THE POTENTIAL OF THE NICKEL ELECTRODE

by

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Outline of Thesis

1. Introduction

The published work concerning the electro-motive force of nickel shows a multiplicity of varying values, rangeing from -0.90 volts to -0.466 volts, compared with the normal calomel electrode as zero. Most of this work has been carried out in concentrated solutions, with little concern towards accuracy. The values recorded are the observed values, without any corrections; in only one case has any attempt been made to calculate a value for the normal electrode potential from the measured value.

Some recent work at the Bureau of Standards (1) seems to indicate that the true potential of nickel lies somewhat higher than the present accepted value of -0.4800 volts, referred to the normal calomel electrode as zero. Furthermore Gerke (2) in his "Summary of Electrode Potentials" does not accept the present value for nickel as reliable in that he does not include it in his table of standard reference electrodes.

Since nickel is such an important metal, especially in the plating industries, an accurate and

careful re determination of the true equilibrium
value was deemed highly advisable.

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2. Review of Literature

Neumann (3), using nickel amalgam for his
electrode, reports the following values for three
different solutions:

Normal nickel sulfate......-0.538 volts [*]

Normal nickel chloride.....-0.540 volts

Normal nickel nitrate......-0.500 volts

He prepared his electrode by plating nickel from a
nickel chloride-boric acid solution, then rubbing it
with mercury and again plating from a boric acid-
ammonium sulfate-nickel sulfate solution until a
thick amalgam was obtained.

Küster (4), in his work on the electrolytic
separation of iron and nickel from solutions of their
sulfates, found nickel to be deposited from neutral
normal nickel sulfate solution at -0.80 volts. He
believed therefore that this was the true value for the
potential of nickel.

[*] These values, as well as those which will follow in
the review, are referred to the normal calomel electrode.
The convention which will be used throughout with regards
to sign will be that adopted by the American Electro-
chemical Society. That is, the sign of the charge on
the metal will be placed before the value for the
electrode potential (28).

Siemens (5) used nickel which was polarized
alternately anodically and cathodically, and found
the value of -0.504 volts.

Euler (6) suggests that rough nickel will
give a more nearly reproducible value than nickel
sheet. He used Kahlbaum's nickel, treated it with
sulfuric acid, then placed it in normal nickel
sulfate and made it alternately anode and cathode,
using a small current density. He allowed his
metal to stand for a few days previous to us. He
obtained the value of -0.466 volts for $N-NiSO_4$ and
-0.472 volts for $N/5-NiSO_4$. He assumes normal nickel
sulfate to be 0.11 normal in nickel ions and cal-
sulates the value of Eo for nickel in contact with
a normal solution of its ions to be -0.460 volts.
With Mond nickel he obtained the potential of
-0.466 volts. Euler advises the expulsion of air
but he took no particular precautions to exclude it
from his electrolyte. He does not mention having
neutralized his solution or having worked at a
constant acidity.

Muthmann and Fraunberger (7) report the
value of -0.883 volts. They believed that the true
potential of nickel is obtained only when passivizing
influences are excluded. They therefore polarized
their nickel with hydrogen in distilled water and

quickly transferred it to a normal nickel sulfate
solution.

Schweitzer (8) using pure powdered nickel
and nickel sheet in normal nickel sulfate, working in
an atmosphere of hydrogen, found the values of -0.613
and -0.590 volts. With powdered nickel and normal
nickel chloride he obtained -0.596 volts.

Pfanhauser (9) gives the value of -0.519
volts, using normal nickel sulfate.

Schoch (10) working in vacuo in order to
remove oxygen and air, using varying grades of nickel
including sheet nickel, Kahlbaum's and his own
electrolytic preparation, obtained values varying
from -0.465 to -0.487 volts. He believes -0.480
volts to be the true value though with powdered
nickel he obtained the value of -0.522 volts. This
powdered nickel he obtained by reducing nickel oxide
(prepared by heating Kahlbaum's nickel nitrate) in a
current of hydrogen. This nickel, laden with hydrogen
gave a potential of -0.590 volts after 36 hours. On
boiling out, to expel the hydrogen, the value of -0.522
volts was attained. In another experiment Schoch
also showed the effect of hydrogen on the potential
of nickel. He boiled a piece of nickel sheet in
concentrated sodium hydroxide and then placed it in

normal nickel sulfate. The potential attained
in this case was -0.875 volts. With nickel treated
with hydrochloric acid and in contact with hydrogen
a potential of -0.62 volts was obtained. After
boiling out the potential of this same nickel dropped
to -0.48 volts. Schoch found the potential of nickel,
in contact with normal nickel chloride, to be -0.42
volts.

Smits and de Bruyn (11), (12), on the basis
of the theory of electromotive equilibrium developed
by Smits (13), believe that when the potential of
nickel is measured in an acid solution, in an
atmosphere of hydrogen, the result will be dependent
on the hydrogen ion concentration of the solution and
will be equal to the potential of the hydrogen electrode.
They measured the potential of a solution saturated
with hydrogen and found that the potentials of nickel
and hydrogen electrodes in this solution both became
constant at -0.640 volts. They then measured the
potential of a normal nickel sulfate solution, working
in vacuo, using a nickel wire as electrode, and found
the value of -0.480 volts, agreeing with that of
Schoch. The present work has shown that nickel of
this form, even with careful evacuation and boiling,
becomes coated with a black oxide after standing for
a short while. It is probable then that the value
measured by both Schoch and Smits and deBruyn may

have been effected by this oxide.

Various other conflicting values and
opinions may be found. W. Bonsdorff (14) reports
that he was unable to obtain a reproducible electrode.
Coffetté and Foerster (15), finding that nickel was
deposited from normal nickel sulfate colution with a
cathode potential of -0.903 volts, support the value
found by Muthmann and Fraunberger. Schildback (16)
in his work on cobalt, assumes the value of Schoch.

Thompson and Sage (17), using spongy nickel
made by electrolyzing a half normal nickel chloride
solution at 90°, with 12.5 volts, obtained the value
of -0.672 volts with an electrolyte of neutral molal
nickel sulfate. With a solution containing 60 gms.
$NiSO_4 \cdot 6H_2O$, 20 gms $(NH_4)_2SO_4$ and 40cc NH_4OH per liter,
electrolyzed at 20° with 8 volts, they obtained a
nickel whose electrode potential was -0.577 volts.
They took no special precautions to expel air or to
get rid of hydrogen.

