>
<td>O</td>
<td>1.08 (in acid)</td>
</tr>
<tr>
<td>Cl</td>
<td>1.31</td>
</tr>
<tr>
<td>OH</td>
<td>1.68 (in acid)</td>
</tr>
<tr>
<td>OH</td>
<td>0.88 (in base)</td>
</tr>
<tr>
<td>SO₄⁻</td>
<td>1.90</td>
</tr>
</tbody>
</table>

Stated it is possible to accomplish the quantitative separa-

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*Frederick H. Getman, Outlines of Theoretical Chemistry, p. 496.*
tion of different metals by means of graded electromotive forces. The salt having the lower decomposition potential will decompose first, and when the deposition of the metal is complete, the current will fall almost to zero. If the electromotive force is then raised above the decomposition potential of the second salt, the metal of that salt will be deposited, and so on. In practice it is necessary to raise the potential slightly above the decomposition potential because of the gradual decrease in the number of ions of the salt whose metal is to be deposited. For example, suppose a mixture of the sulphates of silver, nickel, and zinc is subjected to electrolysis. If the electromotive force is regulated to slightly more than 0.80 volts, the decomposition potential of silver sulphate, and less than 2.09, all of the silver will be deposited. If the cathode is then changed and the electromotive force raised slightly above 2.09 volts and less than 2.35 volts, all of the nickel is deposited. By again changing the cathode and raising the voltage above 2.35 volts, the zinc will be plated out.

In Table II is given the separation potentials of some of the ions for molar concentration, the separation potential of the H⁺ ion being assumed to be equal to zero.

**Electrolytic-Solution Pressure.** In a solution after ionization the positive charges (on the metallic ions) and the negative charges (on the acid radicals) are equal in number. The condition of the solution is unchanged. But
if a plate of iron be immersed in water and a portion of it passes into solution, the ions passing into solution would be positively charges, and an equal amount of negative electricity would appear on the plate. The tendency of a metal to ionize and to pass into solution is known as its "electrolytic-solution pressure," and when elements are arranged in order of their decreasing electrolytic-solution pressures, an absolute electrochemical series results, independent of the radicals present.

Some of these electrolytic-solution pressures\(^5\) are, in atmospheres:

\[
\begin{array}{ll}
\text{Zn} & 9.9 \times 10^{18} \\
\text{Cd} & 2.7 \times 10^{12} \\
\text{Fe} & 1.2 \times 10^{12} \\
\text{Co} & 1.9 \\
\text{Ni} & 1.3 \\
\text{Pb} & 1.1 \times 10^{-3} \\
\text{H} & 9.9 \times 10^{-4} \\
\text{Hg} & 1.1 \times 10^{-17} \\
\text{Ag} & 2.3 \times 10^{-17} \\
\text{Cu} & 4.8 \times 10^{-20}
\end{array}
\]

These considerations show the requisites for depositing a pure metal from a mixed electrolyte are that the voltage be sufficiently high to exceed its solution pressure, that no metal of lower solution pressure be present, and that the voltage be not high enough to deposit those metals of higher solution pressures. On the other hand, the fact can be deduced at this point that, in order to deposit an alloy from a mixed solution, it is necessary to have the following conditions: first, an E.M.F. sufficiently large to deposit

the metal of higher solution pressure; second, a current so large that it cannot be carried by the metal of lower solution pressure; third, an anode of the alloy desired; and fourth, an electrolyte in which all its components are soluble.

The voltage difference caused by solution pressure and osmotic pressure is

\[ E = \frac{RT}{nF} \log \frac{P}{C} \]

where \( R \) is the gas constant in joules per degree, \( T \) the absolute temperature, \( n \) the valence, \( F \) the faraday, \( P \) the solution pressure, and \( C \) the osmotic pressure.

**Overvoltage.** "The electromotive force necessary to overcome the resistance of the chemical reaction at an electrode is termed overvoltage."\(^6\) It has been found that the potential difference necessary for electrolysis is greater than the theoretical amount for the decomposition of the given electrolyte by quantities which vary according to the cathode material. Here overvoltage will refer to that of hydrogen on platinum or nickel. Hydrogen is liberated on polished platinum with an overvoltage of 0.29 volts, and on nickel with 1.05 volts.

**Passivity.** If an anode is employed which is not readily soluble, the electromotive force produced by solution of the anode is not equal to that required for deposition upon

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\(^6\) Frederick H. Getman and Farrington Daniels, *Outlines of Theoretical Chemistry*, p. 494.
the cathode, and therefore a definite potential must be applied in order to cause continuous electrolysis. This failure of a metal to dissolve during the passage of a current is known as "passivity", and is particularly pronounced with nickel. It is well known that pure (or nearly pure) nickel will not corrode readily in a nickel sulphate solution; and in consequence, it is necessary to reduce this passivity, either by intentionally alloying the nickel with carbon, iron, tin, or other elements, or by adding chlorides to the solution. Usually both methods are used in commercial plating.

There is no satisfactory explanation of passivity, but it is certainly associated with, if not entirely due to, the accumulation on or in the metal of a film of oxygen or oxide. This film or oxide prevents solution of the metal until by the application of a sufficient potential difference the film is destroyed. Practically, passivity may be considered as a form of polarization as it requires the application of a certain minimum E.M.F. before any current will flow continuously.

Energy Required for Electrolysis. As is well known, the formation of chemical compounds from the elements usually is accompanied by the evolution of heat, the so-called heat of formation. The heat of formation of a compound is the heat evolved or absorbed when one mole of the compound
is formed from the elements. When the heats of formation are divided by the total valence of the one of the radicals, they stand to each other, when arranged in order of numerical value, in such a manner as to form the electromotive series. This series is shown in Table III. A metal of the series will displace in chemical compounds any metal following it, but will not affect any that precedes it. Thus iron or nickel will replace copper, but copper will not replace either nickel or iron.

Since the amount of metal deposited per hour is a function of the current only, and since it requires the same energy to break down a compound that it gives out when formed, it is obvious that, if the heat of formation be known, the minimum voltage at which the compound will break down with insoluble electrodes can be calculated.

