COMPOSITION OF DIFFICULTLY SOLUBLE NICKEL COMPOUNDS PRECIPITATED BY ALKALI FROM SULFATE SOLUTION, AND THEIR STANDARD ISOBARIC POTENTIALS OF FORMATION

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It is known that nickel ions, as well as many other metallic ions, under the proper conditions form difficultly soluble hydroxides, basic salts and even more complex compounds. However, despite the large number of researches on the subject, the composition and conditions for the formation of difficultly soluble nickel basic salts have not been established up to now. Thus, for example, Britton [1] found that 1.66 equivalents of alkali is required to precipitate all of the nickel from a 0.025 M solution, which fact is evidence that the basic salt is precipitated. On the other hand, Fialkov and Akselrud [2,3] consider the nature of their experimental results as being due to the formation of pure nickelous hydroxide in all of the concentration intervals studied by them. Rotinyan and Zeldes [4] showed that, at low concentrations of nickel sulfate in the potentiometric titration of the solution with alkali the pure nickelous hydroxide $Ni(OH)_2$ is formed, while at the same time for higher concentrations of $NiSO_4$ the solid phase consists of basic salts. Singley and Carriel [5] found that basic compounds are formed when nickel is precipitated by alkali from nickel chloride, nitrate, or sulfate solutions, these compounds with further elevation of the pH undergoing transition into the pure hydroxide.

According to the observation made by Bagno [6], the difficultly soluble nickel compound, precipitated from nickelous chloride solution by a mixture of NaOH and Na_2CO_3, undergoes a change in composition with time. The CO_3'' ions, first found in the precipitate, are replaced by hydroxyl ions with the passage of time.

In the present study we set ourselves the task of establishing the composition of difficultly soluble nickel compounds, elucidate the conditions for their formation, and compute where possible the standard isobaric potentials for the formation of these compounds.

Selection of a method for determining the composition of the solid phase

The composition of the solid phase can be determined by several methods. At first glance, the most reliable composition of the solid phase is obtained by direct chemical analysis of the difficultly soluble compound, separated from its equilibrium solution. However, on closer examination this method very frequently proves to be inaccurate. Actually, if the solid phase is found in equilibrium with the solution only in a definite interval of salt activities and solution acidities, then on removing it from the mother liquor by washing with distilled water a change in the composition of the solid phase takes place toward the formation of a more basic compound. Consequently, this method is adaptable only in the case where constancy in the composition of the solid phase during washing has been established by some other independent method.

Another method [1] consists in the potentiometric determination of the amount of alkali necessary to precipitate all of the metal ions from solution. Calculation of the solid phase composition from the number of equivalents of alkali consumed for 1 equivalent of metal gives a true value only in the case where the precipitate retains a constant composition from the beginning to the end of the titration. Such a situation frequently fails to hold true in practice [7].

It is possible to determine the most trustworthy composition of the solid phase from the slope values for the relation pH vs. log metal salt activity in solution, with a large number of experimental points being plotted [7].

For this method it is necessary to know the pH values of the solutions in equilibrium with the solid phase at different salt activities. The hydrogen ion concentration in the solution found in equilibrium with the solid phase can be obtained by measuring the pH of the solution, brought to a state of visible turbidity by the addition of an alkaline reagent and held in order to attain equilibrium (Gromov * [8]).

* At low salt concentrations the method of Gromov has the disadvantage that a considerable portion of the salt may be lost in the formation of turbidity, and consequently its equilibrium concentration will be substantially different from the initial concentration, which concentration is used in the calculations.

The method of Akselrud and Fialkov [3], in accord with which the hydroxide (or basic salt) is precipitated separately, filtered and then brought into equilibrium with the salt solution (the equilibrium concentration of the salt is analyzed separately), gives the same physical value for the pH. Therefore, it is natural for the experimental data obtained by methods [3] and [8] to coincide with each other.

Other methods, by some means or other, fix the pH at the beginning of solid phase formation in the process of adding alkali to the solution. The initiation of solid phase formation can be detected by the inflection on either the potentiometric or conductometric titration curves, and also from polarographic measurement data [9,10].*

This group of methods usually requires fairly rapid experimental execution, as a result of which the solid phase may consist not of compounds in equilibrium with the solution but of difficultly soluble pseudoequilibrium compounds, for which the pH of formation differs from that of the equilibrium compounds.