The values discussed above are grouped
together in Table I, so that they may be compared at
a glance. The values as given in the literature are
not corrected. When corrected to a solution normal
in nickel ions the values would be about 0.015 volts less.
(This value is obtained by assuming $N-NiSO_4$ to be ionized
to the extent of 31%, as are other salts of this type.

Table I.

Electrode Potential of Nickel as Recorded in Literature.

Worker	Solution	Potential
Neumann	$N-NiSO_4$	-0.538 v.
	$N-NiCl_2$	-0.540
	$N-Ni(NO_3)_2$	-0.500
Küster	$N-NiSO_4$	-0.803
Siemens	$N-NiSO_4$	-0.504
Euler	$N-NiSO_4$	-0.466
	$N/5-NiSO_4$	-0.472
Muthmann and Fraunberger	$N-NiSO_4$	-0.883
Schweitzer	$N-NiSO_4$	-0.613
	$N-NiCl_2$	-0.596
Pfanhauser	$N-NiSO_4$	-0.519
Schoch	$N-NiSO_4$	-0.480
	$N-NiCl_2$	-0.420
Smits and de Bruyn	$N-NiSO_4$	-0.480
Thompson and Sage	$M-NiSO_4$	-0.672
		-0.577

In the case of nickel and other inert
metals the equilibrium potential is only established
under very definite conditions. If the solution is in
contact with air the metal is attacked and the corrosion
leads to a change in the potential in the direction of
greater nobility. Some of the above values, therefore,

when the work was carried out with no particular
care for the exclusion of air, are too low. On the
other hand the results of Muthmann and Fraunberger
and Küster are too high, for they are even higher
than the potential at which nickel can be plated from
its solution. Hydrogen effects the potential, as was
shown by Schoch and also by Smits and de Bruyn, and
it seems possible that the values of Schweitzer were
thus effected. However, just as Foerster assumed
that a small amount of hydrogen was necessary to
attain the equilibrium of the iron electrode, so
Schweitzer suggests that a small amount of this gas
may assist in attaining equilibrium in the reaction
$$Ni - 2(-) \rightleftharpoons Ni^{2+}$$

The presence of an acid will cause a lowering
of the potential, for nickel will displace hydrogen
from acids and the electrode would then act as a
hydrogen electrode.

Because of the unknown activity of metallic
ions in concentrated solutions it is impossible to
correctly calculate a value for the normal electrode
potential from the above work, since all of it was
carried out in concentrated solutions.

Liquid potentials were not eliminated in any
of the older work and since it is well known that there
is sometimes considerable potential between electrolytes
another source of uncertainty is added to the above results.

3. Experimental Details

a. Preliminary Work

For the preliminary measurements, electrodes
of the type described by Smits (13) were used and
filled according to his procedure. One of the elec-
trodes of the cells measured was the normal calomel
electrode. The other electrode consisted of nickel
from different sources, immersed in various solutions,
all normal with respect to nickel sulfate. Connection
between the two electrodes was måde by using the device
suggested by H. E. Haring (18). A 10 cm piece of glass
tubing, drawn out to a capillary was filled with
saturated KCl solution and connected to the side arm
of the calomel electrode vessel by means of a piece
of rubber tubing. The capillary end was then dipped
into another tube, also drawn out, which was filled
with some of the solution whose electrode potential
was being determined. Connection could now be made
with the nickel electrode. By use of this device
contact potential at the liquid junction is practically
eliminated and the diffusion of KCl is decreased.

The results are tabulated in Table 2. The
values given are referred to the normal calomel
electrode.

The electrodes of cells No. 1, No. 2, No. 3

TABLE II

Preliminary Measurements

Time In Days	1	2	3	4	6	8	10	12	15	18	20	22	24	30	35	48
Cell No. 1	.451	.457	.463													.455
2	.452	.457	.460													.451
3	.444	.445	.458													.460
4	.453	.468	.471		.474	.475										.470
5	.492	.516	.517		.512	.510										.502
6	.493	.517	.521		.523	.522										.492
7		.400			.457		.463			.452		.471	.465			
8	.435	.452			.452		.468			.469		.470	.472			
9	.445	.458			.467		.468			.469		.470	.472			
10	.460	.470			.472		.468			.471		.471	.472			
11		.545			.557			.555		.555	.556		.555	.552	.552	.550
12		.539			.542			.535		.532	.530		.526	.518	.523	.500
13	.525		.525											.532		.532
14	.523		.523											.531		
15		.571	.577		.577			.577		.577	.576		.574			
16		.587	.589		.591			.591		.586				.576		
17		.520		.520		.544			.546	.550			.550	.551		
18		.530		.542		.543			.542	.544			.542	.544		
19		.540		.541		.545			.545	.547			.547	.547		
20		.553			.550			.552		.555			.555	.557		
21		.565			.563			.561		.560			.556	.556	.557	.555
22		.565			.563			.561		.560			.556	.554	.556	.550

and No. 4 consisted of nickel wire, obtained from
A. H. Thomas, inserted through the rubber stopper
of the electrode. The electrolyte was a N-NiSO$_4$
solution, which was shaken with Ni(OH)$_2$ previous to
use.

Electrodes of No. 5 and No. 6 consisted of
electrolytic sheet nickel, obtained from the Bureau
of Standards, which had been allowed to stand in the
air for a long period of time. Previous to use the
netal was polished with pumice powder and thoroughly
washed. Strips of it were inserted between the
rubber stopper and the wall of the electrode vessel.
The electrolyte was standard plating solution (see
preparation of materials), normal in NiSO$_4$, to which
sufficient NaOH had been added to bring the pH up to
6.8, i. e. the precipitation point of Ni(OH)$_2$.

The electrode of No. 7 was made by sealing
a piece of the above sheet nickel into a piece of glass
tubing and inserting this into the rubber stopper.
The electrolyte was normal NiSO$_4$ previously treated
with NaOH.