If \( n \) be the valence of the compound and \( E \) the minimum voltage of decomposition, the energy to break up the compound is \( nEF \) watts or \( Q \) cal. per second. Since one cal. per second equals 4.186 watt seconds,

\[
E = 4.186Q/96,500n = Q/23n \quad \text{(Thompson's rule)}.
\]

This is not quite true, a more accurate statement being given by Gibbs-Helmholtz equation

\[
nEF = Q \times 4.186 + \frac{de}{dT}
\]

in which \( T \) equals absolute temperature and \( \frac{de}{dT} \) is the tem-
perature coefficient of the E.M.F. This coefficient is usually small and Thompson's rule suffices for practical purposes.

Conversely, it follows that if the minimum decomposition voltage of a compound for insoluble anodes is known, the heat of formation can be calculated. It also follows that the theoretical deposit of metal per kilowatt-hour may be calculated in advance, though 100 per cent efficiency is never reached in practical work. It is, however, a most valuable guide, for it is possible to get an approximate idea of the power that is going to be required per unit of material produced by making use of the heats of formation.

With soluble anodes the case is entirely different. If copper is being dissolved from an anode as fast as it is being deposited on the cathode, the energy of solution is equal to the energy required for decomposition, so that the current expended is only that needed in overcoming the resistance of the circuit and the internal resistance of the electrolytic cell. It can be seen why it is preferable to carry on electrolytic processes by using soluble anodes rather than to carry on the same process by dissolving the metal by purely chemical means and then depositing it by using insoluble anodes. It is possible to calculate the exact amount of any product that may be produced from the number of amperes at one's disposal, and to check up in this way both the general power efficiency and the ampere
## TABLE III

ELECTROMOTIVE FORCE SERIES OF ELEMENTS

<table>
<thead>
<tr>
<th>Element</th>
<th>Ion</th>
<th>Electrode Reaction</th>
<th>Electrode Potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>Li⁺</td>
<td>Li = Li⁺ + e</td>
<td>+2.9595</td>
</tr>
<tr>
<td>Rb</td>
<td>Rb⁺</td>
<td>Rb = Rb⁺ + e</td>
<td>2.9259</td>
</tr>
<tr>
<td>K</td>
<td>K⁺</td>
<td>K = K⁺ + e</td>
<td>2.9241</td>
</tr>
<tr>
<td>Sr</td>
<td>Sr⁺⁺</td>
<td>1/2Sr = 1/2Sr⁺⁺</td>
<td>2.9320</td>
</tr>
<tr>
<td>Ba</td>
<td>Ba⁺⁺</td>
<td>1/2Ba = 1/2Ba⁺⁺</td>
<td>2.9000</td>
</tr>
<tr>
<td>Ca</td>
<td>Ca⁺⁺</td>
<td>1/2Ca = 1/2Ca⁺⁺</td>
<td>2.8700</td>
</tr>
<tr>
<td>Na</td>
<td>Na⁺</td>
<td>Na = Na⁺ + e</td>
<td>2.7146</td>
</tr>
<tr>
<td>Mg</td>
<td>Mg⁺⁺</td>
<td>1/2Mg = 1/2Mg⁺⁺</td>
<td>2.4000</td>
</tr>
<tr>
<td>Al</td>
<td>Al⁺⁺⁺</td>
<td>1/3Al = 1/3Al⁺⁺⁺</td>
<td>1.7000</td>
</tr>
<tr>
<td>Be</td>
<td>Be⁺⁺</td>
<td>1/2Be = 1/2Be⁺⁺</td>
<td>1.6900</td>
</tr>
<tr>
<td>U</td>
<td>U⁺⁺⁺</td>
<td>1/4U = 1/4U⁺⁺⁺</td>
<td>1.4000</td>
</tr>
<tr>
<td>Mn</td>
<td>Mn⁺⁺</td>
<td>1/2Mn = 1/2Mn⁺⁺</td>
<td>1.1000</td>
</tr>
<tr>
<td>Te</td>
<td>Te⁺⁺</td>
<td>1/2Te = 1/2Te⁺⁺</td>
<td>0.8270</td>
</tr>
<tr>
<td>Zn</td>
<td>Zn⁺⁺</td>
<td>1/2Zn = 1/2Zn⁺⁺</td>
<td>0.7618</td>
</tr>
<tr>
<td>Cr</td>
<td>Cr⁺⁺</td>
<td>1/2Cr = 1/2Cr⁺⁺</td>
<td>0.5570</td>
</tr>
<tr>
<td>S</td>
<td>S⁺⁺</td>
<td>1/2S = 1/2S⁺⁺</td>
<td>0.5100</td>
</tr>
<tr>
<td>Ga</td>
<td>Ga⁺⁺⁺</td>
<td>1/3Ga = 1/3Ga⁺⁺⁺</td>
<td>0.3000</td>
</tr>
<tr>
<td>Fe</td>
<td>Fe⁺⁺</td>
<td>1/2Fe = 1/2Fe⁺⁺</td>
<td>0.4110</td>
</tr>
<tr>
<td>Cd</td>
<td>Cd⁺⁺</td>
<td>1/2Cd = 1/2Cd⁺⁺</td>
<td>0.4010</td>
</tr>
<tr>
<td>In</td>
<td>In⁺⁺⁺</td>
<td>1/3In = 1/3In⁺⁺⁺</td>
<td>0.3360</td>
</tr>
<tr>
<td>Tl</td>
<td>Tl⁺⁺</td>
<td>Tl = Tl⁺⁺⁺</td>
<td>0.3300</td>
</tr>
<tr>
<td>Co</td>
<td>Co⁺⁺</td>
<td>1/2Co = 1/2Co⁺⁺</td>
<td>0.2780</td>
</tr>
<tr>
<td>Ni</td>
<td>Ni⁺⁺</td>
<td>1/2Ni = 1/2Ni⁺⁺</td>
<td>0.2310</td>
</tr>
<tr>
<td>Sn</td>
<td>Sn⁺⁺</td>
<td>1/2Sn = 1/2Sn⁺⁺</td>
<td>0.1360</td>
</tr>
<tr>
<td>Pb</td>
<td>Pb⁺⁺</td>
<td>1/2Pb = 1/2Pb⁺⁺</td>
<td>0.1220</td>
</tr>
<tr>
<td>Fe</td>
<td>Fe⁺⁺</td>
<td>1/2Fe = 1/2Fe⁺⁺</td>
<td>0.0450</td>
</tr>
<tr>
<td>H₂</td>
<td>H⁺⁺</td>
<td>1/2H₂ = H⁺⁺</td>
<td>0.0800</td>
</tr>
<tr>
<td>Sb</td>
<td>Sb⁺⁺⁺</td>
<td>1/3Sb = 1/3Sb⁺⁺⁺</td>
<td>-0.1000</td>
</tr>
<tr>
<td>Bi</td>
<td>Bi⁺⁺⁺</td>
<td>1/3Bi = 1/3Bi⁺⁺⁺</td>
<td>-0.2260</td>
</tr>
<tr>
<td>As</td>
<td>As⁺⁺⁺</td>
<td>1/3As = 1/3As⁺⁺⁺</td>
<td>-0.3000</td>
</tr>
<tr>
<td>Cu</td>
<td>Cu⁺⁺</td>
<td>1/2Cu = 1/2Cu⁺⁺</td>
<td>0.3440</td>
</tr>
<tr>
<td>O₂(18°C)</td>
<td>OH⁻</td>
<td>OH⁻ = 1/2O₂ + 1/2H₂O + e</td>
<td>-0.3970</td>
</tr>
<tr>
<td>Po(18°C)</td>
<td>Po⁺⁺⁺⁺</td>
<td>1/4Po = 1/4Po⁺⁺⁺⁺ + e</td>
<td>-0.4000</td>
</tr>
<tr>
<td>Cu</td>
<td>Cu⁺⁺</td>
<td>Cu = Cu⁺⁺⁺⁺</td>
<td>-0.4700</td>
</tr>
<tr>
<td>I₂</td>
<td>I⁻</td>
<td>I⁻ = 1/2I₂⁻</td>
<td>-0.5345</td>
</tr>
<tr>
<td>Te</td>
<td>Te⁺⁺⁺</td>
<td>1/4Te = 1/4Te⁺⁺⁺</td>
<td>-0.5580</td>
</tr>
<tr>
<td>Ag</td>
<td>Ag⁺⁺</td>
<td>Ag = Ag⁺⁺⁺⁺</td>
<td>-0.7978</td>
</tr>
<tr>
<td>Hg</td>
<td>Hg⁺⁺</td>
<td>2Hg = Hg₂⁺⁺⁺⁺ + 2e</td>
<td>-0.7986</td>
</tr>
</tbody>
</table>