The fact that the pH values determined by methods [8] and [3] at times are higher than the values obtained in the second group of methods is apparently due to the above situation.

To determine the composition of the solid phase we used in the present work the earlier described calculation method based on the slope coefficient values of the linear functions $pH - \log a_{\pm}$ [7]. To verify the obtained results we developed still another method for determining the composition of the deposited solid phase, based on measurement of the electrical conductivity of the coexistent solution. A detailed description of this method is given below.

EXPERIMENTAL

a) Measurement of the pH of formation of the hydroxide and basic salts of nickel by the potentiometric method. The pH values of the solutions coexisting with the solid phase were determined by both method [8] and by the potentiometric method [11].

It should only be emphasized that the potentiometric titration curves are taken in such a manner that each point is the result of measuring the established value of the electromotive force (change in e.m.f. < 1mV after 10-15 minutes). Reproducibility of the results was within ± 0.1 pH. The reagents used were carefully purified. Standard 0.1 N NaOH was used for the titrations.

The pH values corresponding to initial solid phase formation are given in the table. In the table are also given the pH values of the solutions in equilibrium with the solid phase, determined by the method of Bromov. These values for the coordinates $pH - \log a_{\pm}$ are depicted in Fig. 1. First of all it should be mentioned that the obtained results are in excellent agreement with the literatuare data [3,4], with the exception of the experiments performed by Gayer and Garrett [12], in which in dilute nickel chloride solutions the slope coefficient of the relation $pH - \log a_{\pm}$ proves to be 0.5 (i.e., the solid phase consists of pure nickel hydroxide, which agrees with our data) but the absolute pH values in their experiments are shifted by approximately a pH unit when compared with the values depicted in Fig. 1. Apparently, this divergence is caused by some systematic error hidden in the measurements of Gayer and Garrett. Further, it can be seen from Fig. 1 that at concentrations of nickel sulfate up to approximately 0.1 M the compound found in equilibrium with the solution (top curve) is the pure hydroxide (slope coefficient of the straight line is 0.5). At concentrations of nickel sulfate ranging from ~ 0.1 to ~ 1.0 the basic salt of composition $3NiSO_4 \cdot 4Ni(OH)_2$ is found in equilibrium with the solution. The composition of this basic salt is determined from the slope of the linear function $pH - \log a_{\pm}$ according to the formula

$$pH = \frac{\Delta Z^0_{basic}}{2.3nyRT} - \frac{y + bx + dx}{ny} \log a_{\pm} - \frac{1}{ny} \log \frac{b^{(y+bx)} d^{xd}}{\left(\frac{b}{b^{b+d}} \cdot \frac{d}{d^{d+b}}\right)^{y+bx+dx}} - \log K_w \qquad (1)$$

the derivation of which was given earlier [7].

(Here ΔZ^0_{basic} – standard isobaric potential of forming the basic salt in accord with the scheme:

$$(y + bx)\, Me^{n+} + dx\, A^{m-} + ny\, OH' \rightleftharpoons x[Me_bA_d]\, y[Me(OH)_n],$$

* The last method, recently proposed by Kovalenko, is to be preferred when the measurements are made in dilute solutions. Kovalenko determined the moment of initial hydroxide formation and the pH corresponding to it from the decrease in the metal diffusion current, taking a series of polarograms at different pH values.

If the titration is made, given the dropping mercury cathode diffusion potential, then the curve, constructed by Kovalenko from a number of polarograms, is obtained directly.

$a_{\pm}$ – mean salt activity in the solution, K_W – ionic product of water).

TABLE

The Influence of Nickel Sulfate Concentration on the pH of Solutions Coexisting with the Solid Phase