Electrodes of No. 8, No. 9 and No. 10 con-
sisted of nickel amalgam, prepared by electrolyzing
N-NiSO$_4$ solution, for 1 hour at 1.6 amps., using a
cathode of pure mercury and a platinum anode. No. 8
was the liquid portion, No. 9 was the putty-like portion

and No. 10 was the top portion, consisting of almost pure nickel, finely divided. The above amalgams were washed with water and kept under water for four days before use. The electrolyte was $N-NiSO_4$.

Electrodes of cells No. 11, No. 12, No. 13, and No. 14 consisted of a platinum foil plated with a thin coating of nickel from plating solution, using a current of about 1.5 amperes. No. 11 and No. 12 were washed and boiled in water, then were allowed to stand in $N-NiSO_4$ for two days previous to use. They were then filled with $N-NiSO_4$ which had been shaken with $Ni(OH)_2$. After 30 days No. 11 was electrolyzed so that oxygen was discharged on the nickel and No. 12 electrolyzed so that hydrogen was discharged. Oxygen did not effect the potential but hydrogen caused a lowering for just a short while to 0.515 volts. No. 13 and No. 14 were allowed to stand in distilled water, exposed to the air, for several days previous to use.

After 30 days No. 14 was opened for just an instant. Its potential immediately dropped to 0.450 volts, showing the effect of air. When opened for just a second or two longer it dropped to 0.350 volts.

The electrodes of No. 15 and No. 16 consisted of a "tree" of nickel plated on a small platinum wire

from plating solution. No. 15 was washed and used at once, while No. 16 was kept in water for 2 weeks previous to use. Both were immersed in $N-NiSO_4$ treated with $Ni(OH)_2$.

Electrodes of cells Nos. 17 to 22 consisted of a small Pt wire, plated with nickel, in contact with the fine nickel obtained when nickel is plated with a high current density from heated plating solution, using as cathode a small platinum point. No. 17, No. 18 and No. 19 were allowed to stand in contact with $N-NiSO_4$ for four days before filling the electrode vessels. No. 20 was filled with $N-NiSO_4$ at once after plating. No. 21 and No. 22 were allowed to stand in contact with $N-NiSO_4$ for two days previous to filling. After 28 days No. 22 was emptied and refilled with new $N-NiSO_4$ solution.

The cells show different potentials, depending on the method of preparation of the nickel, its previous exposure, treatment of nickel surface, presence of air or hydrogen, etc. By reference to the table it can be seen that the value found by Schoch was duplicated and even a somewhat higher result attained with cells No. 5 and No. 6. It should be remarked that with cells No. 11 to No. 22, where the nickel used was electrolytic, quite noticeably higher values were obtained. With cells where the nickel was

used immediately after plating, the potential given
may have been effected, to some extent, by hydrogen;
but it is highly improbable that nickel, which has
been exposed to the air, or which has been allowed to
stand in contact with water or nickel sulfate solution,
would still contain hydrogen in sufficient amount to
account for such consistently high values. With
amalgam electrodes it is probable that air was not
entirely excluded, for it took a long time to reach
equilibrium. Equilibrium seemed to be reached more
rapidly with electrolytic nickel and for that reason
it was decided to use it in the final measurements.

b. Preparation of Materials

Water. - The water used was obtained by
distillation from a Barnstead still. It was sufficiently
pure for the work, having a pH of about 6.9.

Nickel Sulfate. - Nickel sulfate of the
Industrial Nickel Products Co., obtained from the
Bureau of Standards, was re-crystallized three times
at room temperature. This salt was then dissolved
in water and shaken with $Ni(OH)_2$ for a day in order to
neutralize the H_2SO_4 formed by hydrolysis. By this
means the pH of the solution was brought to about 6.8
This solution was then used to make the more dilute
$NiSO_4$ solutions.

$NiSO_4$ was also prepared by electrolyzing dilute H_2SO_4 using an anode of Mond Nickel. The salt so obtained was further purified by recrystallization and shaking with $Ni(OH)_2$.

A $2N-NiSO_4$ solution, prepared from the Industrial Nickel Products salt was electrolyzed for 200 hrs. at the "break" in the nickel curve, using a platinum-black cathode saturated with hydrogen. The purpose and theory of this electrolysis will be discussed later.

Nickel Hydroxide. - A solution of the recrystallized $NiSO_4$ was treated with NaOH solution until precipitation was complete. The preäipicate so obtained was washed by decantation until the washings were neutral and then filtered through a Buchner funnel.

Mercury. - The mercury used was purified according to the method of Hulett and Minchin(19). Ordinary laboratory mercury was passed several times through a long column of HNO_3 and $HgNO_3$ in the form of a fine spray. This washed mercury was then distilled several times in a current of air under reduced pressure, in an apparatus which was one continuous piece of Pyrex glass.

Mercurous Sulfate. - This salt was prepared according to the method described by Hulett (20). Normal H_2SO_4 was electrolyzed with a current of 0.9 amps. per dm^2, using as cathode a piece of platinum foil and

as anode pure mercury, with which contact was made
by means of a platinum wire, completely covered with
mercury. As the sulfate was formed at the anode a
stirrer, with double paddle, just swept the surface
of the mercury and scraped off the salt. The Hg_2SO_4
so prepared was laden with mercury but this is useful
in preventing oxidation of the salt. It was kept in
a glass stoppered bottle in the dark, covered with
normal H_2SO_4. Before use it was thoroughly washed,
until free from the acid.

Mercurous Chloride. - This salt was pre-
pared by electrolysis according to the method of
Lipscomb and Hulett (21) using the same apparatus
which was used in the preparation of Hg_2SO_4, except
that normal HCl was used as the electrolyte. The
calomel obtained was washed repeatedly with water,
until it was free from HCl and kept in a glass stoppered
bottle in the dark. The calomel was heavily laden
with mercury. This is advantageous in making reproducible
calomel electrodes.

Nickel Chloride. - This salt was made by
electrolyzing dilute HCl using a cathode of platinum
and anode of Mond Nickel. The solution so obtained was
evaporated to dryness to get rid of the HCl. The solid
salt was then dissolved and recrystallized three times
at room temperature, discarding the mother liquor after
each recrystallization. The pure salt was then dissolved

and shaken with $Ni(OH)_2$ prepared as above, but from $NiCl_2$ rather than $NiSO_4$.