7 Handbook of Chemistry and Physics, Chemical Rubber Publishing Company, p. 905.
TABLE III (continued)

<table>
<thead>
<tr>
<th>Element</th>
<th>Ion</th>
<th>Electrode Reaction</th>
<th>Electrode Potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>*Pb</td>
<td>Pb+++</td>
<td>1/4Pb = 1/4Pb+++</td>
<td>+ e</td>
</tr>
<tr>
<td>*Pd</td>
<td>Pd++</td>
<td>1/2Pd = 1/2Pd+++</td>
<td>+ e</td>
</tr>
<tr>
<td>*Pt</td>
<td>Pt</td>
<td>1/4Pt = 1/4Pt+++</td>
<td>+ e</td>
</tr>
<tr>
<td>Br₂</td>
<td>Br⁻</td>
<td>Br⁻ = 1/2Br₂</td>
<td>+ e</td>
</tr>
<tr>
<td>Cl₂</td>
<td>Cl⁻</td>
<td>Cl⁻ = 1/2Cl₂</td>
<td>+ e</td>
</tr>
<tr>
<td>*Au</td>
<td>Au+++</td>
<td>1/3Au = 1/3Au+++</td>
<td>+ e</td>
</tr>
<tr>
<td>*Au</td>
<td>Au⁺</td>
<td>Au = Au⁺</td>
<td>+ e</td>
</tr>
<tr>
<td>*F₂</td>
<td>F⁻</td>
<td>F⁻ = 1/2F₂</td>
<td>+ e</td>
</tr>
</tbody>
</table>

*These values are doubtful, but they indicate the relative activity of the elements and are therefore included.*

The efficiency of a plant.

If the potential difference between two insoluble electrodes is less than the decomposition voltage of the electrolyte, a "diffusion" current will still flow. This is a small current carried by actual migration of ions and tends to produce difference in concentration of the solution until such time that the tendency to produce further changes is exactly balanced by the tendency to diffuse. The migration velocities of various ions have been measured. Some of them are as follows:

Ion Migration Velocities, Centimeters per Second

(potential gradient 1 volt per centimeter, 18°C.)

<table>
<thead>
<tr>
<th>Ion</th>
<th>Velocity</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>0.00326</td>
</tr>
<tr>
<td>NH₄</td>
<td>0.00067</td>
</tr>
<tr>
<td>K</td>
<td>0.00056</td>
</tr>
</tbody>
</table>

---

Ag⁺ 0.00045  
Na⁺ 0.00035  
Li⁺ 0.00180  
OH⁻ 0.00069  
I⁻ 0.00060  
Cl⁻ 0.00064  
ClO₃⁻ 0.00057  
C₂H₅O₂⁻ 0.00042

Non-ionized colloidal particles may also carry charges and migrate.

**Resistance and Heat.** From Ohm's law it is evident that the magnitude of the current which passes through any circuit is determined not only by the E.M.F. applied but also by the resistance of the bath. The total resistance of any plating bath is determined by the size, shape and electrical conductivity of the electrodes; and the resistance of that portion of electrolyte between the electrodes. Since nickel and platinum are relatively good conductors, the actual resistance of the electrodes is small compared with that of the bath. The principal reason that the current is increased by increasing the size of the electrodes is not because of the lower resistance of the large electrodes, but because a larger portion of the solution thereby becomes effective in conducting the current. We are therefore concerned principally with the resistance of the solution. The energy consumed in the passage of a current through a solution is equal to the power multiplied by the time:

\[
\text{Energy} = \text{Electromotive force} \times \text{Current} \times \text{Time} = EIT
\]

But since \( E = IR \), we may write
Energy = IR x It = I²Rt.