Nickel concentration		$\gamma_{\pm}$	$a_{\pm}$	pH potentiometrically determined at		pH determined by the method of Gromov at
g/liter	M			20°	50°	20°
0.10	0.0017	0.66	0.00112	7.94	7.04	7.66
0.15	0.0025	0.60	0.00150	7.90	6.86	7.87
0.20	0.0034	0.55	0.00187	7.85	6.82	7.78
0.30	0.0051	0.49	0.00249	7.77	6.80	7.70
0.40	0.0068	0.46	0.00309	7.58	6.68	7.62
0.49	0.0083	0.43	0.00355	–	–	7.53
0.50	0.0085	0.42	0.00361	7.61	6.62	7.63
0.60	0.0102	0.40	0.00413	7.58	6.45	7.56
0.70	0.0119	0.38	0.00458	7.44	6.56	7.56
0.80	0.0136	0.37	0.00503	7.36	6.52	7.55
0.90	0.0153	0.35	0.00543	7.34	6.46	7.48
0.96	0.0163	0.34	0.00562	–	–	7.48
1.0	0.0170	0.34	0.00578	7.24	6.42	7.52
1.0	0.0170	0.34	0.00578	–	–	7.38
1.5	0.0255	0.29	0.00739	7.10	6.38	–
1.88	0.0320	0.26	0.00848	–	–	7.38
2.0	0.0341	0.26	0.00886	7.08	6.32	7.30
2.14	0.0364	0.26	0.00937	–	–	7.38
3.0	0.0511	0.23	0.01175	6.92	–	–
5.0	0.0852	0.18	0.01533	6.78	5.94	7.28
10	0.1704	0.12	0.02044	6.51	5.70	7.17
20	0.3408	0.075	0.02556	6.41	5.36	6.98
30	0.5146	0.065	0.03345	6.15	5.16	6.88
40	0.6815	0.055	0.03748	6.10	5.14	6.77
50	0.8519	0.050	0.04259	6.04	4.98	6.72
60	1.0223	0.045	0.04600	5.84	4.94	6.67

b) Study of the composition of basic salts by the electrical conductivity method. We will examine the case where the addition of alkali to a nickel sulfate solution results in the formation of a difficultly soluble compound in accord with the reaction

$$(x + y)\,NiSO_4 + 2yNaOH = x\,NiSO_4 \cdot yNi(OH)_2 + yNa_2SO_4. \quad (2)$$

To perform the experiment we chose such concentrations of salt and alkali that, first, the conductivity of the mixed solution as a first approximation was additively composed of the conductivities of the individual component solutions and, second, that in the selected concentration interval the change in the specific conductance of the solution was proportional to the salt concentration.

With progress of reaction (2) the conductivity of the solution should drop due to decrease in nickel sulfate concentration and simultaneously it should rise due to the formation of sodium sulfate. The change in the specific conductance of the solution during solid phase formation is influenced by both factors.

If the experiment is conducted in such a manner that to a constant volume of nickel sulfate solution of concentration C_1 there is added V ml of alkali solution of concentration C_2, the solution made up to constant volume W with distilled water, next filtered and the specific conductance of the filtrate determined, then, in accord with the equation for the reaction, the change in nickel sulfate concentration is expressed by

$$\Delta C_1 = \frac{\Delta(C_2V)}{W} \cdot \frac{(x + y)}{2y}. \quad (3)$$

Here C_1 and C_2 are expressed in moles per milliliter.

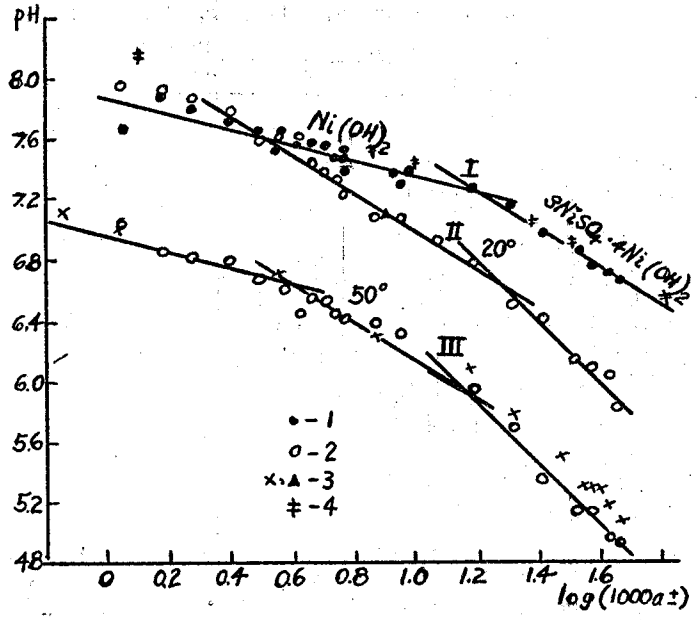

Fig. 1. Relation of the pH of initial solid phase formation vs. the logarithm of nickel sulfate activity in solution.