Plating Solution. - The plating solution used was the ordinary "Standard" nickel solution used in the plating industry. It was N in $NiSO_4$, N/4 in NH_4Cl and M/4 in H_3BO_3.

Fine Nickel. - The nickel used for measuring electrode potentials in the final results was prepared by plating from the above "Standard" solution. The solution was previously boiled, under reduced pressure, to expel air. It was electrolyzed, at a temperature of about 70°, with a current of about 1.6 to 2 amperes. A platinum wire about 8 mm long served as cathode, with another platinum wire as anode. The nickel was removed from the platinum wire, from time to time, by touching it with a stirring rod. The nickel obtained by this means was finely divided. It was thoroughly washed with some of the solution whose electrode potential was going to be measured, previously boiled out, and was then allowed to stand in the same solution for two days before being introduced into the electrode vessel.

At no time was the nickel exposed to the air, except when it was quickly transferred from one vessel to another, and then only when moistened with solution.

It was at first attempted to prepare fine spongy nickel by electrolyzing pure normal nickel sulfate

solution, at about 1.6 amps., with electrodes
of platinum wire. But the nickel so obtained
had mixed with it a green deposit, probably of
$Ni(OH)_2$. Such impure nickel could not have been
used for electrodes and the above described method
was then developed.

Hydrogen. - The hydrogen used in the
electrolysis of the $NiSO_4$ solution was prepared
by the electrolysis of NaOH solution. An electrolytic
hydrogen generator, of the type described by Clark
(22) was used. The gas was purified from oxygen by
passing through a tungsten filament lamp.

c. Apparatus and Method.

The type of electrode vessel used and
the arrangement of the apparatus for filling are
shown in Figure I. This is a modification of the
apparatus used by Smits (13). The upper portion
shows the electrode vessel, E. A piece of platinum
wire was sealed into the bottom of the vessel at S
so that external contact could be made with the
nickel. Mercury filled the tube M.

Some of the solution, previously boiled out,
was poured into the flask F and into the electrode
vessel E. The fine nickel, carefully washed, was
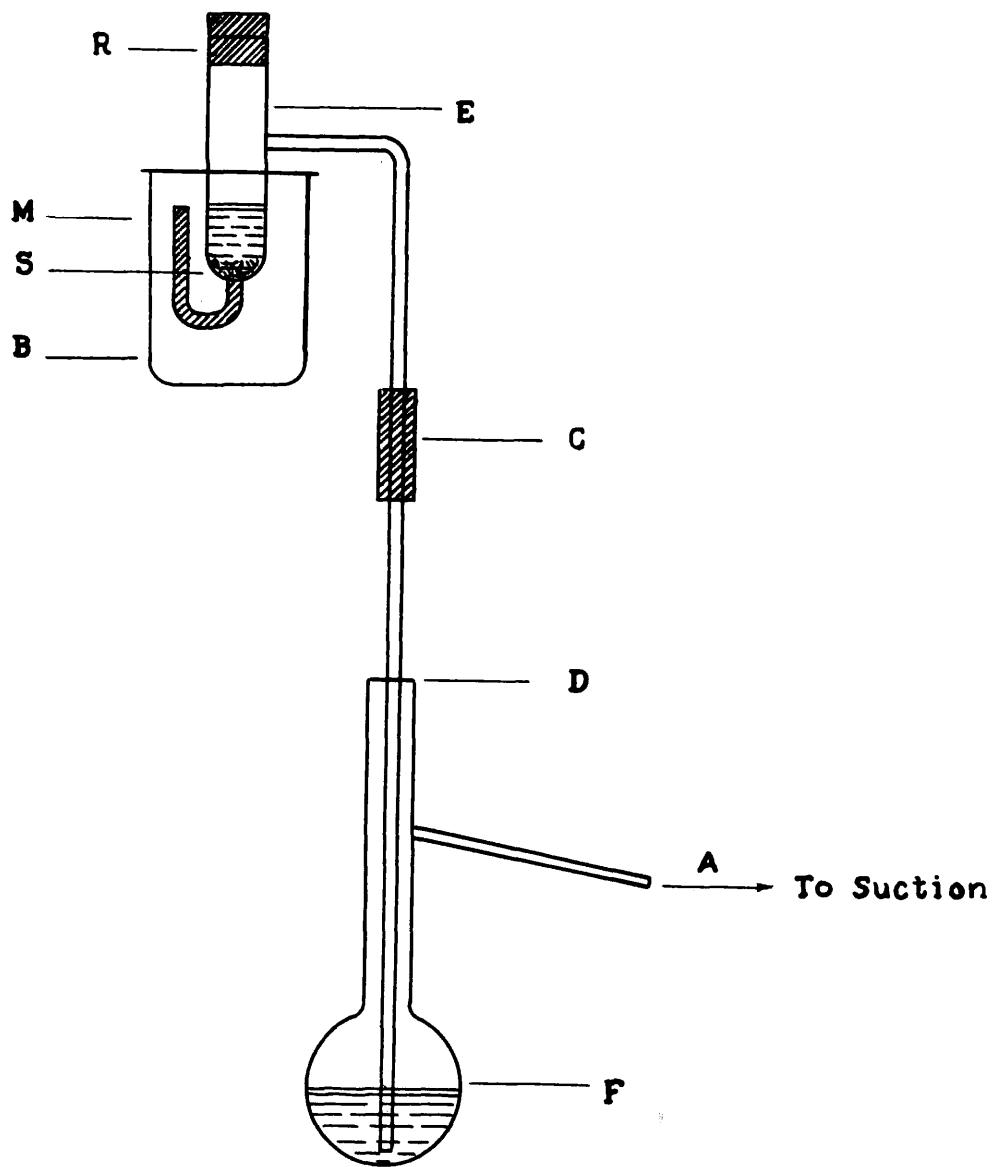introduced into the electrode vessel in a sufficient

Figure I.

