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FERMENT, George R., 1939-CURRENT-POTENTIAL EFFECTS OF TRACE IMPURITIES IN MANGANESE ELECTRO-WINNING.

Newark College of Engineering, D.Eng.Sc., 1965 Engineering, chemical

University Microfilms, Inc., Ann Arbor, Michigan

CURRENT-POTENTIAL EFFECTS OF TRACE IMPURITIES IN MANGANESE ELECTROWINNING

BY

GEORGE R. FERMENT

A THESIS

PRESENTED IN PARTIAL FULFILLMENT OF

THE REQUIREMENTS FOR THE DEGREE

OF

DOCTOR OF ENGINEERING SCIENCE IN CHEMICAL ENGINEERING

AT.

NEWARK COLLEGE OF ENGINEERING

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ABSTRACT

The purpose of this investigation was to study the effects of trace metallic impurities, found in manganese electrowinning solutions, on cathode current-potential curves.

This investigation led to the development of a novel analytical tool, emphasizing polarization curves as a means of detecting trace metallic impurities in manganese sulfate electrolytes. The method possesses two distinguishing features: (a) it uses the competing hydrogen evolution reaction as a means of detecting metallic impurities, and (b) it enables one to establish if the electrolyte is sufficiently pure for efficient electrolysis.

Nine metallic impurities were studied, consisting of: nickel, cobalt, silver, copper, zinc, molybdenum, cadmium, magnesium, and sodium. In the first series of runs, the individual effect of each metallic impurity on the standard polarization curve was determined for a range of concentrations. Not all of the impurities affected the polarization curve; i.e. cadmium, magnesium, and sodium had no effect. Nickel, cobalt, silver, copper and zinc significantly affected the standard curve yielding a correlation between transition current and concentration of impurity. Molybdenum had an effect on the polarization curve which could not be correlated.

In the second series of runs, the effects of binary mixtures of impurities were studied to see if the transition current of the mixture could be predicted from knowing the values for the individual constituents. However, it appeared that interactions occurred between impurities which prevented the prediction of the transition current of the mixture by a simple additive law.

APPROVAL OF THESIS

FOR

DEPARTMENT OF CHEMICAL ENGINEERING

NEWARK COLLEGE OF ENGINEERING

BY

FACULTY COMMITTEE

APPROVED:

NEWARK, NEW JERSEY

JUNE, 1965

ACKNOWLEDGMENT

I would like to express my appreciation to Dr. C. L. Mantell for his advice during this investigation.

I would also like to express my sincere appreciation to my wife, Barbara, for her patience and encouragement, and for her painstaking task in typing this thesis.

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INTRODUCTION

The commercial importance of hydrometallurgy as an economic method of recovering pure metals from their ores has been well established in the last forty years. The first commercial units for electrowinning copper from low grade ores were placed on stream just past the turn of the century. Later this new technique was applied to electrowinning zinc, followed by cadmium, and still later manganese. Naturally, the commercial success of any chemical process is dictated primarily by economics. At the time, there existed no commercial process which could favorably compete with electrolytic copper for metal recovery from low grade ores. Pyrometallurgy was a strong competitor of electrolytic zinc and manganese, but this competition soon vanished when quantitative methods were evolved for maintaining electrolyte purity.

The successful electrowinning of zinc and manganese relied heavily upon maintaining a high purity electrolyte. Because of necessity, elaborate purification schemes were developed to remove practically all of the heavy metals, and magnesium and calcium of the light metals. Extensive investigations have been undertaken to determine the effects of trace metallic impurities on cell efficiency in zinc and manganese electrowinning. Although fairly accurate concentration limits have been established for single impurities, still relatively little is known about the effects of mixtures. With high purity electrolytes, favorable cell efficiencies are consistently obtained; but with impure solutions, there is usually an appreciable reduction in efficiency.

Along with the rapid rise to commercial prominence of electrochemical processes, there has been an equally significant lag in developing rapid analytical methods for determining whether an electrolyte is sufficiently pure for efficient electrolysis. At present, the most sensitive test for impurities is the behavior of the electrochemical cell, a situation which has existed for nearly four decades. Impure electrolytes will cause a serious reduction in cell efficiency, and in many cases, metal deposition will be completely prevented. However, the deleterious effects of trace impurities are not usually evident until after long periods of electrolysis, resulting in a disruption of the commercial process and the inherent loss of profits. Thus it would be highly desirable to have an analytical method which could predict the behavior of an electrolyte, in terms of cell efficiency, prior to reaching the commercial cell. With this in mind, the present thesis is an attempt to develop and evaluate such an analytical tool for manganese electrowinning based on cathode colarization curves.

SCOPE AND PURPOSE

Naturally, a complete study of the effects of trace impurities in manganese electrolytes would necessarily involve a study of both organic and inorganic species and mixtures of them. Such a task, of course, would be impossible; so the present study was restricted to a selected group of metallic impurities normally found in commercial baths. Being selective allows one to study the effects of various groups within the Periodic Table, such as: the alkaline-earth metals, the alkali metals, the transition metals, and the zinc family without necessarily studying each element. Such a cross-section would enable a trend to be observed within a particular group which may then be compared with other work on the same impurities in order to establish a qualitative relationship between the polarization curves and the cell efficiency. Once such a relationship has been established, the determination of a simple current-potential curve would permit the investigator to predict how an electrolyte will behave under given conditions of electrolysis.

The effects of nine metallic impurities on the polarization curve were studied in this investigation. The nine impurities: nickel, cobalt, silver, copper, molybdenum, zinc, cadmium, magnesium, and sodium have been studied by other investigators and their effect on cell efficiency is well established. In the first series of runs, the individual effect of each impurity was established; while a second series considered the effects of mixtures.

HISTORICAL

Early commercial interests in electrolytic manganese were stimulated by two very important factors: (a) the United States dependency upon foreign suppliers for high grade manganese ore which was used extensively in the manufacture of ferro-alloys, and (b) our vast reserves of low grade manganese ore.

The early studies of Arsdale and Maier (7) demonstrated that manganese could be cathodically deposited from neutral sulfate solutions. Later, Allmand and Campbell (3, 4) studied manganese deposition from both aqueous sulfate and chloride electrolytes, but their only success was in preparing small quantities of the pure metal. During the early years, just past the turn of the century, many other investigators attempted to develop an efficient electrochemical process for winning manganese (21, 22, 50), but all met with some degree of difficulty. Finally, through the pioneering efforts of Shelton and Royer, a promising hydrometallurgical process was developed for electrowinning manganese (46, 61, 77, 78). Through these studies efficient operating conditions were established and the deleterious effects of trace impurities were recognized. Again, as in electrolytic zinc, the successful electrowinning of manganese from sulfate solutions was possible because of the high purity of the electrolyte.

DETERMINATION OF THE EFFECTS OF IMPURITIES

Numerous methods have been employed for studying the effects of metallic impurities in electrolytes and they depend primarily upon the specific nature of the problem. For example, in metal deposition, the prime concern is how the impurity affects the cell efficiency and the quality of the deposit; so methods are employed that measure these parameters. Typical of this technique were the investigations of Jacobs et al (44), who studied the effects of metallic impurities in manganese electrowinning. The first method that was developed was based on a two hour plating run performed in a small electrolytic cell. Here, it was necessary to determine the concentration of impurity that would lower the current efficiency by two per cent. Comparing the results with commercial specifications, it was found that this test was too insensitive. A second method was based on a minimum current density. Initially manganese was plated at a current density of 45 asf, then the current density was gradually decreased in uniform steps of equal time intervals. Metal deposition would continue until a minimum current density was reached, at which point, manganese would begin to redissolve and the cathode potential would exhibit a rapid positive shift. The addition of impurity would cause the minimum current density to increase. Thus a critical concentration of impurity was defined as that

which would cause a significant increase in the minimum current density. Although this test proved to be more sensitive than the first, it still lacked the degree of control necessary for a good analytical tool. The final method was based on a 24 hour plating run, performed in a relatively large test cell. Here, current efficiencies were calculated with and without impurities in the electrolyte, and the critical concentration was established as the maximum amount of impurity that the electrolyte could tolerate before there would be a serious loss in efficiency. Also, it was found that the amount of impurity that could be tolerated decreased as the plating time incircased, indicating deposition of the impurity. Because this test, in essence, duplicated the conditions of commercial practice, it was found to be extremely sensitive to metallic impurities. However, because of the long duration of the test, it was not practical as a method of analysis.