In simple electrolysis, in which there is no evolution of hydrogen or oxygen and in which the anode and cathode are alike both physically and chemically, all the energy expended in the passage of the current is converted into heat. The amount of heat produced may be expressed in joules, but it is more convenient to employ the calorie. A joule is equal to 0.239 cal. The above equation may therefore be written:

Calories produced by electrolysis = I²Rt x 0.239.

The temperature reached by the bath as a result of electrolysis depends upon the rate at which the heat is being carried away. The last depends upon the temperature of the room, the conductivity of the container, and the rate of evaporation of the solution.

Expression and Determination of Hydrogen Ion Concentration. Hydrogen ion concentration is usually expressed as pH. The expressing "pH" involves the logarithm of the reciprocal of the hydrogen ion concentration.

The hydrogen electrode and the quinhydrone electrode are the most accurate methods of determining pH. The quinhydrone electrode is preferable because of the ease of operation and the fact that the hydrogen electrode is so readily poisoned by oxidizing solutions. When the quinhydrone electrode is used, only pH values below eight can be measured. The quinhydrone electrode was therefore used throughout
this work except in basic solutions used in quantitative work. Here the colorimetric method was used.

Referred to the saturated calomel half cell, the quinhydrone electrode gives

\[
\text{pH} = \frac{(0.4530 - \text{Eq})}{0.059}
\]

where Eq is the electromotive force set up by the cell.

**Buffer Action.** Since nickel cannot be deposited electrolytically in highly acid solutions, it is necessary to use buffers to keep the pH within a limited range. The types of buffers usually used were weak acids or their salts in a slightly acid solution for the electroplating. The buffer action of this solution is due to the fact that the hydrogen ions formed in electroplating are taken out of the field of action by the acid radicals of the weak acid salts. In the quantitative work there was an excess of the hydroxide radicals which readily take the hydrogen ion from the solution to form water.

**The Electrolyte.** The character of the electrolyte determines to a great extent the properties of the deposit on the cathode, the corrosion of the anode, and the energy necessary for the electrolytic process. One of the most important factors to be considered is the choice of the proper salt of the metal which is to be electroplated. Listed below are factors to be considered in the choice of the salt of the metal to be used as given by Blum and Hogaboom:

(a) High solubility in order to yield a high metal
concentration.
(b) Good conductivity.
(c) Stability, i.e., resistance to hydrolysis (formation of basic salt) and to oxidation or reduction.
(d) A low metal ion concentration, such as is possessed by complex cyanides.
(e) The ability to corrode the anode nearly quantitatively. This is required especially for metals such as nickel which have a tendency toward anode passivity.
(f) Good throwing and covering power. In certain cases the conditions that will produce good throwing power are such as to decrease the average rate of deposition, or to increase the required voltage. Whether in any given operation the conditions are desirable, must be determined by economic considerations, such as the relative cost of the metal, and the time and labor involved.
(g) A sufficient low price to permit economic operation in the light of its relative advantages.\(^9\)

No single salt has all of these properties and therefore other substances must be added to give the electrolyte as many of the properties as possible. Solutions should be kept as simple as possible in order to avoid complicated reactions as to facilitate analysis of the solutions. Wherever it is possible to employ a single substance to accomplish two or more purposes it should be used. Some of the purposes for which substances may properly be added to plating solutions are the following:

(a) to increase the solubility either of the metal salt or of the oxide or basic compounds that may be formed. Thus the presence of sulphuric acid in a copper sulphate solution prevents the formation of basic cupric or insoluble cuprous compounds. Similarly the presence of excess cyanide prevents

the precipitation of insoluble cyanides.

(b) To increase the conductivity. This may be accomplished by the addition of an acid to acid solutions, such as copper sulphate, of a base to alkaline or cyanide solutions, and of a well conduction salt to solutions which must be kept nearly neutral.

(c) To regulate the acidity or, more specifically, the hydrogen ion concentration of such plating solutions as zinc and nickel, which must not have excessive acidity. For this purpose weak acids (or their salts) may be used, such as acetic and boric acids.

(d) To reduce the metal ion concentration. In the case of simple solutions this may be effected by the addition of a salt with a common ion, e.g., sodium or magnesium sulphate to metal sulphate solutions. If we consider a complex salt, such as a double cyanide, as the major compound, it already has a low metal ion concentration which can be further reduced by the addition of an excess of cyanide.

(e) To aid anode corrosion and decrease the anode polarization, for example, the addition of nickel chloride or alkali chlorides to a nickel sulphate solution and the addition of hydroxides or cyanides to an alkaline zinc solution.

(f) To increase the throwing power. Most conduction salts and addition agents tend to improve this property.

(g) To form colloids (or other dispersoids) which will migrate to the cathode and reduce the size of the crystals. These may be added directly in the form of glue, gelatin, casein, albumen, etc., or in the form of substances which will yield colloids by hydrolysis or reducing action.

(h) To exert a reducing action at the cathode or in the solution. This may possibly be associated with (g).

(i) To yield ions of a more negative metal (such as sodium, potassium, magnesium, etc.). Whether this effect is independent of (d) has not been definitely determined.10

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10 William Blum and George B. Hogaboom, Principles of Electroplating and Electroforming, p. 110.
CHAPTER III

RESULTS

The experimental work was conducted in two parts. The first experiments were all devoted to the quantitative deposition of nickel by electrolysis, and the second period was spent in the study of electroplating. The discussion will be taken up in that order.