Apparatus for Filling Electrode Vessel

quantity so that the platinum wire was completely
covered. A solid rubber stopper R was then
sealed in place with de Khotinsky cement. Connection
was then made between the electrode vessel and the
flask F by means of a piece of heavy pressure
tubing C. The flask was an ordinary 200 cc dis-
tilling flask, of Pyrex glass, with an inner seal
at D. The solution in the flask and water in the
beaker B were then heated and suction applied at A.
When solutions in both E and F had boiled vigorously
for some time the water pump was disconnected and
liquid immediately rushed into E, completely filling
the vessel. By this means all traces of oxygen and
hydrogen were completely removed.

After cooling the vessel was disconnected
at C and the end was placed immediately in a small
beaker containing some of the same solution, with
pure mercury in the bottom. The side arm dipped
under the surface of the mercury. This served as a
seal for the exclution of air and was broken only
when measurements were being made.

The vessel for the mercurous sulfate
electrode, which was used as the standard half-cell,
was of exactly the same type as that of the nickel
electrode. Sufficient mercury was placed in the
bottom to cover the platinum wire and over this a
layer of Hg_2SO_4, carefully washed with the solution

to be used. The vessel was then filled with some
of the $NiSO_4$ solution whose potential was to be
measured, though in this case saturated with Hg_2SO_4
by shaking with some of the washed salt.

The cells were placed in a darkened air
bath kept at $25^\circ \pm 0.5$. Measurements of the potential
were made with a Leeds and Northrup Student Potentio-
meter.

Since boiling effected the concentration of
the solution in the electrode vessel, it was necessary
to determine the nickel concentration in each electrode
vessel after the equilibrium potential had been
measured. This was done by the electrolytic method
described by Treadwell and Hall (23). To a quantity
of solution containing about 0.2 to 0.3 gms. nickel,
8 gms. $(NH_4)_2SO_4$ and 35 cc concentrated NH_4OH were
added, together with sufficient water to bring the
total volume up to 150 cc. This solution was
electrolyzed with a current of 0.6 amps., using as
cathode a weighed platinum gauze. Electrolysis was
continued until the solution showed no further pre-
cipitation with dimethyl glyoxime. The molarity of
the solution could thus be easily calculated.

d. Data on Nickel Sulfate.

Table VII gives the density of nickel
sulafte solutions of varying normality. It is

necessary to know the density of a solution in order
to calculate its molality (mols of salt to 1000 gms
water) from the molarity. Some of the values given
are taken from Landolt-Bornstein (24) and the others
were determined at $25^{\circ}C$, using a 50cc sp. g. bottle,
in the course of this investigation. A curve was made
by plotting normality against density and then the
densities of the solutions which filled the electrode
vessels could be easily read with sufficient pre-
cision.

Cells of the following type were measured:

$$Ni \ \mid \ NiSO_4 \quad (aq.) \ \mid \ Hg_2SO_4 \ \mid \ Hg$$
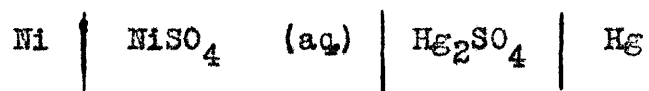
They contained no liquid junction. In Table III are
given the results using the Cleveland Nickel Products
Co. recrystallized salt at concentrations of approxi-
mately 0.05, 0.10, and 0.15 molar. In Table IV are
given the measurements with the $NiSO_4$ prepared from
Mond Nickel at concentration of 0.05 molar and in
Table V are given the measurements with the electrolyzed
$NiSO_4$ at the same concentration.

Table VI shows the change of potential with
time. The cells became constant after about 4 or 6
days and maintained a constant value for about 15 days.
These results are representative of all the measure-
ments given in Tables III to V, and were not choosen
because of any particular consistancy.

Table III

Recrystallized NiSO$_4$ as Electrolyte.

Cell No.	Molarity	Molality Calc.	E.M.F. Measured	γ	E$_0$ Calc.
26	0.0507	0.0508	0.968	0.215	-0.852
27	0.0510	0.0511	0.968	0.214	-0.852
28	0.0503	0.0504	0.967	0.215	-0.852
29	0.0505	0.0506	0.968	0.215	-0.852
30	0.0515	0.0516	0.968	0.213	-0.852
31	0.1016	0.1018	0.958	0.157	-0.852
32	0.1050	0.1052	0.958	0.154	-0.852
33	0.1015	0.1017	0.958	0.157	-0.852
34	0.1018	0.1020	0.958	0.157	-0.852
35	0.1022	0.1024	0.958	0.156	-0.852
36	0.1501	0.1504	0.954	0.129	-0.853
37	0.1613	0.1617	0.954	0.120	-0.853
38	0.1545	0.1548	0.953	0.127	-0.852
39	0.1540	0.1543	0.952	0.127	-0.851
40	0.1516	0.1519	0.953	0.128	-0.852
41	0.1500	0.1503	0.953	0.129	-0.852

Table IV.

$NiSO_4$ from Mond Nickel as Electrolyte.

Cell No.	Molarity	Molality Calc.	E.M.F. Measured	γ	Eo Calc.
42	0.0511	0.0512	0.967	0.214	-0.851
43	0.0508	0.0509	0.967	0.215	-0.851
44	0.0510	0.0511	0.967	0.214	-0.851
45	0.0503	0.0504	0.967	0.215	-0.851
46	0.0505	0.0506	0.967	0.215	-0.851

Table V.

Electrolyzed $NiSO_4$ as Electrolyte.

Cell No.	Molarity	Molality Calc.	E.M.F. Measured	γ	Eo Calc.
47	0.0514	0.0515	0.970	0.213	-0.854
48	0.0514	0.0515	0.968	0.213	-0.852
49	0.0503	0.0504	0.969	0.215	-0.853
50	0.0506	0.0507	0.971	0.215	-0.855
51	0.0524	0.0525	0.971	0.212	-0.854

Table VI.

Change of Potential with Time.