It had long been known that small amounts of impurities significantly affected the hydrogen overvoltage at a metal surface, increasing or decreasing it depending upon the nature of the impurity. However, it was Bockris (13) who first quantitatively established the limit for the onset of poisoning at 10^{-10} moles/L. The effects of impurities were studied by means of potential-time curves produced at a constant current density. The technique was to establish a

of impurity until it had a significant effect on the potential-time curve. Although such a method was shown to be quite sensitive, the technique did not lend itself to rapid analyses because it took several hours to establish stable potential-time curves.

Serfass and co-workers (63-73) developed various colorimetric and spectrophotometric techniques for analyzing plating baths for trace impurities. The procedures are complex and lengthy, usually requiring isolation of the impurity by one or more of the following methods: (a) Precipitation and filtration, (b) distillation, (c) oxidation or reduction, (d) extraction, and (e) adsorption. Once the species had been isolated, it was necessary to establish a color complex with organic compounds. Here, the method of analysis was based upon the detection of a specific ion, and in no way established the behavior of an electrolyte during electrolysis when that particular species was absent.

Previous analytical methods have been based on constant current densities or on the detection of specific ions. The proposed method for analyzing manganese sulfate electrolytes for trace metallic impurities is based on the production of dynamic current-potential curves. This analytical method possesses two distinguishing features:

(a) it utilized the competing hydrogen evolution reaction as a means of detecting the presence of deleterious

\$

impurities, and

 (b) it enables one to predict directly from the polarization curve if an electrolyte is sufficiently pure for efficient electrolysis.

The polarization curves are produced by continuously changing the cell voltage at a programmed rate. Starting with a clean stainless steel cathode, the cell voltage is initially adjusted to yield zero current; the program is then started and the current is plotted as a function of the cathode potential. A typical current-potential curve is depicted in figure 1. Initial region (A) is where the hydrogen evolution reaction predominates and the polarization curve is essentially that for hydrogen evolution on a stainless steel cathode. As the cathode potential becomes more negative, a limiting or transition current is reached, at which point, there is a large negative potential shift (region B) with relatively little change in current. When the potential shift is completed, manganese is freely codepositing with hydrogen and the polarization curve once more exhibits an inflection point. A further increase in cell voltage will now cause a small increase in cathode potential and a relatively large increase in current (region C).

A standard curve is now produced for the pure electrolyte or an electrolyte that is known to yield an acceptable



FIGURE 1



CATHODE POTENTIAL

current efficiency. Since a major portion of the polarization curve is devoted to hydrogen evolution. it should be sensitive to factors that affect the hydrogen overvoltage. Impurities which affect the character of the cathode surface, thus altering the hydrogen overvoltage, should affect the polarization curve in a noticeable manner. Poisons and activators should have opposite effects on the standard current-potential curve, causing a positive or negative displacement of the transition current density. Thus a correlation is possible between transition current density and concentration of impurity. However, a quantitative correlation need not be evident for this method of analysis to be of value, since any deviation of the polarization curve from its standard characteristics will signify the presence of impurities in the electrolyte. So it is only necessary to establish a relationship, however qualitative, between the polarization curves and the operation of a commercial cell.

HYDROGEN ELECTRODE KINETICS

Because of the major role the hydrogen evolution reaction plays in the proposed method of analysis, it was deemed necessary to review the established kinetics of this reaction. For all intensive purposes, this survey will be primarily descriptive and the author refers the readers to other references (9, 12, 26, 45, 51, 53) for a more quantitative development of the governing theories.

It has now become generally accepted that one or more of only three reactions control the rate of cathodic hydrogen evolution. Thus in aqueous solutions a proton approaching a cathode (M) during electrolysis undergoes,

Discharge:

S-H^{*} + M-e \Rightarrow M-H + S (1) Desorption: either M-H + M-H \Rightarrow 2M + H₂ (2) or S-H^{*} + M-H + M-e \Rightarrow 2M+H₂+S (3)

where S represents a solvation sheath, either H₂O or OH, and M the metal cathode. The above reactions have been commonly referred to as: (1) discharge, (2) catalytic, and (3) electrochemical. Attention should be drawn to the fact that discharge must always occur, while the catalytic and electrochemical reactions may be either alternative or simultaneous reactions. Analysis of the above three reactions will reveal that the overall hydrogen evolution reaction must be controlled by one of two types of reactions: (a) one involving ions or (b) one involving atoms. Thus the specific rate of the catalytic reaction should not be affected by the existence of an electrical potential across the metal-solution interface, since the chemical potentials of its components are only dependent upon the activity of atomic hydrogen. Hence, the velocity of the catalytic reaction would be of the simple form $v=ka_{H}^{2}$, where a_{H} is the activity of atomic hydrogen. Such a mechanism would give rise to a limiting rate when the electrode surface became saturated with atomic hydrogen. The chemical potentials of the other two reactions are very much dependent upon electrical potential, so that in turn, the reaction velocities are also dependent upon it.

Hydrogen electrode kinetics developed out of the Transition State Theory (36, 37). Let us consider a solvated proton at position A (figure 2) before making its transition to the electrode and make the initial assumption that there exists a zero metal-solution potential. Then the free energy of activation is given by ($G_x - G_a$), and the rate of the forward reaction is

$$\mathbf{r} = \mathbf{K} \mathbf{a}_{\mathbf{n}} \exp(-\mathbf{\Delta}\mathbf{G}^*/\mathbf{R}\mathbf{T})$$
(4)

ĺ

where K is a constant and a_r is the product of the

/3



FIGURE 2



DISTANCE FROM ELECTRODE

FREE ENERGY

activities of the reactants. Now let a potential difference $\triangle V$ exist across the metal-solution interface. The free energy of activation must necessarily increase by the electrical work done in transporting the charged particle from position A to plane X. The free energy of activation new becomes

$$\Delta G = \Delta G^* + nF^3 \Delta V \qquad (5)$$

where nF is the electrical charge. The new reaction rate is now given by

$$\mathbf{r} = K a_{\mathbf{r}} \exp(-\Delta G^*/RT) \exp(-nF\beta \Delta V/RT)$$
(6)

and the current

$$-$$
 i = nFr (7)

Combining equations 6 and 7, and letting $A = n\beta$, the forward current is

$$i_{f} = K_{f} a_{r} \exp(-\Delta G_{f}^{*}/RT) \exp(-\alpha F \Delta V/RT)$$
(8)

the reverse

$$i_{b} = K_{b} a_{p} \exp(-\Delta G_{b}^{*}/RT) \exp(-nF(1-\beta)\Delta V/RT)$$
(9)

and

$$\Delta V = \Delta V_e + \gamma \tag{10}$$

where ΔV_e is the equilibrium potential and γ the overvoltage.

Now consider the system at equilibrium,
$$7 = 0$$

 $i_f = i_b = i_0$ (11)

and

$$i_{o} = K_{f} a_{r} \exp(-\Delta G_{f}^{*}/RT) \exp(-\alpha F \Delta V_{e}/RT)$$
(12)
= $K_{b} a_{b} \exp(-\Delta G_{b}^{*}/RT) \exp(-nF(1-\beta)\Delta V_{e}/RT)$

where i_0 is defined as the exchange current.