1) Our data at 20°, obtained by the Gromov method; 2) our data, obtained from the potentiometric titration curves at 20° and 50°; 3) data of Rotinyan and Zeldes at 50° [4] and at 20° [11]; 4) data of Akselrud and Fialkov [3].

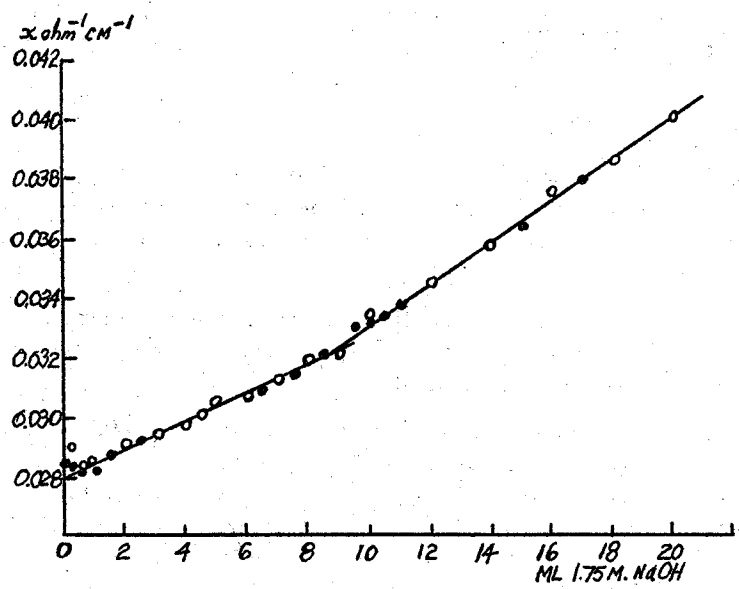

Fig. 3. Change in the specific conductance of the solution during the precipitation of nickel from sulfate solution with alkali.

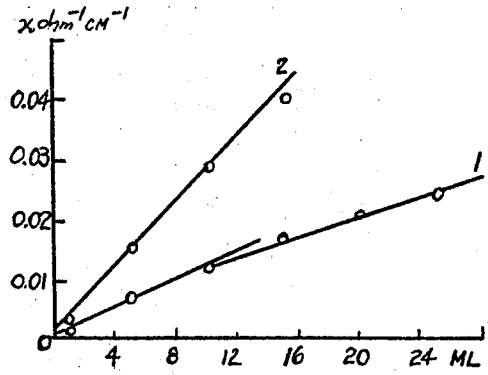

Fig. 2. Change in the specific conductance of nickel and sodium sulfate solutions with change in concentration.

1) Relation between the specific conductance of nickel sulfate solution and salt concentration, expressed in milliliters of 0.681 M $NiSO_4$ solution in 50 ml of solution, 2) Analogous curve for sodium sulfate; initial concentration of $NaSO_4$ solution 1 M.

When the above indicated conditions are observed in the experiment the change in the specific conductances of nickel and sodium sulfates will be:

$$\Delta \kappa_{NiSO_4} = -K_1 \Delta C_1 = -K_1 \frac{\Delta (C_2 V)}{W} \frac{(x+y)}{2y}; \quad (4)$$

$$\Delta \kappa_{Na_2SO_4} = K_2 \frac{\Delta (C_2 V)}{2W}. \quad (5)$$

Consequently, the total change in conductivity will be determined by the expression

$$\Delta \kappa_{\Sigma} = \frac{\Delta (C_2 V)}{2W} \left[K_2 - K_1 \frac{(x+y)}{y} \right], \quad (6)$$

from which it is seen that the change in the specific conductance of the solutinn during precipitation of the basic salts or hydroxides should as a first approximation be proportional to the amount of added alkali. In other words, the relation $\kappa_{\Sigma} - C_2 V$ should be expressed by a straight line in the whole concentration interval for the original salt in which a precipitate of constant composition is obtained.

With changes in the composition of the precipitate the indicated straight line will suffer breaks.

The tangent to the slope of each straight portion is equal to

$$\frac{\Delta \kappa_{\Sigma}}{\Delta (C_2 V)/2W} = K_2 - K_1 \frac{(x+y)}{y}. \quad (7)$$

Equation (7) makes if possible to determine the composition of the precipitate (values x and y) from the slope of the linear function $\kappa_{\Sigma} - C_2V$, provided constants K_1 and K_2 are known.