Cell No.	Time in Days 1	2	4	6	12	18
36	0.952	0.954	0.953	0.953	0.953	0.952
37	0.951	0.953	0.954	0.954	0.954	0.952
38	0.952	0.953	0.953	0.953	0.952	0.951
39	0.947	0.952	0.952	0.953	0.952	0.951
40	0.950	0.953	0.953	0.953	0.952	0.952
41	0.952	0.953	0.953	0.953	0.953	0.953

Table VII.

Density of NiSO$_4$ Solutions.

Normality	D 25/4	Source
0.050	1.0010	Experimental
0.100	1.0051	Experimental
0.125	1.0067	Landolt-Bornstein
0.175	1.0109	Landolt-Bornstein
0.200	1.0132	Experimental
0.250	1.0168	Landolt-Bornstein
0.300	1.0209	Experimental
0.500	1.0360	Landolt-Bornstein
1.000	1.0741	Landolt-Bornstein

4. Discussion

a. Theoretical.

When two Faradays of electricity pass through the cell

$$Ni \mid NiSO_4(aq) \mid Hg_2SO_4 \mid Hg$$
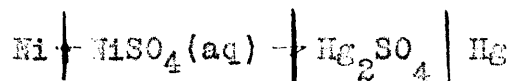
the following reaction takes place

$$Ni + Hg_2SO_4 \rightleftharpoons NiSO_4 + 2Hg \qquad (1)$$
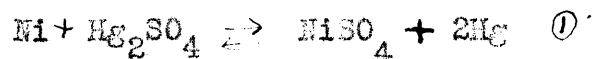
According to Van't Hoff (31), the maximum work which can be derived from the reaction at constant temperature T is given by the expression

$$W = RT \cdot \ln K - RT \cdot \ln \frac{[NiSO_4][Hg]^2}{[Ni][Hg_2SO_4]} \qquad (2)$$

where K is the equilibrium constant, R the gas constant and the values in brackets represent the concentrations of the respective substances. If the maximum work is expressed in terms of electrical energy we have

$$W = nFE \qquad (3)$$

in which n is the number of unit charges transferred, F is the Faraday and E is the electromotive force of the cell. On substituting we have

$$nFE = RT \cdot \ln K - RT \cdot \ln \frac{[NiSO_4][Hg]^2}{[Ni][Hg_2SO_4]} \qquad (4)$$

or

$$E = RT/nF \cdot \ln K - RT/nF \ln \frac{[NiSO_4][Hg]^2}{[Ni][Hg_2SO_4]} \qquad (5)$$

but $RT/nF \cdot \ln K$ is a constant which is called Eo, the

normal electrode potential of the metal, so that we have

$$E = Eo - RT/nF \cdot \ln \frac{[NiSO_4][Hg]^2}{[Ni][Hg_2SO_4]} \qquad (6)$$

According to Lewis (25), when the ratio of the effective ion concentrations, C_2/C_1, of two solutions of an electrolyte is calculated from the electromotive force of a concentration cell and from conductivity measurements, the values do not agree. That is C_2/C_1 is not equal to $\gamma c_2/\gamma c_1$, where c is the concentration of the electrolyte and γ is the degree of dissociation. The ratio of the effective ion concentrations $C_2/C_1 = a_2/a_1$ is called the activity coefficient, represented by the symbol γ. Accordingly $a = \gamma c$.

The activity of a substance in its standard state is chosen as unity. Hence equation (6) above, where Hg, Ni and Hg_2SO_4 are in their normal states, simplifies to the form

$$E = Eo - RT/nF \cdot \ln(a_{NiSO_4}) \qquad (7)$$

and we are concerned only with the activity of $NiSO_4$. But the activity of a salt is the product of the activity of its ions, so that for $NiSO_4$ we have

$$a_{NiSO_4} = (a_{Ni}^{++})(a_{SO_4}^{=})$$

or, since $a = \gamma c$ and the values of γ and c are the same for both Ni^{++} and $SO_4^{=}$ ions, we have

$$E = Eo - RT/nF \cdot \ln(m\gamma)^2, \qquad (8)$$

where m is the concentration expressed as molality.
Introducing the values for R, T, n and F, and
changing from Naperian to Briggsian logarithms, we
arrive at the equation

$$E = Eo - 0.05912 \log(m).$$

It was at first believed that the low value
for the electrode potential of nickel might be due, in
part, to the presence in the electrolyte of ions of
metals below nickel in the displacement series. Should
an electrode of nickel be placed in such a solution,
nickel would displace the metal ion and the electrode
would then function as an electrode of the metal against
its ions. In order to prevent this a $2N-NiSO_4$ solution
was electrolyzed as described under the preparation of
materials. The cathode of platinum black was kept
saturated with hydrogen during the electrolysis. The
theory of the procedure was this:- When hydrogen is
discharged in the process of electrolysis (as is always
the case with metals above hydrogen) the pressure of
the gas may be less than one Atmosphere. Hence the
potential of the hydrogen would be more positive and
current would be utilized in its removal from solution.
This means that the efficiency of removal of metals
below nickel would be diminished. Keeping the electrode
saturated with hydrogen would reduce the tendency of
hydrogen to leave the solution and so increase the
efficienty of removal of the other metallic impurities.

Metals showing high hydrogen overvoltage should also
be useful in this direction. Therefore as another
experiment a solution was electrolyzed, using as
cathode a layer of pure mercury in the bottom of the
container. But, since $(Ni(OH)_2$ was kept in the
solution in order to maintain a constant acidity, it
settled to the bottom and covered the mercury.
Consequently this method was not feasible.

      b. Choice of Results

      The measurements given represent only a
part of the total number made. Thus 5 other cells
were measured, using 0.0625 molar $NiSO_4$ solution as
electrolyte. These gave a value of 0.966 volts $\pm$ 0.001.
Other cells were measured with 0.15 molar solutions,
but their values also fell within the average value
of the cells given for this concentration, i. e $\pm$ 0.001
volts. Still other cells containing 0.1 molar solution
were studied in which the nickel was prepared just
before filling the vessels, through washed. The
potential of these was around 0.970 volts at first,
but it began to drop, showing the effect of occluded
hydrogen. With 0.05 molar $NiSO_4$ electrolyzed, 12 other
cells were measured, but all values fell between the
limits of those given in Table III. However, none of
these were calculated to Eo since the nickel concentra-
tion was not determined after the electrode potential
was measured.

c. Calculation of Results

As there are no available data from which
the activity coefficients of $NiSO_4$ can be calculated,
the values for $CuSO_4$ were taken at corresponding
concentrations. The justification for doing this
arises from the fact that bivalent salts, as a class,
behave very similarly. Thus Hampton(26), in his
measurements of the potential of the iron electrode,
assumed the activity coefficients of $FeCl_2$ to be the
same as the values for $BaCl_2$. Also Lewis and Randall
give values for several salts of the type $MeSO_4$ and
these are found to be practically the same, especially
for the more dilute solutions, such as were used in
this research. Furthermore the constancy of the results
of this work, when calculated to Eo, is perhaps the
best evidence that salts of the type $MeSO_4$ would have
the same activity coefficient.