Combining equations 8, 9, 10, and 12, the net cathodic current is given by

$$i_{c} = i_{f} - i_{b}$$
(13)

or

$$i_{c} = i_{0} \left\{ exp(-\alpha \gamma F/RT) - exp((n-\alpha)\gamma F/RT) \right\} (14)$$

for .075v) $\pi \langle -.075v$

$$i_{c} = i_{o} \exp(-\alpha \gamma F/RT)$$
(15)

and rearranging

$$7 = (RT/AF) \ln(i_0/i_c) = a - b \log(i_c)$$
 (16)

which is the Tafel Equation.

From the preceding equations, it is apparent that in order to have a net cathodic current it is necessary to increase the equilibrium potential by the overvoltage, η .

The physical significance of overvoltage now becomes clear, it represents an energy term which is proportional to the quantity by which the free energy of activation at the reversible potential must be reduced in order to force the overall reaction to proceed at a specified rate. It is also evident that the rate of the hydrogen evolution reaction is very much dependent upon two other factors, α and the free energy of activation. The free energy of activation is primarily a function of cathode material and surface condition; while the quantity α is dependent upon the nature of the metal-solution interface.

Theoretical treatment of hydrogen electrode kinetics has been very helpful in establishing diagnostic criteria (20, 51) principally for determining the overall reaction path and estimating the rate controlling step. Two important criteria that have been extensively used to distinguish the discharging entity are the pH and salt effects. These effects were long recognized, but it was deBethune (24) who first developed a quantitative relationship to explain the observed experimental results. For example, when a proton is discharged from a hydronium ion and it is followed by either fast catalytic or fast electrochemical desorption, reducing the pH or concentration of neutral salt will cause the hydrogen overvoltage to decrease. Similar effects should also be observed for fast discharge followed by slow electrochemical desorption. However, when

the source of protons originate from water molecules, theory predicts that the converse effects should be expected. The theoretical pH and salt effects are in fair agreement with experiment (5, 40, 56, 58, 59, 76) particularly for mercury electrodes (25, 53).

In recent years, a great deal of emphasis has been placed on the effect of electrode material in relation to the rate of the hydrogen evolution reaction (23, 52, 57). However, this concept was not new for it was Horiuti and Polanyi (1) who first showed that the rate of the hydrogen reaction was dependent upon electrode material when proton discharge was rate controlling. It was their postulate that the reaction rate was a specific function of the heat of adsorption of hydrogen atoms on the metal surface. An increase in the heat of adsorption would cause a corresponding decrease in the heat of activation. This, in turn, reduces in which decreases the overvoltage and causes the reaction rate to increase. However, at present, no quantitative application of the heat of hydrogen adsorption can be made in relation to overvoltage, since a great deal of controversy still exists as to what are the rate controlling mechanisms on the different metal electrodes. Experimental evidence (5, 11, 14, 17, 19, 54) indicates that the rate of the hydrogen evolution reaction increases in accordance with the sequence Hg, Ag, Cu, Ni, and Pt. Table 1 shows

a selected list of the Tafel parameters a, b, and $\tilde{\gamma}$. Thus it is evident that there is a large increase in rate in going from Hg to Ag, while the difference in reaction rates is almost indistinguishable between Ag and Cu. Again, there are increases in going from Cu to Ni and from Ni to Pt. Table 2 shows the relationship between the heat of atomic hydrogen adsorption and overvoltage on various metal surfaces. Thus, for the metals selected, a definite relationship is apparent. In the final analysis, it is apparent that although the hydrogen evolution reaction has been extensively studied (55), a critical survey (10,20) will reveal that the complex mechanisms are still not widely understood even in the purest solutions, and in impure solutions, even less is known about the effects of impurities.

TABLE 1

PARAMETERS OF THE TAFEL EQUATION

7 = a - b log(i)-3 2 2 10 amps/cm

Metal	y volts	a <u>volts</u>	b	Reference
Pt	-0.03	-0.114	0.03	11
Ni	-0.28	-0.64	0.12	11
Cu	-0.406	-0.771	0.122	19
Ag	-0.435	-0.81	0.125	14
Hg	-1.056	-1.395	0.113	18
· 1			· · · · ·	•

TABLE 2

HEAT OF H ADSORPTION (57)

Metal	volts	∆ H Kg-cal/atom
Pt	.0127	62.9
NÌ	•32	60.2
Fe	. 40	60.5
Cu	• 46- • 57	58.5
Ag	• 59	57.5
Pb	•85	55.6
Zn	-	54.3
Cđ	•99	53.9
Hg	1.04	52.9

IMPURITY EFFECTS IN HYDROGEN EVOLUTION

Levina and Sarinsky (2) were the first to recognize the effect of impurities on the hydrogen evolution reaction. However, it was Bockris and Conway (9, 13) who quantitatively established the concentration of 10^{-10} moles/L as sufficient to significantly affect the hydrogen reaction. Small quantities of As_20_3 , CO, CS_2 , and KCN poisoned the reaction, while traces of PtCl₄ lowered the overvoltage on silver and nickel electrodes towards that of a platinized platinum electrode.

The effects of large organic molecules, such as the amyl and octyl alcohols (53), were also studied. It was postulated that the poison had two primary effects: (a) to change the nature of the double layer, causing an increase in the Tafel "b" slope, and (b) to saturate the adsorptive power of the surface by raising the energy levels of the other sites, causing an increase in the heat of activation.

Hillson (41) studied the effect of capillary-active materials on many different electrodes. He postulated that the surface adsorption of the molecules tends to block the discharge of hydrogen ions and also reduces the surface activity of atomic hydrogen.

A qualitative attempt (23) has been made to explain

the sensitivity of the transition metals to poisoning by substances such as H_2S and CO in terms of "d" band character. The "d" band character is related to the number of unpaired electrons in the metal"d" band. Since both H_2S and CO have lone pair electrons, they will donate these electrons to fill the metal "d" band. This, in turn, increases the metal "d" band character, lowering the energy for atomic hydrogen adsorption, and thus decreasing the rate of the primary discharge reaction.

It is quite evident that a large degree of uncertainty still exists in understanding the overvoltage phenomena associated with impurities. Although some attempts have been made to qualitatively explain these phenomena, they have usually lacked rigorous quantitative proof. Even less information exists on impurities that tend to accelerate the hydrogen reaction and theoretical treatment has not even been attempted.
IMPURITY EFFECTS IN METAL DEPOSITION

C. A. Hansen (39) in 1919 was the first to recognize the deleterious effects of metallic impurities in relation to zinc electrowinning. Certain metallic impurities present in the electrolyte would cause a serious reduction in current efficiency. It soon became evident that the performance of the zinc cell was more sensitive to trace impurities than any analytical methods yet developed for chemical identification and determination. Thus the operation of the zinc cell was established as the final test of the thoroughness of the purification scheme; a commercial practice which has not encountered much change to the present day.

Continuing the work of Hansen, Laist et al (47) established the critical concentrations of several metallic impurities, above which there would be an appreciable loss in current efficiency. Later, Tainton and Clayton (74) confirmed and supplemented Laists original list.

Steintveit and Holtan (79) investigated the effect of as many as four impurities present simultaneously in a Zinc sulfate electrolyte. They found that no simple additive law could explain the effect of mixtures on the current efficiency. For example, the presence of only one of two impurities may have no harmful effect at all, while the

18.00

presence of both simultaneously would seriously reduce the current efficiency.

Jacobs et al (44), in electrowinning manganese, encountered problems similar to those for zinc; trace impurities would seriously affect the current efficiency of the process. Through his efforts critical concentration limits were established for a large number of metallic impurities.