1. Quantitative Electrodeposition of Nickel

The nickel salts used for quantitative work were nickel sulphate, nickel nitrate, nickel chloride, and nickel acetate. These salts were made up in solutions which contained approximately 0.3000 gram of nickel in fifty cubic centimeters. Each solution was then analyzed by standard gravimetric and electrolytic methods as described by Treadwell-Hall.1

The determination of nickel as nickel glyoxime was made the gravimetric method. Fifty cubic centimeters of the neutral or slightly acid solution of nickel salt were diluted to about 400 cubic centimeters and heated nearly to boiling. This was treated with a one per cent solution of dimethylglyoxime in alcohol until it was in slight excess. Ammonium hydroxide was carefully added until the solution gave a

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1F. P. Treadwell and William T. Hall, Analytical Chemistry, p. 135.
slight odor of ammonia. The solution was allowed to stand for an hour or more, filtered through a Gooch crucible, washed with hot water and dried at 110° to 120° C. for 45 minutes. The precipitate contained 20.31 per cent nickel.

The determinations by electrolysis were made with apparatus set up as shown in Figure 1.

The electrodes were solid sheet platinum, the cathode being cylindrical and the anode a small strip capable of being suspended inside the cathode. For every 0.25 to 0.30 gram of nickel present, 5 to 10 grams of ammonium sulphate and 30–40 cubic centimeters of concentrated ammonium hydroxide were added. This solution was diluted with distilled water to a volume of 150 cubic centimeters and electrolyzed with a current density of 0.6–2.0 amperes per square decimeter for three to four hours.

Figure 1. Electrolytic Apparatus

A = Ammeter
B = Source of current
C = Electrolytic cell
R = Rheostat
V = Voltmeter
To clean the cathode it was placed in a small beaker of six normal nitric acid and heated for about fifteen minutes. This treatment was necessary to remove the last traces of nickel.

**TABLE IV**

**COMPARISON OF GRAVIMETRIC AND ELECTROLYTIC DETERMINATIONS**

<table>
<thead>
<tr>
<th>Salts</th>
<th>Test</th>
<th>Gravimetric Determination</th>
<th>Electrometric Determination</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiSO₄</td>
<td>1</td>
<td>.2993 gm.</td>
<td>.2995 gm.</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>.2991 &quot;</td>
<td>.2995 &quot;</td>
</tr>
<tr>
<td>NiCl₂</td>
<td>1</td>
<td>.2997 &quot;</td>
<td>.2998 &quot;</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>.2997 &quot;</td>
<td>.2997 &quot;</td>
</tr>
<tr>
<td>Ni(NO₃)₂</td>
<td>1</td>
<td>.3010 &quot;</td>
<td>.3006 &quot;</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>.3008 &quot;</td>
<td>.3001 &quot;</td>
</tr>
<tr>
<td>Ni(C₂H₃O₂)₂</td>
<td>1</td>
<td>.3000 &quot;</td>
<td>.3001 &quot;</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>.2998 &quot;</td>
<td>.3000 &quot;</td>
</tr>
</tbody>
</table>

It will be noted that slightly larger amounts were obtained by electrolysis in the analysis of nickel sulphate and nickel acetate. These discrepancies, however, are well within experimental error. In the presence of nitrites practically no nickel was deposited.

In determining the types of solutions from which nickel could be deposited, ammonium hydroxide, sodium hydroxide, potassium hydroxide, and calcium hydroxide were used to give a basic reaction. Nickel was obtained quantitatively
only from the ammoniacal solutions. This was probably due to the formation of the complex nickel ammonium cation, as shown by the equation

\[ \text{Ni}^{++} + 4\text{NH}_3 \rightleftharpoons \text{Ni(NH}_3)_4^{++} \]

The ammonia here probably served a two-fold purpose in that it decreased the concentration of the nickel ion, which is necessary for a good plating solution, and also prevented the formation of the insoluble nickel hydroxide.

The ammoniacal solutions in general gave a bright deposit, while the solutions of the other hydroxides tended to give from blue to almost black deposits.

Nickel could not be deposited quantitatively from ammoniacal solutions alone. So it was necessary to determine what additional reagents were necessary. Each of the basic solutions mentioned above was tried in combination with the following reagents:

- Ammonium acetate
- Ammonium carbonate
- Ammonium chloride
- Ammonium citrate
- Ammonium fluoride
- Ammonium fluoroborate
- Ammonium formate
- Ammonium nitrate
- Ammonium oxalate
- Ammonium sulphate
- Ammonium tartrate
- Boric acid
- Di-sodium hydrogen ortho-phosphate
- Sodium bromide
- Sodium carbonate
- Sodium chloride
- Sodium cyanide
- Sodium di-hydrogen ortho-phosphate
- Sodium iodide
- Sodium nitrate
- Sodium orthophosphate

It was found that only the ammonium salts of the acetate, chloride, fluoride, formate and sulphate, and boric acid could be used to determine nickel quantitatively.
Table V gives in parts per thousand the amount of nickel left in solution when .3000 gram of nickel was electrolyzed from the solutions, each containing one of the six suggested addition reagents.

**TABLE V**

**PARTS PER THOUSAND OF NICKEL LEFT FROM .3000 GRAM**

<table>
<thead>
<tr>
<th></th>
<th>(NH)₄SO₄</th>
<th>NH₄C₂H₃O₂</th>
<th>NH₄CHO₂</th>
<th>NH₄F</th>
<th>NH₄Cl</th>
<th>H₃BO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiSO₄</td>
<td>0.</td>
<td>0.</td>
<td>0.</td>
<td>1.</td>
<td>1.</td>
<td>2.</td>
</tr>
<tr>
<td>NiCl₂</td>
<td>0.</td>
<td>0.</td>
<td>1.</td>
<td>0.</td>
<td>2.</td>
<td>1.</td>
</tr>
<tr>
<td>Ni(NO₃)₂</td>
<td>2.</td>
<td>3.</td>
<td>1.</td>
<td>2.</td>
<td>3.</td>
<td>2.</td>
</tr>
<tr>
<td>Ni(C₂H₃O₂)₂</td>
<td>0.</td>
<td>0.</td>
<td>0.</td>
<td>0.</td>
<td>1.</td>
<td>0.</td>
</tr>
</tbody>
</table>

Another test was made to determine the merit of these six addition reagents by dissolving exactly .3000 gram of nickel powder in acid, and electrolyzing by each of the methods. The results of these determinations are shown in Table VI where the weights of nickel are given in grams recovered.