In column 5, of Tables III, IV and V are
given the activity coefficients, for the concentrations
indicated, obtained by plotting the values which have
been calculated by Lewis and Randall.

As an example for calculation let us take
the first measurement given under Table III. Substitut-
ing in equation (9) we have

$$0.968 = Eo - 0.05912 \log(0.0508)(0.215)$$

or $\quad$ Eo $\quad = 0.852$ volts.

Then, accepting the sign convention adopted by the American Electrochemical Society, we simply put down our value for Eo in column 6 as -0.852 volts.

d. The Normal Electrode Potential.

The values as given in Table III, column 6, represent the normal electrode potential of nickel as referred to the Hg, $Hg_2SO_4(s)$, $\overset{=}{SO}_4$ electrode. Lewis and Randall give for this electrode the value of 0.6213 volts. Adding this to the average value for Eo in column 6, Table 2, we arrive at the value for the normal potential of nickel, with $H_2 | \overset{+}{H}$ taken as zero. Then by subtracting 0.283 from this latter value we obtain the normal electrode potential referred to the normal calomel electrode. We thus get -0.514 volts $\pm$ 0.002 as the true value for the normal electrode potential of nickel.

Calculated on the old basis of arriving at the electrode potential this value would be about -0.58 volts. We can thus see that the electrode potential of nickel has been raised about 0.1 volts above the present accepted value.

e. Errors.

The standard cell used in connection with the potentiometer was an Eppley Cell which was calibrated

against a Bureau of Standards cell and found to be
accurate within the limits that could be read on the
instrument (0.0001 volts).

In each case, when cells were made from a
solution of a given strength, several reference
electrodes were always set up and checked among
themselves. They were found to be constant and re-
producible to within 0.0001 volts.

The air bath was regulated at $25^{\circ} \pm 0.5^{\circ}$.
This was sufficiently accurate for the work, since a
change of 0.5° will produce a change of only 0.0001
volts in the electrode potential, as calculated from
equation (9).

All of the volumetric apparatus and the set
of weights were calibrated previous to doing any of the
analytical work. The thermometer used was a Bureau of
Standards calibrated thermometer.

Boiling changes the concentration of the
solution and for this reason the nickel concentrations
of the solutions were determined after the equilibrium
potential had been reached. These concentrations, as
given in column 2 of the E.M.F. tables, are accurate to
within $\pm$ 0.0005 M. But this change in concentration
would not effect the value of the potential as
measured. The density determinations are accurate to

within $\pm 0.1\%$, but this would not change the calculated molality sufficiently to appear in the final measured value.

The student potentiometer is accurate to within 0.0005 volts. But no attempt was made to measure the values of the E.M.F. further than the third place. The true equilibrium potential as reported in this work is therefore probably accurate to ± 0.002 volts.

Though but little difference was found between the electrode potential of electrolyzed and non-electrolyzed salt, spectroscopic analysis revealed an interesting fact. The two samples, through the kindness of the Bureau of Standards, were tested by means of arc spectra, portions of the samples being burned on graphite electrodes and photographed. Neither sample contained copper. Sample No. 1, the non-electrolyzed salt, was found to contain a considerable amount of cobalt. Sample No. 2, was entirely free from cobalt, but contained slight trances of aluminum, manganese and sodium. The sodium had been added in the form of the hydroxide in order to keep the solution at pH 6.8. The source of the aluminum and manganese was probably from the Pyrex dish in which the electrolysis was carried out. The difference in cobalt content would show that the electrode potential of nickel/is probably above that of cobalt, which is contrary to the present accepted

values for these two metals. Otherwise the electrolysis,
using a current whose value was just at the "Break" in
the I/E curve of nickel, would not have removed a more
negative metal. This point is now under investigation in
this laboratory.

The lowering of the electrode potential of
nickel is more readily effected by oxygen than by any
other impurity. In the preliminary work, before the
apparatus shown in Figure I was used, it was impossible
to completely remove air, the potentials always varied
and seldom were duplicate results obtained. On the
other hand, with the more careful boiling and evacuation
air could be so thoroughly removed that it did not
effect the potential. The nickel used in the preliminary
work was always found to contain black oxide on the
surface when removed from the electrode vessel. But
with the more careful boiling no oxide was visible on
the nickel and it always retained its grey metallic
appearance.

When a metal is deposited at a high current
density, such as was used in plating the nickel for this
work, hydrogen is always plated out. The effect of
hydrogen has been shown to raise the potential. However,
with careful washing of the nickel, allowing it to stand
for some time in contact with the solution to be tested,
and finally thorough boiling and evacuation of the
apparatus before filling the electrode vessel, it is

almost certain that all of the hydrogen has been
completely removed. The best proof for this is
perhaps found in the fact that the electrodes pre-
pared act as truly reversible electrodes. According
to Luther (27) the most important criteria of
irreversibility is a change in electromotive force
which is not proportional to the logarithm of the
concentration of the ions. A glance at the values
in Table III will reveal that for the cells measured
the electrode potential varied with the nickel ion
concentration just as it should according to the
Nernst equation. Had the electrode functioned as
a hydrogen electrode such variations would not have
been possible. Furthermore, when Cells No. 11 and No.
12 were polarized anodically and cathodically so
that hydrogen and oxygen were discharged on the
nickel, after a short while they returned to their
former value, showing that the electrode is a reversible
one.