Organic and inorganic impurities have been studied in relation to copper deposition by a great many investigators (15, 48, 75). With the addition of amino and hydroxy acids (62) to the copper electrolyte, there existed a parallelism between the increase in polarization and decrease in crystal size. In all systems studied, the impurity usually increased the polarization which resulted in a reduction in cell efficiency.

In electrolytic chlorine-caustic cells, Angel et al (6) showed that trace amounts of graphite in the presence of magnesium or aluminum appreciably reduced the current efficiency. It was proposed that a layer of hydroxide forms on the mercury cathode to which the particles of graphite adhere, making good electrical contact. The resulting loss in current efficiency was attributed to the low hydrogen overvoltage which existed on graphite compared to that on mercury.

Bockris and Drazic (16) found in studying the reduction of iron that the presence of impurities does not alter the mechanism of the deposition reaction, but that they do increase the rate of the hydrogen evolution reaction which reduces the cell efficiency.

Ewing and co-workers (28-35) studied impurities in relation to their effects on the physical properties of the electroplate. They developed standard procedures for testing a plated panel for appearance, adhesion, salt-spray corrosion resistance, ductility, and hardness. An attempt was made to develop a correlation between these properties and metallic impurities. Again, the tests were somewhat lengthy and relied heavily upon visual observations.

It is acknowledged that there exists a vast amount of work on the effects of trace impurities in metal deposition. However, because of the complexity of these effects, they have not yet yielded to theoretical treatment; and so relatively little is known about the nature of these phenomena.

EXPERIMENTAL

Apparatus

Since the proposed analytical method is based on current-potential curves, it is necessary to provide a means for measuring these quantities. The cell current was measured in terms of a voltage drop across a precision resistor, while the cathode potential, relative to a saturated calomel electrode, was measured directly by a high impedance vacuum tube voltmeter. Both of these signals were then fed to a X-Y recorder which automatically plotted the polarization curve. The entire experimental system is shown by an electrical schematic in figure 3, where the symbols refer to the following list.

- P is a DVIII transistor power supply manufactured by the Model Rectifier Corporation. It is rated at 30 volts and 2 amperes. In this investigation, a standard setting of 10 volts was used for the experiments.
- R₁ is a programmed variable resistor, rated at 30 ohms and 5 watts, and manufactured by the Clarostat Corporation. This motor driven potentiometer was used to continuously change the cell voltage at a programmed rate.

 R_2 and R_3 are respectively 10 ohm and 4 ohm variable

CIRCUIT SCHEMATIC

FIGURE 3



resistors. Their sole purpose was to function as a pair of voltage dividers, coarse and fine control, so that the starting cell voltage could be adjusted to give zero current.

R₄ is a 10 ohm precision resistor used to measure the cell current. It is manufactured by the Precision Resistor Corporation.

R_r is a standard 20 ohm resistor.

- SCE is a Beckman saturated calomel electrode with a fiber junction which is used as a reference electrode for measuring the cathode potential.
- SB is the necessary salt bridge which provides electrical contact between the working cathode and the calomel reference electrode.
- SC is an EPLAB Students' Cell which is used to supply a bucking voltage opposite to that of the cathodecalomel couple. The average measured voltage for the standard cell was 1.01789 volts.
- V is a Model 413AR Hewlett Packard DC Null Voltmeter which is used to measure the cathode potential. This particular model has a millivolt output proportional to the voltage input. The millivolt

signal was sent to a Moseley 135 X-Y Recorder which plotted the cathode potential as a function of current.

M is a Synchron Timing Motor which is used to drive the potentiometer R_1 . A 2 rph motor was used in this study, and for this particular experimental system it produced an average voltage change of 0.10 v/min.

A picture of the entire experimental apparatus is shown in figure 4; while figure 5 shows the electrode assembly, standard cell, and motor-driven potentiometer.

System

Because the proposed analytical method was intended for commercial practice, it was highly desirable to select a system which measured up to commercial specifications (49). The standard system used entirely in this investigation is depicted in table 3. The few experiments which depart from this standard system will be so indicated at the point where they occur.

Solutions

The stock manganese sulfate-ammonium sulfate electrolyte was made up in batches of 16 liters at a time. All

EXPERIMENTAL APPARATUS

FIGURE 4



ELECTRODE ASSEMBLY

FIGURE 5



TABLE 3

STANDARD SYSTEM

Mn	30 g/L
(NH) 50	120 g/L
4 2 4 pH	7.2005
Temperature	30.0 - .2 [°] C
Anode	Pb-1% Ag
Area Diaphragm	l in. Filter Paper
Cathode	S.S. 316
Area	2 0.196 in
Polarization Rate	0.10 v/min.

reagent grade salts were used in the preparation of the stock solution which was initially adjusted to pH 7.0 with ammonium hydroxide. The resulting solution was then purified by the commercially used metal sulfide precipitation. In this step, ammonium sulfide solution, in the ratio 2ml per liter of stock solution, was added to the batch to precipitate the interfering metal ions. The batch was then stirred for two hours, allowing for complete precipitation, and filtered. Just prior to filtration, the batch was adjusted to pH 7.20[±].05. The entire preparation and purification sequence is shown in figure 6.

The stock solution contained an excess of both the manganese and ammonium salts because the test samples were made by diluting 100 ml of stock solution with a 5 ml additive. After dilution, the resulting solution contained the standard salt concentrations specified in table 3. The 5 ml additive may or may not contain impurity depending upon the nature of the run. If there was no impurity present, a standard polarization curve was produced. When an impurity was present, it was detected by the nature in which it affected the standard polarization curve.

The 5 ml additive contained the metallic impurity in such a concentration that when diluted to 105 ml the result-

SOLUTION PREPARATION

FIGURE 6



PURE ELECTROLYTE

S	0	LI	17	T	01	4 T	MP	UR	I	TI	ES
•	•								•		

Ion	Concentration mg/L
Cobalt	0-0.600
Nickel	0-4.00
Copper	0-9.85
Silver	0-30.0
Zinc	0-15.00
Molybdenum	0-4.00
Cadmium	0-200.0
Magnesium	200.0
Sodium	200.0

Table 4 lists the concentration ranges for the metallic impurities studied in this investigation.

The solutions that contained the metallic impurities were prepared from reagent grade sulfate salts. For each impurity, a base solution was prepared by accurately weighing the sulfate salt (\pm 0.1 mg) and diluting it to the desired volume. Solutions that contained impurity concentrations less than the base were prepared by successive dilution of the base. In the preparation of all solutions, liquid volume measurements were made with Class A glassware.

Electrodes

It was previously established that the hydrogen evolution reaction was very sensitive to electrode material and its surface condition. Thus before any analytical method could be evaluated, it was necessary to standardize on a cathode material and a method of preparation that would give reproducible results.

During the course of this investigation, five cathode materials were tested: stainless steel 316, nickel, monel, copper, and aluminum. All, but the stainless steel, gave such poor results that they were eliminated. So the stainless steel cathode was used exclusively in evaluating the analytical method.

A physical method was finally selected for conditioning

the electrode. Polishing with silicon carbide sandpaper not only regenerated a fresh cathode surface but gave good reproducible results. The entire preparation sequence is depicted in figure 7. In each polishing step, the electrode was stroked 40 times, alternating direction after every 10 strokes. Preplating was only necessary when the electrode was not in continuous use, and it was performed just like a normal run, which will be outlined in the following section. The electrode was rinsed first with running tap water and then with distilled water. The manganese plate was stripped for two minutes in 5% sulfuric acid.