To determine the time necessary for the electrolytic deposition of nickel from each the still and rapid methods, three electrolytes were used. They were made up as follows: The first was a solution containing .2995 of a gram of nickel as nickel sulphate, 10 grams of ammonium sulphate
and 40 cubic centimeters of concentrated ammonium hydroxide
made up to 150 cubic centimeters of solution; the second

TABLE VI

GRAMS OF NICKEL RECOVERED FROM EXACTLY .3000 GRAM
OF NICKEL POWDER WHEN THE SUGGESTED ADDITION
REAGENTS WERE USED

<table>
<thead>
<tr>
<th>Addition Reagents</th>
<th>(NH₄)₂SO₄</th>
<th>NH₄C₂H₃O₂</th>
<th>NH₄CHO₂</th>
<th>NH₄F</th>
<th>NH₄Cl</th>
<th>H₃BO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount In grams added</td>
<td>10</td>
<td>10</td>
<td>8</td>
<td>6</td>
<td>8</td>
<td>4</td>
</tr>
<tr>
<td>Nickel recovered</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Test 1.</td>
<td>.3001</td>
<td>.2999</td>
<td>.3000</td>
<td>.2999</td>
<td>.2998</td>
<td>.2999</td>
</tr>
<tr>
<td>Test 2.</td>
<td>.3000</td>
<td>.3000</td>
<td>.2998</td>
<td>.2997</td>
<td>.2996</td>
<td>.2998</td>
</tr>
</tbody>
</table>

contained .2997 of a gram of nickel as nickel chloride, 5
grams of ammonium chloride, and 40 cubic centimeters of con-
centrated ammonium hydroxide made up to 150 cubic centimeti-
ers of solution; and the third contained .3000 of a gram
of nickel as nickel acetate, 10 grams of ammonium acetate
and 40 cubic centimeters of concentrated ammonium hydroxide
made up to 150 cubic centimeters of solution. Several
beakers of the first electrolyte were made up and the first
subjected to electrolysis for fifteen minutes, the second
for thirty minutes, the third for forty-five minutes, and
so on until complete deposition was reached. The potential
was set at a current density of 1.25 amperes per square
decimeter and this setting maintained throughout the series.
This was done in order to make sure that each solution
Figure 2. Electrolysis of Nickel Sulphate in an Electrolyte of Ammonium Sulphate and Ammonium Hydroxide
Figure 3. Electrolysis of Nickel Chloride in an Electrolyte of Ammonium Chloride and Ammonium Hydroxide
Figure 4. Electrolysis of Nickel Acetate in an Electrolyte of Ammonium Acetate and Ammonium Hydroxide
would receive the same treatment. After the still method was run in this manner, the rapid method was run in the same way at time intervals of ten minutes. These data are shown in Figures 2, 3, and 4. It will be seen that stirring the solution decreases the time to less than one-half. When the sulphate was used electrolysis was found to be more rapid than when the chloride was used, which in turn was slightly more rapid than when the acetate was used.

**Acidity of the Solution.** The importance of controlling the acidity of nickel solutions in electrolysis is evident from a consideration of the relative positions of nickel and hydrogen in the electromotive series, in which nickel is .22 of a volt$^2$ more electronegative than hydrogen. From this relation we may predict that in the electrolysis of a hypothetical solution which is normal both in nickel and hydrogen ions, only hydrogen would be liberated at the cathode unless the potential were increased very much above the discharge potential for hydrogen. By decreasing the hydrogen ion concentration and increasing the nickel ion concentration, we may bring the two potentials closer together and make it easier to deposit metallic nickel. The overvoltage of hydrogen upon nickel also plays a large part in the deposition of nickel in slightly acid solution. The fact that this overvoltage increases with the current den-

---

Figure 5. Nickel Recovered From .2995 of a Gram When an Electrolyte of Nickel Sulphate, Ammonium Sulphate and Ammonium Hydroxide Was Used

A - No ammonium sulphate was used.
Figure 6. Nickel Recovered From .3014 of a Gram When an Electrolyte of Nickel Acetate, Ammonium Acetate and Ammonium Hydroxide Was Used

A - No ammonium acetate was used.
Figure 7. Nickel Recovered From .2994 of a Gram When an Electrolyte of Nickel Chloride, Ammonium Chloride and Ammonium Hydroxide Was Used

A - No ammonium chloride was used.
Figure 8. Nickel Recovered From 0.2996 of a Gram
When an Electrolyte of Nickel Nitrate, Boric
Acid and Ammonium Hydroxide Was Used
A - No boric acid was used.
sity also makes plating possible in more acid solutions.

From the above considerations it is evident that for the quantitative deposition of nickel, electrolysis must be carried on in an alkaline solution. A series of experiments were made in order to determine the alkalinity necessary for the quantitative deposition of nickel. The pH determinations were made at the end of a three to four hour period of electrolysis. This pH measurement was made at the end of electrolysis to make sure the value was correct for the time when the least amount of nickel was present. The variations in pH were made by varying the amounts of ammonium hydroxide with respect to the desired amount of the addition reagent, and then varying the addition reagent with respect to the ammonium hydroxide. The results obtained in these experiments show that the pH must be around 9.2 to 10 depending upon the reagents used. In addition to this evidence it was found that there was a minimum amount of the addition reagent which could be used, and that greater amounts could be used without altering the results. Drops noted in graphs at high pH values are due to the lack of addition reagents rather than the value of the pH. These results are given in Figures 5, 6, 7, and 8.

2. Nickel Plating

Unfortunately there was no method of quantitatively recording the value of the deposits from the various baths as regards smoothness, adherence, luster and softness.
The description of the deposits will therefore be compared by a word description of their general appearance and properties.

**Nickel Salts Used.** The first experiments conducted on electroplating were with the pure salts of nickel sulphate, nickel chloride, nickel nitrate and nickel acetate. Pure nickel electrodes were used. The conductivity of the solutions was poor, heat being produced when high current densities were used. The solutions were very slightly acid; but when subjected to electrolysis, they quickly became very acid, and large amounts of hydrogen were evolved at the cathode. When the acetate was used the anode corrosion was very poor. The plates obtained were exceedingly chalky, adhered poorly, and ranged in color from a dark gray to a black.

