[Contribution from the Department of Physical Chemistry, University of Cape Town]

THE SINGLE POTENTIAL OF THE NICKEL ELECTRODE

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Received January 10, 1929 Published May 6, 1929

The single potential of nickel has been the subject of numerous investigations during the past thirty-five years but so far no work has been done which has inspired sufficient confidence for the values obtained to be accepted as standard. Each investigator claims accurate reproducibility for his particular results and yet the variety of opinion is surprising. Some give positive values, some negative, and the range between extremes is of the order of one volt. The whole position is therefore highly unsatisfactory and the following work was undertaken with the view in the first place of investigating the reasons for these extraordinary variations and in the second place of deciding whether it is possible to assign any definite single potential to this metal.

Possible sources of variations in results are: (1) impurities in the electrode, (2) impurities in the electrolyte, (3) variations in nature of electrode surface, (4) changes in electrolyte during measurements, and (5) chemical action between electrode and electrolyte.

1. Pure nickel free from cobalt and iron has been used by most of the investigators. In the course of this work various samples from the purest available to markedly impure material containing iron, cobalt and up to 2% of copper were used, but no difference could be detected which could be ascribed definitely to these impurities. Extreme purity of nickel from other metals appears therefore to be of small importance for the purpose in hand.

Gaseous impurities, however, are in another category. Experiments were tried using the carefully cleaned metal in an atmosphere of nitrogen with air-free solutions. When air was admitted and even bubbled through the solution, no change could be detected. Oxygen is therefore an unimportant impurity, contrary to the opinion of certain investigators. On the other hand, hydrogen has a powerful effect. This gas is very appreciably soluble in metallic nickel and if present in any considerable quantity may transform the nickel into a hydrogen electrode. Freshly prepared electrolytic nickel contains large quantities of hydrogen and the single potential of such an electrode may differ by as much as 0.5 volt from that of a similar electrode free from the gas. Hydrogen is therefore a dangerous impurity and must be rigidly excluded. The values recently obtained by K. Murata[1] are invalidated for this reason.

2. Chemically pure nickel salts are available but preliminary experiments tried with crude commercial samples showed no variations which

[1] Murata, *Bull. Chem. Soc. Japan*, **3**, 57–69 (1928).

could be definitely ascribed to this source. Extreme purity of the electrolyte appears therefore to be a matter of little importance.

3. In the case of copper, recently investigated, it was found that variations in the nature of the electrode surface had little or no effect upon the single potential. In striking contrast to this, it has been found that the difference of potential between a highly polished and a very rough nickel surface is of the order of 0.4 volt and further that reproducible results at any stage between these limits could be obtained by choosing different grades of emery or glass paper for preparing the surface.

4. Nickel sulfate, the salt generally used for this purpose, is very stable in solution and there appears to be no reason for ascribing any appreciable influence to this factor.

5. Judging by the rapid changes of potential which occur when a nickel electrode is first placed in a solution of a nickel salt, there is no doubt that chemical action does occur between electrode and electrolyte. Such action is, however, extremely small though its effect upon the single potential is great. A highly-polished nickel rod immersed in a solution of nickel sulfate for several hours is unchanged in appearance even under the microscope, although its single potential may have changed by 0.3 volt during the period.

Experimental

The apparatus used was identical with that previously described for copper electrodes.

Especially pure nickel sulfate free from cobalt and iron was used for making up the solutions and the electrodes were made from Merck's A.R. nickel in the form of sheet 0.5 mm. thick or small rods 2 mm. thick. The electrodes were in most cases covered with hard white sealing wax leaving 1 sq. cm. exposed. This was done in order to avoid the possible interference of surface actions at the liquid–air boundary, but it is probable that this precaution is unnecessary.

It is essential that electrodes be kept in motion with respect to electrolyte during observations of single potential. An electrode which has been left at rest for some time in the electrolyte shows a sudden change of potential of the order of 0.2 volt when moved. This is most probably due to local concentration changes in the film of electrolyte in contact with the electrode and such changes can only be avoided by rapid relative motion between electrode and electrolyte. Where rods were used, they were rotated at speeds of about 500 r. p. m., and where plates were used a small spiral glass stirrer was rotated at the same speed close in front of the plate.

(a) In view of the success of Nielsen and Brown[2] in preparing a standard copper electrode by using a two-phase amalgam, this method was adopted for the first mode of attack. The amalgam was prepared by electrolyzing a solution of pure nickel chloride using a cathode of especially pure electrolytic mercury and an anode of pure sheet nickel. After washing, the amalgam was heated to the boiling point of mercury to expel any traces of hydrogen, and preserved under a half-molar solution of nickel sulfate.