Procedure

First, the test sample was prepared by mixing 5 ml of additive with a 100 ml of stock solution in a 250 ml Erlenmeyer flask. The sample was then placed in a 30°C temperature bath where it was allowed to equilibrate for at least one hour. It was then transferred into a 150 ml beaker and placed in the plexiglass temperature bath. A filter paper diaphragm was placed around the lead anode. The stainless steel cathode was conditioned according to the scheme developed in the preceding section. After the final water rinse, it took 45 seconds to mount the cathode in the holder and immerse the entire electrode assembly into the test sample. The cathode was not wiped dry; a film of water was allowed to remain on the cathode surface. For

ELECTRODE PREPARATION

FIGURE 7



two minutes the electrical circuit remained open while all of the electrical connections were made. The circuit was then closed, the voltage dividers adjusted to yield zero current, and the system was allowed to stabilize for five minutes. Then the motor-driven potentiometer was activated and the polarization curves were automatically plotted. The analytical test was performed in an unstirred solution and it was completed within 40 minutes.

EXPERIMENTAL RESULTS

The results of this investigation are presented in tables 5 through 19. Here, the effects of impurities are presented as a function of the transition current.

Throughout this text the term transition current will be used, but since the cathode used throughout this investigation had a fixed area of 0.196 in.², current and current density are synonymous.

Generally, the following tables refer to data taken from the standard system (table 3), all exceptions will be noted at the place where they are included.

EFFECT OF TEMPERATURE ON THE TRANSITION CURRENT

Run	Temperature	Transition	Transition Current		
		<u>BM</u>	avq		
3a	22.0	22.5	23.2		
3 b	22.0	23.8			
1	30.0	28.0			
2a	39.1	40.0	41.3		
26	39.1	42.6			

EFFECT OF AGITATION ON THE TRANSITION CURRENT

Run	Agitator <u>Setting</u>	Transition 	Current avg
4a	O Still	30.0	
4b		30.0	
5	5	29.1	
6a	6	33.5	33.4
6b	×	33.3	
7a	8 Turbulent	34.3	33.5
7b		32.6	

EFFECT OF PH ON THE TRANSITION CURRENT

Run	РН	Transition Cur <u>ma</u>	rent avq
11a	3.70-4.30	31.2 3	1.1
115	3.70-4.20	31.0	
10a	5.10-6.00	32.0 3	0.9
10b	5.10-5.90	29.8	
9a	6.20	30.8 3	1.8
9b	6.25	32.7	
Ba	7.25	31.4	
8b	7.20	29.0	
12a	7.75	27.5 2	6.2
12b	7.70	24.8	
13	8.10	25.5	

TABLE 8	
---------	--

EFFECT OF MnSO4 ON THE TRANSITION CURRENT

Run	Mn504 9/1	Transition Current <u>ma</u> avq
14a	75.0	30.8
14b	75.0	30.6
15a	60.0	35.5 35.4
15b	60.0	35.2
16a	52.7	33.3 34.7
16b	52.7	36.0
17a	37.5	33.5 34.8
17b	37.5	36.0

TA	BL	Ε	9
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EFFECT OF Co⁺⁺ ON THE TRANSITION CURRENT

Run	Co ⁺⁺ <u>mg/l</u>	Transition Current <u>ma</u> avo
18a	0	29.5
18b	0	28.8
19a	0.195	38.0 37.0
19ь	0.195	36.0
20a	0.293	36.0 44.8
20b	0.293	43.5
21a	0.390	55.5 54.9
21b	0.390	54.2
22a	0.469	65.7 62.8
2 2 b	0.469	59.9
23a	0.527	76.3 74.2
23b	0.527	72.1
24	0.600	

EFFECT OF Cu++ ON THE TRANSITION CURRENT

Run	Cu ⁺⁺ <u>mg/1</u>	Transition Current <u>ma</u> <u>avq</u>
25	0	29.0
26a	2.46	30.4 31.7
26b	2.46	33.0
27a	4.93	35.4 35.6
27b	4.93	35.7
28a	6.02	37.7 38.9
286	6.02	40.0
29	7.01	39.2
30	9.85	

TABLE 11

EFFECT OF Ni⁺⁺ ON THE TRANSITION CURRENT

Run	Ni ⁺⁺ <u>mg/1</u>	Transition Current <u>ma avq</u>
31a	0	27.4
31b	0	28.7
32a	0.50	36.7 36.0
3 2b	0.50	35.3
33a	1.00	45.7 45.2
33b	1.00	44.6
34a	1.40	55.8 54.9
34b	1.40	54.0
35a	1.60	60.3 61.0
3 5b	1.60	61.7
36	1.80	67.7
37	2.00	75.9
38	4.00	

EFFECT OF Zn⁺⁺ ON THE TRANSITION CURRENT

Run	Zn ⁺⁺ mg/1	Transition Current
39	0	27.3
40	.31	22.0
4 1a	•63	21.0 20.8
415	•63	20.5
42a	5.00	18.3 18.3
426	5.00	18.3
43	10.00	17.5
44	15.00	16.2

Run	Ag ⁺ mg/l	Transition Current <u>ma avq</u>
80 a	. 0	28.1
80b	т. О	27.5
81a	10.0	34.5 33.5
81b	10.0	32.5
82a	20.0	37.9 37.3
825	20.0	36.8
83a	30.0	41.0 40.8
83b	30.0	40.5

EFFECT OF Ag⁺ ON THE TRANSITION CURRENT

EFFECT OF Cd⁺⁺ ON THE TRANSITION CURRENT

Run	Cd ⁺⁺ mg/1	Transition Current <u>ma</u> avq
46 a	0	25.7
46b	0	27.3
47a	5.0	28.2 27.9
475	5.0	27.5
48a	25.0	30.1 30.1
4 8b	25.0	30.1
50	50.0	30.0
49a	100.0	30.5 30.5
49b	100.0	30.5
51	200.0	29.8

EFFECT OF MISCELLANEOUS IMPURITIES ON THE TRANSITION CURRENT

Run	Impurity	Conc. Tran	nsition Current
52	None		29.6
53	Molybdenum	2.00	
54	Molyb denum	4.00	
55	Na ⁺	200.0	30.5
56	Mg ⁺⁺	200.0	30.0

EFFECT OF NI⁺⁺ ON THE TRANSITION CURRENT

Programmed Voltage Rate = 0.15 v/min.

Run	Ni ⁺⁺ <u>mg/1</u>	Transition Current
75a	0	30.5 29.4
7 5b	0	28.3
76a	0.50	34.7 34.0
76b	0.50	33.3
77a	1.00	39.1 38.4
77ь	1.00	37.7
78a	1.60	43.8 43.9
78b	1.60	44.0
79	2.00	50.0

EFFECT OF BINARY MIXTURES ON THE TRANSITION CURRENT

Run	Impurity <u>Mixture</u>	Conc. mg/l	Transition Current <u>ma avq</u>
57a		0	30.5
57b		0	29.2
58a	Ni ⁺⁺	0.50	53.0 51.3
58b	Co ⁺⁺	0.195	49.5
59a	Ni ⁺⁺	0.50	46.9 46.7
59Ъ	Cu ⁺⁺	4.93	46.5
60a	Ni ⁺⁺	0.50	25.3 24.9
60b	Zn ⁺⁺	0.63	24.5
61	Ni ⁺⁺	0.50	36.7
	Cd ⁺⁺	5.00	
62	Ni ⁺⁺	0.50	
	Molybdenum	2.09	
63	Zn ⁺⁺	0.63	28.5
	Cd ⁺⁺ .	100.00	
64	Zn ⁺⁺	0.63	23.8
	Cd ⁺⁺	5.00	
65	Zn ⁺⁺	0.63	29.0
	Cu ⁺⁺	4.93	
66	Zn ⁺⁺	0.63	31.1
	Co ⁺⁺	0.527	