The latter are determined from the individual conductivity measurements of pure nickel sulfate and sodium sulfate solutions at different concentrations. 0.681 M Nickel sulfate solution and 1.000 M sodium sulfate solution were used to determine the constants K_1 and K_2. Both salts were carefully purified beforehand.

The different amounts of salt solution were made up to 50 ml with distilled water, after which the electrical conductivity of the solution was determined with the aid of the ordinary bridge scheme. The determination results are given in Fig.2, from which it can be seen that under experimental conditions the change in specific conductance with change in concentration is indeed linear.

Inasmuch as constants K_1 and K_2 denote the change in the specific conductance of $NiSO_4$ and Na_2SO_4 solutions with unit change in concentration, then evidently

$$K_1 = \frac{\Delta \kappa_{NiSO_4}}{\Delta C_{NiSO_4}} \quad \text{and} \quad K_2 = \frac{\Delta \kappa_{Na_2SO_4}}{\Delta C_{Na_2SO_4}}. \quad (8)$$

We started with a solution of nickel sulfate in our experiments. Consequently, for calculating K_1 in the initial experimental stages it is necessary to take the slope coefficient of the straight line corresponding to the higher concentrations of nickel sulfate, while for calculating K_2 it is necessary to use the values corresponding to low concentrations of sodium sulfate.

The calculation of constants K_1 and K_2 under these conditions gives:

$$K_1 = \frac{8.3 \cdot 10^{-4} \cdot 50 \cdot 1000}{0.681} = 61.8$$

$$K_2 = \frac{26.5 \cdot 10^{-4} \cdot 50 \cdot 1000}{1} = 132.5.$$

At low concentrations of nickel sulfate

$$K_1 = \frac{11.5 \cdot 10^{-4} \cdot 50 \cdot 1000}{0.681} = 84.4$$

A number of solutions were prepared for the nickel precipitation experiments, the solutions containing 25 ml of 1 M $NiSO_4$ and various amounts of 1.75 M NaOH; after this the solutions were made up to 50 ml. The solutions were filtered and the specific conductances were determined at 20°, either on the following day or immediately. The results of two parallel experiments, in which the solutions were filtered and the specific conductances determined on the second day after precipitation of the nickel with alkali, are given in Fig. 3. The starting solution was acidified slightly, as a result of which the first portions of alkali were consumedin neutralizing the excess acidity and the specific conductance dropped. From Fig. 3 it can be seen that the obtained data arrange themselves along two linear sec - tions.

The slope coefficient corresponding to the higher concentrations of nickel sulfate is

$$\frac{4.4 \cdot 10^{-4} \cdot 10 \cdot 1000}{1.75} = 25.1,$$

while for more dilute solutions it is

$$\frac{7.1 \cdot 10^{-4} \cdot 10 \cdot 1000}{1.75} = 40.5$$

The values x and y are determined from these slope coefficient values and the constants K_1 and K_2.

For the first section $x = 0.74\ y$, while for the second,* $\frac{x+y}{y} = 1.09$, i.e., as an approximation $x = 0$ and $y = 1$.

*In calculating the composition of the solid phase in this case $K_1 = 84.4$ and $K_2 = 132.5$. The last constant was used on the assumption that it is valid up to fairly high concentrations of sodium sulfate.

As a result, from the conductivity measurements it follows that the precipitate corresponding to the first section of the curve in Fig. 3 has the composition $3NiSO_4 \cdot 4Ni(OH)_2$, while the second section corresponds to $Ni(OH)_2$.

The experiments in which the precipitate was not allowed to stand with the solution gave analogous results, and consequently are not presented here.

The developed method has the advantage that it permits determining the composition of the precipitated compound, even if the latter is not found in equilibrium with the solution, whereas the determination method based on the slope of the linear function $pH - \log a_{\pm}$ assumes that the solid phase is in equilibrium with the solution.

DISCUSSION OF RESULTS

First of all it should be mentioned that the slope coefficient and electrical conductivity methods are in excellent agreement as regards the composition values obtained for the solid phase. Both the calculations according to Equation (1) and the conductivity method lead to the conclusion that in dilute solutions pure nickelous hydroxide is formed, whereas in more concentrated solutions the basic salt $3NiSO_4 \cdot 4Ni(OH)_2$ is precipitated.