**Addition Reagents.** A study was then made of the effect which the various addition reagents have upon the plating from solutions of the above mentioned nickel salts. It was found necessary to decrease the nickel ion concentration in order to obtain a bright surface of metallic appearance. This was accomplished by two methods. The first was to increase the acid radical of the solution by the addition of sodium sulphate, sodium chloride, sodium acetate, or sodium nitrate to a dilute solution of the corresponding nickel salt. The second was by forming complex nickel ions with ammonia or cyanide. When the sodium salts of the acid rad-
icals were used, the plates were found to be dark and splotched with chalky deposits. When the complex ion of ammonia was formed, it was found possible to secure very lustrous coatings which were as smooth as the surface upon which they were deposited, and which adhered well to a cathode of nickel, copper, lead, or carbon. The complexes of cyanide usually gave dark coats. When the best plates were obtained by the use of cyanide, the anode corrosion was poor, and this made the electrolyte unfit for plating.

Merits of the various salts used were noted for conductance and anode corrosion. It was necessary to use salts of metals high in the electromotive series because of the position of nickel in the electromotive series. It was noted that large quantities of the alkali metals tended to darken the deposits, while ammonia salts gave brilliant deposits. The best deposits were obtained with the use of ammonium sulphate and ammonium fluoroborate. Good deposits may be obtained from the use of nickel and ammonium chloride baths, but the tendency of this solution is to darken the deposit. The nitrate was very unsatisfactory. The chloride salts were seen to give the best anode corrosion with the use of a pure nickel anode which tends to become passive. It was necessary to use chlorides to get the best anode corrosion. This corrosion is due more to the acidity of the solution than to the type of salt used, and will be discussed further in that connection.
Control of pH and Its Effect. From the discussion given on acidity in quantitative deposition, it is seen to be of fundamental importance in the electrolysis of nickel.

It is desirable to keep the solution slightly acid in order to maintain proper anode corrosion. Weak acids are used for this purpose. Those tried in this work were boric, citric, tartaric, oxalic, fluoroboric, and acetic.

![Graph showing titration curve for 50 c.c. of different solutions](image)

**Figure 9. Titration Curve for 50 c.c. of:**

- A - N NaSO$_4$
- B - N NaSO$_4$; 0.5 - M H$_3$BO$_3$
- C - N NaSO$_4$; 0.5 - M H$_3$BO$_3$; 0.2 - N NaCl
- D - N NaSO$_4$; 0.5 - M H$_3$BO$_3$; 0.1 - N NaF
- E - N NaSO$_4$; 0.5 - M H$_3$BO$_3$; 0.2 - N NaF
- F - N NaSO$_4$; 0.5 - M H$_3$BO$_3$; 0.1 - N HF

Boric acid is probably the most used for this purpose. Curves A and B in Figure 9 show that between pH 3 and 6.5 a nickel sulphate solution is practically unbuffered, as is seen on the addition of a small amount of acid or alkali a great change of pH occurs. The addition of boric acid flattens the slope of the curve considerably, especially between the pH range of 5 and 6.5 and the solution is thereby much better buffered.

While the buffer effect of boric acid is very notice-

\[ \text{Figure 10. Titration Curve for 50 c.c. of:}^4 \]
\[ G = 0.3 \text{ M } \text{NiSO}_4 - (\text{NH}_4)_2\text{SO}_4 \]
\[ H = 0.3 \text{ M } \text{NiSO}_4 - (\text{NH}_4)_2\text{SO}_4 - 0.3 \text{ M } \text{H}_3\text{BO}_3 \]

\[ ^4 \text{(Taken from) M. R. Thompson, op. cit. p. 346.} \]
able in the case of nickel sulphate, as seen in curves A and B, Figure 9, it is just barely evident, if at all, in the case of nickel ammonium sulphate (curve G and H, Figure 10). It appears therefore that nickel borate does not exist in approachable concentrations in the presence of ammonium salts. If a fluoride in the form of the acid or the salt is added to a solution containing boric acid, there is then present some complex and indefinite compounds generally referred to as fluoroboric acid or fluoroborates. These mixtures possess remarkable buffer action in proportion to the amount of the fluoride present provided the boric acid is in excess. This is shown by comparing curve D, E and F with curves A and B, Figure 9. In the latter type of solutions, it is evident that widely different anode and cathode efficiencies must occur in order to produce rapid changes in pH.

In the experimental work, it was found that electrolytes of the borates or fluoroborates gave ideal deposits and that the solutions maintained nearly a constant pH after several hours of plating. This is when the anode is not of pure nickel but contains small amounts of iron. Citric acid was found to serve this purpose fairly well, while none of the other acids added greatly to the properties of the solution.

The effect of pH on current efficiency is shown in Figure 11 as prepared by M. R. Thompson. It was found that in solutions with a pH below 4 pitting was common. Usu-
Figure 11. Cathode Efficiency of Nickel Deposits\(^5\)

A = 1.5 amp./dm\(^2\)  (13.9 amp./sq. ft.)
B = 0.2 amp./dm\(^2\)  (1.9 amp./sq. ft.)
   In NaISO\(_4\) 0.25 M H\(_3\)BO\(_3\)  - 0.1 N NaCl
C = 1.5 amp./dm\(^2\)  (13.9 amp./sq. ft.)
D = 0.2 amp./dm\(^2\)  (1.9 amp./sq. ft.)
   In NaISO\(_4\) 0.25 M H\(_3\)BO\(_3\)  - 0.1 N NaF

ally the plate was very bright, but at high current densities, a chalky deposit was obtained. This chalky deposit was probably due to the co-precipitation of hydrogen.

In discussing the deposition of nickel at low pH, William Blum lists the following advantages and disadvantages:

Advantages

1. Increase in plating range. It is possible to use a higher current density without

\(^5\) (Taken from) M. R. Thompson, op. cit., p. 349.
peeling or cracking at the edges. The decreased time due to the use of the higher current density permits a better use of the equipment.
2. Better anode corrosion.
3. No turbidity in the bath if the pH is kept sufficiently low (below about 3.0).
4. The nickel is supplied to the solution from the anodes instead of by the addition of nickel salt, thus giving lower costs.