EFFECT OF Ni⁺⁺-Zn⁺⁺ MIXTURES ON THE TRANSITION CURRENT

Run	Impurity <u>Mixture</u>	Conc. <u>mg/l</u>	Transition Curro	ent v <u>q</u>
67a	Nickel	0	28.1	
67b	Zinc	0	30.5	
60a	Nickel	0.50	25.3	
60b	Zinc	0.63	24.5 24	•9
69a	Nickel	1.00	26.8 25	•7
69Ъ	Zinc	0.63	24.5	
71	Nickel	1.60	32.6	
	Zinc	0.63		
70a	Nickel	2.00	54.8 52	•2
7 0b	Zinc	0.63	49.5	
72a	Nickel	2.00	31.4 30	•6
72b	Zinc	1.25	29.8	
73a	Nickel	2.00	23.5 24	.8
73b	Zinc	2.50	26.1	
74a	Nickel	2.00	21.7 21	•9
74b	Zinc	5.00	22.0	

COMPARISON OF CALCULATED AND OBSERVED TRANSITION CURRENT

Mixture	Conc. mg/l	Transition Observed, ma	Current <u>*Calculated, ma</u>
Nickel	0.50		•
Cobalt	0.195	51.3	43.9
Nickel	0.50		
Copper	4.93	46.7	42.5
Nickel	0.50		
Zinc	0.63	24.9	27.7
Nickel	0.50		
Cadmium /	5.0	36.7	34.8
Zinc	0.63		
Cadmium	100.0	28.5	22.2
Zinc	0.63		
Cadmium	5.0	23.8	19.6
Zinc	0.63		
Copper	4.93	29.0	27.3
Zinc	0.63		
Cobalt	0.527	31.1	65.9

* The calculated values were based on the assumption that each impurity acts independently and that the effect of each impurity was additive.

DISCUSSION OF RESULTS

This investigation was divided into two major phases. In Phase I, the experiments were designed to determine the nature of the current-potential curves and to establish the effect of certain variables so they may be controlled within the proper limits. In this sequence such experimental variables as: temperature, agitation, pH, and manganese salt concentration were studied. While in Phase II, the effects of metallic impurities were studied.

Phase I

The effects of temperature, agitation, pH, and manganese salt concentration on the polarization curves, relative to the standard curve, are shown in figures 17 through 33 in the data section of the appendix. Tables 5 through 8 show the effects of these variables on the transition current.

The general characteristics of the current-potential curves may be briefly reviewed with the aid of figure 8. The initial region of ascent (A) was characterized primarily by the evolution of hydrogen and it was considered to be only a function of the hydrogen overvoltage on the basis metal cathode. Since it was previously established that the hydrogen overvoltage was sensitive to the state of the electrode surface, any metallic impurity that would affect the character of the surface, should have an effect on this POLARIZATION CURVE

FIGURE 8



CATHODE POTENTIAL

portion of the curve. As polarization continued, a point of inflection was reached where the curve exhibited a large change in potential with essentially no change in current (region B). When the potential shift was completed, another inflection point appeared, and the slope was characterized by a sharp increase in current with a relatively small change in potential (region C). At this point, both hydrogen and manganese were freely codepositing.

Experiments of Phase I were designed to study the nature of the hydrogen evolution reaction and to establish reasonable operating limits for the experimental variables. Such an investigation should allow one to determine whether or not region B can be defined as resulting from a true limiting current. A limiting current will only occur when some step in the reaction sequence is proceeding at its maximum rate.

A study of classical hydrogen electrode kinetics will reveal that only when catalytic desorption is rate controlling, can there exist a true limiting current density. Thus in order to establish the significance of the first inflection point and region 8, it was necessary to determine the mechanism of the hydrogen reaction. The mechanisms for this reaction have already been reviewed and diagnostic
criteria based on pH and salt effects have been used to distinguish the discharging entity and predict the reaction path.

Variations in pH and manganese salt concentration, shown in figures 23 through 33, do not significantly effect the standard polarization curve or the transition current (tables 7 and 8). However, a trend was indicated; a reduction in the hydrogen ion concentration resulted in a slight increase in the hydrogen overvoltage. A similar effect was also noticed when the manganese sulfate concentration was increased. In both cases, the activity of the hydrogen ions in the double layer was probably reduced which decreased the rate of the hydrogen reaction.

The effect of agitation was also small as indicated by figures 19 through 22 and table 6. Agitation increased the diffusion rate of hydrogen ions into the double layer which resulted in a net increase in the reaction rate.

As expected, temperature had a significant influence on the reaction kinetics as shown by figures 17 and 18 and table 5. Thus, it was evident that strict temperature control was a necessary criterion for reproducible results.

The experimental pH and salt effects indicated that protons were discharged from hydronium ions. It could also be concluded that the hydrogen reaction on a stainless steel cathode must be governed by one of the following paths:

- (a) slow discharge followed by fast catalytic desorption,
- (b) slow discharge followed by fast electrochemical desorption,

Although the exact mechanism could not be determined from existing data, it was sufficient to know that none of the above paths would give rise to a limiting current density. Thus a new perspective was necessary in evaluating the significance of the transition region (8).

From the polarization curves, the first inflection point occurred very close to the equilibrium potential of manganese, approximately -1.45v relative to a saturated calomel electrode (sce). Now, since it is known that manganese deposits upon itself with a relatively large overvoltage, and if it is assumed that manganese deposits upon stainless steel close to the equilibrium potential; then a possible explanation of the significance of the transition region (8) can be developed.

For example, as the stainless steel cathode is polarized, it becomes more negative changing as a function of the hydrogen overvoltage. When the deposition potential of manganese on stainless steel is reached, the metal will start to codeposit with hydrogen. As a layer of manganese covers the surface, the cathode undergoes a transition from a stainless steel to a manganese electrode. However, the hydrogen overvoltage changes abruptly in transcending from one metal to the other, being relatively larger on manganese. Therefore, in order to sustain the same reaction rate on manganese, the cathode potential must shift to become more negative. Also, since manganese deposits upon itself with a substantial overvoltage, a potential increase is necessary in order to maintain the manganese reaction once the stainless steel surface has been covered with a monatomic layer of manganese.

This hypothesis implies that the significance of the first inflection point is represented by the deposition potential at which manganese deposits on a stainless steel cathode. The region of potential shift is indicative of two simultaneous events:

- (a) the transition of the hydrogen reaction from a stainless steel to a manganese electrode, and
- (b) the transition of the manganese reaction from a stainless steel to a manganese electrode.

Thus the constant current resulting from these transitions is more appropriately defined as the transition current as opposed to limiting current.

Again referring to figure 8, a few general remarks can be made about the current-potential curves. When an impurity is added to the electrolyte, it may affect the polarization curve in two possible ways:

- (a) change the initial deposition potential of manganese on stainless steel, and/or
- (b) alter the hydrogen overvoltage on the basis metal surface.

Ideally considering case (a), the impurity would affect only the initial deposition potential of manganese and not alter in any way the primary hydrogen reaction. The resulting polarization should follow a path similar to curve (2), and the inflection point should shift along the potential axis relative to that for the standard curve. With case (b), the impurity affects only the hydrogen reaction and not the deposition potential of manganese. The polarization should now follow curve (3), and the inflection point should be displaced only vertically along the current axis. The ideal cases just cited represent two extremes because the behavior of a real impurity would probably possess both of the above mentioned properties. The transition current can be used as a correlating parameter, the same as limiting current in polarography.

Phase II

In this phase, an effort was made to determine how trace metallic impurities affect the current-potential curves. Again the study was sub-divided into two parts: (a) a study of single impurities, and (b) a study of binary mixtures. Emphasis was placed on evaluating the experimental technique to see if it were suitable as an analytical tool for determining the purity of manganese electrolytes. Here, a pure electrolyte is not to be taken in its absolute sense, but it refers to an electrolyte which is sufficiently pure to yield an acceptable current efficiency when subjected to electrolysis.