Basic conclusions may be derived from a comparison of the results obtained by the "equilibrium" method of Gromov and the "rapid" potentiometric titration method. If the data obtained with these methods agree with each other at low concentrations of nickel sulfate, then significant and regular differences exist in more concentrated solutions.

The conductivity method shows that in the case of rapid titration the composition of the precipitate is such that it is in equilibrium with a more concentrated nickel sulfate solution.

This circumstance makes it possible to interpret the data of the potentiometric titration method.

Specifically, from Fig. 1 it follows that at low salt concentrations the pure nickelous hydroxide is formed, and then, insofar as the solid phase in all cases is in equilibrium with the solution, the pH values obtained from the potentiometric titration curves and by the Gromov method coincide with each other. In more concentrated nickel sulfate solutions the basic salt is formed during titration, which only after a long period of time is transformed into pure nickelous hydroxide (cf. left section of Curve II).

The composition of the pseudoequilibrium compound under the given conditions corresponds to $3NiSO_4 \cdot 4Ni(OH)_2$, i.e., it corresponds to the composition of the basic salt found in equilibrium with the solution in the region of higher nickels sulfate activities. It should be mentioned that the slope coefficient for this section of Curve II (Fig. 1) is equal to the slope coefficient of the extreme right section of equilibrium Curve I.

At even higher nickel sulfate concentrations the first precipitated basic salt has a less basic character than before, which with the passage of time is transformed not into the pure hydroxide but instead into a more basic salt, namely $3NiSO_4 \cdot 4Ni(OH)_2$.

If the composition of the second pseudoequilibrium salt is calculated from the slope coefficient of Curve II (right section), then it corresponds to the formula $3NiSO_4 \cdot 2Ni(OH)_2$.

Under equilibrium conditions this salt is probably formed at extremely high nickel sulfate activities, which activities were not attained in our experiments; consequently, on the equilibrium Curve I the section with the same slope coefficient is not shown.

Curve III (Fig. 1), obtained by the potentiometric method at 50°, shows that the slope coefficients remain constant when the temperature is raised. This condition serves as evidence that the same difficultly soluble compounds are formed at 50° and at room temperature.

It should also be mentioned that our data are in satisfactory agreement with the earlier obained values [4].

On the basis of the obtained data, it may be concluded that in general the potentiometric titration method, as well as the other "rapid" methods for determining the pH at the beginning of solid phase formation, do not give the right to calculate the free energy of formation of the salt.

In conclusion, we wish to state that the possibility of forming pseudoequilibrium compounds limits even more the practical use of the so-called pH series for the precipitation of hydroxides [1,2], for the solution of concrete problems is governed, not by the equilibrium pH values existing at the beginning of solid phase formation, but by those pH values that are established under the given process rate.

Calculation of the standard isobaric potentials on the basis of the equilibrium curve leads to the following values.

The standard isobaric potential for the formation of nickelous hydroxide from the ions is −20.8 kcal/mole, whereas the value −18.9 kcal/mole was obtained earlier.

The standard isobaric potential for the formation of the basic salt $3NiSO_4 \cdot 4Ni(OH)_2$ (ΔZ^0_{basic}) is −96.0 kcal for 1 mole of basic salt and the standard isobaric potential for the addition of 3 moles of nickel sulfate to 4 moles of nickelous hydroxide ($\Delta Z^0_{addn.}$) is −20.4 kcal for 1 mole of basic salt.

SUMMARY

1. The method of analyzing the equilibrium curves pH−log $a^{\pm}$ was used to determine the compositions of difficultly soluble nickel salts formed in the treatment of $NiSO_4$ solutions with alkali solutions.

2. The obtained results were verified by the method of analyzing the conductivity curves for the mother liquors during the precipitation of basic nickel salts with alkali.

3. It was shown that at low nickel sulfate activities the pure hydroxide is formed, while at higher activities the basic salt $3NiSO_4 \cdot 4Ni(OH)_2$ is formed. The standard isobaric potentials for the formation of these compounds were calculated, as was also the standard isobaric potential for the addition of nickel sulfate to nickelous hydroxide with the formation of $3NiSO_4 \cdot 4Ni(OH)_2$.

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