Disadvantages
1. There is a greater initial tendency for a low pH bath to cause pitting.
2. The cathode efficiency is lower.
3. Too high anode corrosion under some conditions.
4. Trouble will result if the pH is allowed to become high.
5. There is a tendency for the pH to increase gradually, thus making it more difficult to control pH values.
6. Since it is desirable to operate the low pH baths at high temperatures, the tanks and linings are restricted to materials which will permit such temperatures.
7. For bright nickel plating the low pH bath gives best results at low temperatures, while the high pH bath can be operated over a wider temperature range.
8. The low pH bath is not suitable for plating zinc base die castings. It might be desirable to discuss these advantages and disadvantages in detail.6

Current Density. Increasing the current density tends to give better deposits up to a certain value. At too high current densities the deposits become coarse and spongy with a characteristic burnt appearance. An increase in metal concentration will tend to decrease these faults.

Mechanical Agitation of the Solution. The use of high

current densities was found to give better results in agitated solutions; that is, there was less tendency for the plate to show burned spots. This was due to the fact that an even distribution of nickel was maintained throughout the solution.

In a paper presented to the American Electrochemical Society by C. W. Bennett, H. A. Kenny and R. P. Dugliss, it was shown that mechanical agitation decreased the cathode efficiency.\(^7\) The explanation of this is that in using

![Figure 12\(^8\)]


stationary electrodes, as hydrogen is evolved, a film of ammonium hydroxide is built up around the cathode which permits a larger ratio of nickel to hydrogen to be deposited. When agitation is employed, this film is destroyed.

Figure 12 shows the results in efficiency with time when rotating cathodes are used. The electrolyte contains seven grams of nickel ammonium sulphate, one gram of nickel chloride and one hundred cubic centimeters of water. The current density was 1.5 amperes per square decimeter.

The effect of the accumulation of ammonium hydroxide at the anode is shown in Figure 13 and shows an increase in efficiency with time when varying amounts of ammonium

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Figure 13

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⁹(Taken from) C. W. Bennett, H. C. Kenny and R. P. Dugliss, op. cit., p. 341.
hydroxide are used with stationary electrodes.

Figure 14 gives the effect of varying the degree of agitation by using the same solutions as before.

\[\text{Efficiency} \]

\[\text{Minutes} \]

\[\text{Figure 14}^{10}\]

\[\text{(Taken from) C. W. Bennett, H. C. Kenny and R. P. Dugliss, op. cit., p. 343.}\]
CHAPTER IV

A. Quantitative Electrolytic Deposition

Recommendations. These solutions are suggested for obtaining nickel quantitatively from the salts of nickel sulphate, nickel chloride or nickel acetate when there is from .2 to .3 of a gram of nickel in solution. A current density of 1.6 to 2.5 amperes per square decimeter may be used.

Solution A.

Thirty-five to forty-five cubic centimeters of concentrated ammonium hydroxide, five to ten grams of nickel sulphate and the nickel salt made up to a volume of 150 cubic centimeters.

Solution B.

Thirty-five to forty-five cubic centimeters of concentrated ammonium hydroxide, four to eight grams of ammonium chloride and the nickel salt made up to a volume of 150 cubic centimeters.

Solution C.

Thirty-five to forty-five cubic centimeters of concentrated ammonium hydroxide, six to twelve grams of ammonium acetate and the nickel salt made up to a volume of 150 cubic centimeters.

Solution D.

Thirty-five to forty-five cubic centimeters of concentrated ammonium hydroxide, four to eight grams of ammonium fluoride, and the nickel salt made up to a volume of 150
cubic centimeters.

Conclusions.

1. The use of ammonium hydroxide for the quantitative deposition is important for two reasons: first, to decrease the hydrogen ion to such an extent that the nickel will deposit in very dilute solutions; and second, it reduces the nickel ion concentration, which is necessary for good plating and for preventing the formation of a nickel hydroxide precipitate.

2. The presence of too little ammonium hydroxide results in the deposition of black nickel hydroxide on the anode.

3. For best results an addition agent is used to increase the conductivity of the solution. For this purpose ammonium sulphate, ammonium acetate, ammonium chloride, ammonium fluoride, ammonium formate or boric acid may be satisfactorily used; however, ammonium sulphate or ammonium acetate is preferable.

4. Agitation decreases the time of deposition.

B. Electroplating

Recomendations.

Solution A

<table>
<thead>
<tr>
<th>Reagents</th>
<th>Grams per liter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel sulphate (\text{NiSO}_4\cdot 7\text{H}_2\text{O})</td>
<td>100</td>
</tr>
<tr>
<td>Ammonium sulphate (\text{(NH}_4\text{)}_2\text{SO}_4)</td>
<td>15</td>
</tr>
</tbody>
</table>
Solution A (continued)

Reagents                  Grams per liter

Ammonium chloride \( \text{NH}_4\text{Cl} \) 15
Boric acid \( \text{H}_3\text{BO}_3 \) 20

For the best operation the plating is done at a current density of one to two amperes per square decimeter.

Solution B

Reagents                  Grams per liter

Nickel sulphate \( (\text{NiSO}_4 \cdot 7\text{H}_2\text{O}) \) 250
Ammonium fluoride \( (\text{NH}_4)_2\text{F}_2 \) 10
Boric acid \( \text{H}_3\text{BO}_3 \) 35

This solution may be used satisfactorily with an average current density of from three to five amperes per square decimeter.

Conclusions.

1. Better deposits may be secured in acid solutions with a high current density.

2. When low current densities are used, the pH should be comparatively high.

3. Deposits made in highly acid solutions are brighter and more brittle than those with a high pH.

4. With pH values up to approximately four the deposits are bright but very likely to show cracking and pitting. A pH of approximately four is therefore the lower limit of good deposition.

5. In basic solutions the deposits are likely to be
dark and curling, and cracking is often noted.

6. Increasing the concentration of the nickel salt permits the use of a higher current density.

7. Agitation permits the use of a high current density.

8. Agitation decreases the cathode efficiency.  

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