<u>Single Impurities</u>. The effects of cobalt and nickel on the current-potential curves are shown in figures 34 through 39, appearing in the data section of the appendix. It was

evident that both species were active in reducing the hydrogen overvoltage and that the activity was a function of the impurity concentration. Copper and silver were not quite as active as the previous two species, as indicated by their polarization curves (figures 40-43). Zinc was the only impurity that poisoned the stainless steel cathode; the hydrogen overvoltage increased as shown in figures 44 through 46. All of these impurities showed a correlation between transition current and concentration (figures 9-13).

The metallic impurities: cadmium, magnesium, and sodium did not affect the standard polarization curve (figures 47-51), and so no correlation existed.

Molybdenum was the only impurity that was not added as the sulfate but as ammonium molybdate. Figure 51a shows the effect this impurity had for eliminating the transition region and the apparent insensitivity of the polarization curve to concentration. The hydrogen overvoltage was practically unaffected by the presence of this impurity, but it appeared to have a significant effect on the initial deposition potential of manganese. The observed phenomenon is not fully understood.

A selected list of half-wave potentials is presented in table 20. From this table, it is evident that all

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metallic impurities used in this investigation except magnesium and sodium should be electrochemically precipitated before manganese. For experimental confirmation, a chemical spot test (38) was performed for nickel on a black residue that remained on the cathode after the manganese was stripped with 5% sulfuric acid. The test was positive and so it was assumed that the metallic impurities deposited on the cathode surface, and in doing so, altered the hydrogen overvoltage. Since magnesium and sodium are not electrochemically precipitated, their presence in the electrolyte should not affect the hydrogen reaction. Therefore, the standard polarization curve should remain unchanged; this was supported by experimental data.

Further indication that the impurities deposit on the electrode was furnished by an investigation of their diffusion rates. This was done by replacing the 2rph motor with a 3rph one, which caused in an increase in the rate of polarization. Since the deposition of impurity was under diffusion control, the rate of polarization was a factor. The longer it takes to traverse the voltage span; the more impurity diffuses to and deposits on the cathode. Thus an increase in the polarization rate should reduce the amount of impurity deposited and thereby decrease the rate of the hydrogen evolution reaction. This was in agreement with the experimental results presented in

figure 14. Another interesting outcome from this particular study was that the sensitivity of the test could be changed by varying the polarization rate.

If the impurities do deposit on the stainless steel cathode, one would expect to find a limiting concentration which corresponds to a condition where the electrode surface is completely covered with the reduced impurity. Further additions would have no effect on the hydrogen evolution reaction, and the transition current would now become independent of concentration. Zinc was the only impurity to exhibit such an effect.

The other impurities exhibited a critical concentration. For example, the critical concentration for cobalt was 0.527 mg/L. Above the critical value, the effect of the impurity was uncertain and not at all understood. The transition from a stainless steel to a manganese electrode usually was never completed; thus manganese did not cover the entire electrode surface. When the current was held constant, manganese began to redissolve along with a positive potential shift. Examples of polarization curves for cobalt and copper at concentrations above the critical value are shown in figures 35 and 40, respectively. Critical concentrations for nickel, copper, and silver are 2.00, 7.01, and 30.0 mg/L, respectively. Above the critical

concentration, the correlation between transition current and concentration does not exist.

From the experimental results, the ability of metallic impurities to catalyze the hydrogen evolution reaction may be arranged in the decreasing sequence: Co > Ni > Cu > Ag> standard electrode > Zn. Since it has already been assumed that the impurities deposit on the cathode, it is reasonable to assume that their catalytic activity is related to how actively the respective metals support the hydrogen evolution reaction.

Metals widely differ in their ability to catalyze the hydrogen reaction; this is shown by the diversity in hydrogen overvoltages on the different metals, being low for the platinum metals and high for the zinc group. Hydrogen electrode kinetics have been extensively studied on nickel, copper, and silver electrodes (5, 11, 17, 19, 54). There is agreement that the rate controlling step is the slow discharge of protons. No data was available for cobalt, but its behavior was expected to be similar to that of nickel. No reliable data existed for the hydrogen reaction on zinc or cadmium, but these metals were expected to behave like lead and mercury which possess a rate controlling discharge step.

In hydrogen electrode kinetics extensive use is made

of the Tafel Equation,

$$\gamma = a - b \log(i) \tag{17}$$

where γ is the overvoltage at a specific current density (i), and (a) and (b) are constants. A selected list of the parameters of the Tafel Equation were given in table 1. It is obvious that the hydrogen overvoltage follows the following decreasing sequence: Ag \rangle Cu \rangle Ni. This is in agreement with the present experimental results for the effects of impurities on the hydrogen overvoltage.

In recent years, emphasis has been placed on establishing a relationship between hydrogen overvoltage and heat of H adsorption. An increase in the heat of adsorption decreases the heat of activation and should result in a lowering of the overvoltage when proton discharge is rate controlling. A comparison between the heats of adsorption and overvoltage (table 2) for various metals showed good agreement with the above theory.

In light of the above discussion, an explanation of the experimental results may now be attempted. It was evident from the data that certain metallic impurities significantly affected the polarization curves. As previously established, they could: (a) change the deposition potential of manganese, (b) change the hydrogen overvoltage, and (c) simultaneously do both.

From the polarization curves, it was apparent that the inflection point was shifting to more negative values indicating a possible change in the deposition potential of manganese. However, this small increase may be due to an overvoltage-current density effect; thus the effect of impurity on the manganese overvoltage is not immediately obvious and cannot be distinguished. The accompanying vertical displacement of the inflection point or transition current is reflected by a significant change in the hydrogen overvoltage. Cobalt and nickel impurities produced marked effects on the hydrogen overvoltage, while the effects of copper and silver were not as pronounced. Assuming that proton discharge is the rate controlling step, this change in hydrogen overvoltage may possibly be related to the catalytic activity of the reduced impurity or the change in the heat of H adsorption. For example, as nickel deposits, one would expect the overvoltage to approach that of a nickel electrode. If the catalytic activity were greater on nickel than on stainless steel, one would expect to see the hydrogen reaction accelerated, which was the experimental result. If the impurity reduced the catalytic activity of stainless steel, such as zinc, the converse result would occur. Also, the observed catalytic activity of the reduced impurity appears to be a function of the heat of H adsorption. For cobalt and nickel, the heat of adsorption is relatively large, decreasing

through copper and silver, and being the lowest for cadmium and zinc. This is the same decreasing sequence for the catalytic activity on the respective metals. Thus the activity of the stainless steel cathode appears to be altered by the deposition of metallic impurities which may affect the heat of atomic hydrogen adsorption on the surface. Bockris et al (9, 13) also noticed an activation of silver and nickel electrodes when studying the hydrogen reaction in the presence of platinum chloride. Other investigators (42, 60) studying hydrogen deposition on metal alloys found that the individual constituents definitely contribute to the overvoltage.

The effect of reduced impurities on the hydrogen evolution reaction may be treated analytically. However, before attempting an analytical development, certain simplifying assumptions must be made, such as:

- (a) the reduced impurity does not form an alloy with the stainless steel electrode,
- (b) the stainless steel and the reduced impurity act independently in supporting the hydrogen evolution reaction, and
- (c) the cathode potential is held constant.

First, consider the evolution of hydrogen on the stainless steel electrode where the total current (I_t) is given by

 $I_{t} = I_{s}$ (18)

where the subscript (s) refers to stainless steel and I_s refers to the rate at which hydrogen evolves from the stainless steel surface. Now consider the hydrogen reaction when the stainless steel surface is contaminated with some reduced metallic impurity. A small fraction of the electrode surface is now covered with the reduced impurity, and hydrogen is now evolving simultaneously from the stainless steel and the reduced impurity surfaces. The electrical analogue of this system is a parallel circuit and the total current of a parallel circuit is given by

 $I_t^{\dagger} = I_s^{\dagger} + I_r$ (19) where the subscript (r) refers to the reduced impurity.