Variations in the physical state of the
metal or at least of its surface, will often times
produce considerable variability in the electrode
potential. Schoch (10) found a difference of 0.03
volt between sheet nickel and finely divided nickel.
Hampton(26) found that the potential of annealed iron
is much lower than the potential of finely divided iron
and accepts the potential of the finely divided iron

as the best equilibrium value. Allmand and
Ellingham (29) state that a metal which is
deposited electrolytically at a high current
density, giving a loose deposit, may be practically
free from strain. Lewis and Lacey (30) suggest
that electrodes of fine metal seem to be free
from the surface strains which characterize
electrodes plated with a coherent film. These
electrodes give much more exposed surface and on
standing in contact with solution rapid local
action will remove any portion of the metal
which might still have a high potential. Lewis
and Lacey used finely divided metal in determining
the potential of both silver and copper.

The nickel used in this work was of a
very fine form and contained no oxide such as the
reduced oxide of Schoch must have contained.

5. The Potential of Nickel Against Nickel Chloride

Cells of the following type were measured:

$$\text{Ni} \left| \text{NiCl}_2 \ (.05m), \right| \text{Hg}_2\text{Cl}_2 \left| \text{Hg}. \right.$$
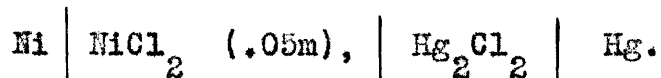
These cells contained no liquid potential. The
results are given in Table VIII.

The nickel chloride and mercurous chloride
electrode vessels were filled according to the same

method used in filling the sulfate cells. The
nickel used was the fine electrolytic nickel. The
potential was measured under the same conditions
as previously.

Nickel chloride in such dilute solutions
was found to hydrolyze very readily. In the
electrodes of cells No. 52, No. 53 and No. 54 a
precipitation of $Ni(OH)_2$ covered the nickel. This
undoubtedly had the effect of lowering the electrode
potential. In order to prevent hydrolysis a very
small amount of dilute HCl (about 3cc per liter of
solution) was added to the electrolyte. The pH
of the solution was 4.9. Electrodes of cells No.
55, No. 56, No. 57, No. 58 and No. 59 were filled
with this solution. Electrodes of cells No. 60,
No. 61, No. 62, No. 63 and No. 64 were filled with
$NiCl_2$ to which a somewhat larger amount of acid had
been added (about 6cc per liter of solution). The
pH of this solution was about 2.8.

In the last five cells there was a visible
evolution of hydrogen, with gas rising to the top of
the vessel. The potential measured was therefore below the
true equilibrium potential of nickel, for, as previously
stated, the electrode was in this case functioning as a
hydrogen electrode against hydrogen ions. On the other

hand in the other electrodes, to which acid had
been added in just sufficient amount to clear the
precipitate of $Ni(OH)_2$, there was no evolution of
hydrogen and the measurements of these cells
represent a value nearer to the true equiilbrium
value.

The potentials given were attained after
about 16 days. With cells No. 52 to No. 59 the
values started at from -0.640 to -0.620 volts and
dropped to the values given. Cells No. 60 to 64 attained
their potentials very rapidly, though the values given
represent the measurements after 16 days.

According to equation (7) the electromotive
force of these cells is given by the expression:

$$E = Eo \quad -RT/nF \cdot \ln(a_{NiCl_2}), \qquad (10)$$

where a_{NiCl_2} is the activity of $NiCl_2$ and is equal to
$4(m\gamma)^3$, since the activity of a salt is the product
of the activities of its ions. (Thus $a_{NiCl_2} = (a_{Ni}^{++})$
$(a_{Cl}^-)^2 = (m\gamma)(2m\gamma)^2$, m being concentration expressed
as molality). Substuting the proper values, the above
equation simplifies to the form:

$$E = Eo \quad -0.03 \cdot \log 4(m\gamma)^3 \qquad (11)$$

As there are no available data on the activity
coefficient of $NiCl_2$, the value of γ was assumed to be
the same as that for $BaCl_2$, which was taken from Lewis
and Randall (25).

No attempt was made to determine the
nickel concentrations of the solutions after the
E.M.F. was measured since the precision of the
potential arrived at would not warrant it. The
value for the molality consequently represents the
concentration of the solution before boiling, assuming
molarity to be the same as molality for such a dilute
solution.

The value given for Eo is referred to the
standard calomel electrode as zero. Since the potential
of the standard calomel is -0.270 referred to the
hydrogen electrode and that of the normal calomel is
-0.283 referred to hydrogen, the average values, as
given in the table, would be -0.460, -0.490, -0.440
volts respectively, referred to the normal calomel
electrode.

Table VIII

Electrolyte of 0.05 Molal $NiCl_2$

Cell No.	γ	E.M.F. Measured	Eo Calc.	Remarks
52	0.568	0.567	-0.447	$Ni(OH)_2$ over Nickel
53	0.568	0.568	-0.448	" " "
54	0.568	0.565	-0.445	" " "
			-0.447	Average
55	0.568	0.596	-0.476	HCl added. No H_2
56	0.568	0.595	-0.475	" " " "
57	0.568	0.599	-0.479	" " " "
58	0.568	0.599	-0.479	" " " "
59	0.568	0.599	-0.479	" " " "
			-0.478	Average
60	0.568	0.563	-0.443	H_2 Escaped
61	0.568	0.545	-0.425	" "
62	0.568	0.545	-0.425	" "
63	0.568	0.540	-0.420	" "
64	0.568	0.540	-0.420	" "
			-0.427	Average

6. Summary

1. The normal electrode potential has been carefully re-determined and found to be -0.514 volts ± 0.002 volts, referred to the normal calomel electrode as zero.

2. The finely divided electrolytic nickel was found to reach equilibrium most rapidly and gave the most reproducible results.

3. Oxygen has been shown to be the cause of the apparently low potentials.

4. It has been shown that cobalt and nickel are misplaced in our present accepted electrode potential series. Nickel should be above cobalt in the series, rather than immediately below it.

5. Nickel chloride gave the approximate value of -0.48 volts. Though this is not the true equilibrium potential, it serves as a check on the value determined with nickel sulfate.

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