The effect of the reduced impurity, at a given cathode potential, may be represented by the following ratio,

$$\frac{I_{t}}{I_{t}} = \frac{I_{s}^{i} + I_{r}}{I_{s}}$$
(20)

The current terms may be written as current densities (i) according to the equation

I = (A)(i) (21)

where (A) represents the area of the cathode surface.

If the reduced impurity occupies only a small fraction of the total electrode area, then, the area occupied by

the stainless steel surface may be considered essentially constant and I^e will be approximately equal to I_s. Now, equation (20) may be written as

$$\frac{I_t}{I_t} = 1 + \frac{I_r}{I_s}$$
(22)

The current densities (i) can be represented by the equations

$$i_{s} = i_{os} \exp(-\alpha_{s} \gamma_{s} F/RT)$$
(23)

and

$$i_{r} = i_{or} \exp(-\alpha_{r} \frac{\eta}{r} F/RT)$$
 (24)

where

$$\overline{\gamma}_s = \overline{\gamma}_r$$
 (25)

For most metals, the (\measuredangle) terms are approximately equal; and the exchange currents (i_{os}) and (i_{or}) have already been defined by equation (12).

Using equations 21, 23, 24, and 25, equation 22 may now be written in the form

$$\frac{I'}{I_t} = 1 + \frac{A_r i_{or}}{A_s i_{os}}$$
(26)

From equation 26, the reduced impurity should alter the cell current as a function of the ratio of the products of the area times the exchange current for the respective metal surfaces. For example, the ratio of exchange currents for hydrogen evolution on a platinum surface to that on a

zinc surface is about 10⁵ (22b). Hence, if even a small fraction of a zinc electrode be covered with platinum, a significant change in the rate of hydrogen evolution may be expected.

A quantitative application of equation 26 to the present experimental data is impossible, since there exists no knowledge of the individual surface areas or the exchange currents. However, qualitatively, it is presented to show that the presence of trace quantities of metallic impurities in manganese electrolytes may significantly effect the hydrogen evolution reaction, and thus alter the polarization curve.

The discussion up until now has been emphasizing the concept that the metallic impurities deposit on the basis electrode and raise its activity to a level approaching that of the reduced metal. However, some experiments performed with nickel as the cathode material produced conflicting results. Manganese was deposited at current densities similar to those for a stainless steel cathode; and when nickel was added to the electrolyte as an impurity, the activity of the nickel cathode was significantly increased (figure 54). Although the results with the nickel cathode were not reproducible, they did indicate that further investigation was necessary before the phenomena

associated with metallic impurities could be fully understood.

From this investigation, it can be concluded that polarization curves can be used for the detection of trace amounts of metallic impurities, in the parts per million range, in manganese electrolytes. More specifically, certain metallic impurities may be correlated by the parameters, transition current and impurity concentration. A relationship exists between the transition current and the current efficiency of a commercial manganese cell. Impurities which increase the transition current above the standard value, decrease the current efficiency; while those which decrease it, increase the current efficiency. Thus, polarization curves would be valuable in the electrowinning of manganese. From the nature of the curve, one would be able to predict not only whether or not minute traces of impurities were present in the electrolyte, but also how these impurities would affect the current efficiency of the commercial process.

From this investigation, it can also be established that it is necessary to attain a minimum current density before one can deposit manganese. This minimum current density changes in the presence of impurities, and it changes as a function of their concentration. Thus, in the event

a commercial process is operating inefficiently, the polarization curve should enable one to recommend a new operating current density in order to overcome the effect of the impurity.

This investigation has also shown that the addition of zinc to an impure manganese electrolyte will suppress the deleterious effect of the impurity (figures 15 and 16). The above situation may now be corrected not only by changing the operating current density, but also, by adding small quantities of zinc to the impure manganese electrolyte.

<u>Binary Mixtures</u>. The effects of binary mixtures on the polarization curves are shown in figures 55 through 64. Tables 17 and 18 show their effects on the transition current. Table 19 compares the observed transition current with one calculated on the assumption that each impurity contributes independently to the total effect. However, this assumption is not valid, for there appear to be interactions between the various impurities which usually amplifies the effect of one or both components. This complex relationship is shown in more detail in figures 15 and 16 for nickel-zinc mixtures. Similar complex effects were discovered by Huq and Rosenberg (43) when studying the hydrogen reaction on nickel compounds. At present, the effects of mixtures appear to be highly complex and cannot be explained.





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<u>Reproducibility</u>. The majority of the runs were at least duplicated, and the reproducibility was good as determined by the transition current. Statistical analysis of the results showed that the transition current had associated with it an experimental error of $\frac{+}{2}$ 1.6 ma.

CONCLUSIONS

- 1. Polarization curves can be used to determine if manganese sulfate electrolytes are sufficiently pure for efficient electrolysis. For example, impurities that reduce the current efficiency, such as: nickel, cobalt, silver, copper, and molybdenum, are detected by an increase in the transition current relative to a standard value or by a noticeable change in shape of the polarization curve.
- 2. For the single impurities: nickel, cobalt, silver, copper, and zinc, there is a quantitative relationship between transition current and impurity concentration up to the critical concentration.
- 3. The effects of binary mixtures of impurities on the transition current generally do not follow a simple additive law based on the effects of the individual components. However, for some mixtures, the additive law may apply for a limited range of concentrations.

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APPENDIX

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TABLE 20

SELECTED HALF-WAVE POTENTIALS*

@ 25°C versus SCE

Ion	Supporting Electrolyte	E1 volts ²
Cd++	$1M NH_3 + 1M NH_4^+$	-0.81
Co ++	1M NH3 + 1M NH4+	-1.30
Cu++	$1M NH_3 + 1M NH_4^+$	-0.50
Ni ⁺⁺	$1M NH_3 + 1M NH_4^+$	-1.09
Zn++	$1M NH_3 + 1M NH_4^+$	-1.33
Mn ⁺⁺	$1M NH_3 + 1M NH_4^+$	-1.65
Mg ⁺⁺	tetramethyl - NH4	-2.20
Na ⁺⁺	tetramethyl - NH _A +	-2.07

* <u>Polarography</u>, Kolthoff and Lingane, Interscience Pub., New York, 2nd ed., 1952.

TABLE 21

STANDARD CELL VOLTAGE

Date	E Volte
	101103
10/15/63	1.01787
10/18/63	1.01809
11/22/63	1.01748
12/10/63	1.01828
2/14/64	1.01803
4/8/64	1.01767
5/18/64	1.01798
7/10/64	1.01768
Average	1.01789

TABLE 22

POTENTIALS OF THE SATURATED CALOMEL ELECTRODE*

Temperature	E <u>Volts</u>
20	0.2453
25	0.2415
30	0.2377

* - Principles of Physical Chemistry, Maron, S. H. and Prutton, C. F., Third Edition, New York: The MacMillan Co., 1958, p. 519.
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George R. Ferment was born on

. He attended the public schools of Clifton, New Jersey and graduated in 1957. The same year he entered Fairleigh Dickinson Universit to major in chemistry. Two years later, he transferred to Newark College of Engineering, where he received a B.S.Ch.E. in 1961. Also, in 1961, he received a three year National Defense Education Act Fellowship for graduate study in chemical engineering at Newark College of Engineering. In 1962, under this program, he received a M.S.Ch.E. For his doctoral thesis, under Dr. C. L. Mantell, he investigated the currentpotential effects of trace metallic impurities in manganese sulfate electrolytes.

He is married to the former Barbara Balasa and has one child.

He is presently employed as a research engineer with Celanese Corporation of America at Summit, New Jersey.

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