The cell $\mathrm{NiHg} \mid \mathrm{NiSO_4}\ M/2 \mid \mathrm{Hg_2SO_4} \mid \mathrm{Hg}$ was then made up and immersed in a thermostat at 25°. This cell gave very erratic readings varying between 0.22 and 0.35

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[2] Nielsen and Brown, THIS JOURNAL, 49, 2423 (1927).

volt when first made up and rising to nearly 0.7 volt after standing for two hours. A small spiral glass stirrer was then introduced to stir the amalgam surface during observations. The readings then obtained were much steadier but still varied between 0.4 and 0.55 volt. Similar experiments with more dilute amalgam gave similar results. With the use of twentieth molar nickel sulfate solution, still more erratic values were obtained.

A dropping electrode was then tried for the amalgam but the values given were extremely irregular, varying between 0.3 and 0.65 volt for no apparent reason. Further work with the amalgam was therefore abandoned.

(b) The method which proved successful with copper whereby the "instantaneous" potential of a rapidly rotating rod is measured during the actual process of immersion was now tried.

The cell used was Ni | $NiSO_4$ $M/2$ | Hg_2SO_4 | Hg, the mercury electrode being contained in a separate vessel communicating with the main vessel through 25 cm. of 1-mm. tubing, and the whole apparatus immersed in a thermostat at 25°.

The rotating electrode holder was attached to a stand fitted with rack and pinion for raising and lowering, and the main vessel was closed with a cork through which a glass tube passed, just wide enough to admit the rotating electrode. Other tubes allowed the vessel to be filled with air or nitrogen at will.

It was soon found that reproducible results could be obtained if the electrode was prepared in the same way, even with different samples of metal, some of which were certainly impure. If, however, the method of preparation of the surface was varied, the values obtained also varied widely. For each abrading or polishing material used, there appears to be a fairly definite limiting potential produced. With the finer polishing agents this limit is only obtained after long-continued and repeated application, whereas the coarser agents give a constant value at once. The values obtained with the various agents are given in the following table.

Polishing agent	E.m.f. of cell, volt	Polishing agent	E.m.f. of cell, volt
No. 1 emery cloth	0.63	Soft filter paper	0.45
No. 00 emery cloth	.59	Agate burnishers	.40
No. 000 emery paper	.56	Agate followed by selvyt cloth	.25

Since it was found that the value of 0.45 volt could be repeatedly obtained by using a certain sample of filter paper, various modifications were introduced while keeping to this polishing agent. (1) Previous heating of the electrode to redness in high vacuum had no effect. (2) Previous boiling of the solutions, cooling in an atmosphere of nitrogen and carrying out the measurements in an atmosphere of nitrogen had no effect. (3) Immersing the electrode in concentrated potassium hydroxide solution, washing and drying, lowered the e.m.f. of the cell from 0.45 to 0.40 volt. (4) On allowing the rotating electrode to remain in the solution, a fairly rapid *rise* to 0.53 volt occurs. (5) After (3) above, the electrode was abraded with No. 1 emery cloth, when the value 0.63 volt was again obtained. (6) Repeating (4) with the electrode after (5) treatment, a *fall* to 0.53 volt was observed.

From the above observations we conclude (1) that the presence of oxygen has no appreciable effect upon the single potential of nickel, (2) that immersion in alkali does not render nickel passive, since the single potential of passive nickel differs from that observed by about 1.2 volts and (3) that the value of 0.53 volt appears to be some kind of equilibrium value for the cell.

(c) The experimental electrode was now fitted up in a cell containing 0.5 *M* nickel sulfate together with a secondary nickel electrode and a standard mercurous sulfate electrode and connected to a commutator circuit for measuring back e.m.f., just as has been employed for measuring over-voltage.

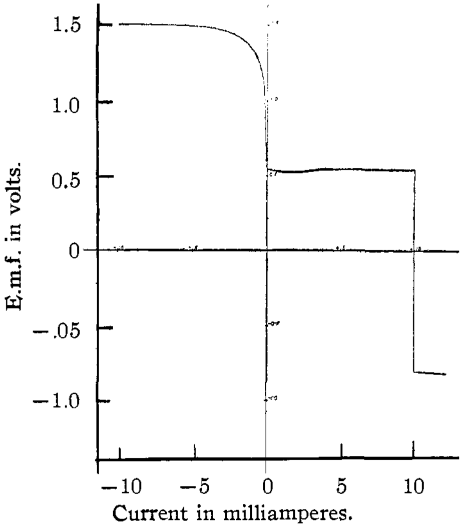

Fig. 1.

When the experimental electrode was made the cathode, the back e.m.f. of the cell rose very rapidly to over 1 volt with a current of 0.1 milliampere and hydrogen gas was liberated. When the same electrode was made the anode, the back e.m.f. fell slowly to 0.53 volt with a current of 2 milliamperes, then rose to 0.55 volt with a current of 4 milliamperes and retained this value up to a current of 10 milliamperes. At this stage after passing current for about one minute the back e.m.f. suddenly changed from 0.55 volt to −0.81 volt due to the electrode becoming passive. The accompanying curve illustrates these changes and should be compared with that obtained for copper in the same way.

These experiments show very clearly the dangerous nature of hydrogen as an impurity when measuring the single potential of nickel. A current of 10^{-5} ampere is sufficient to alter the value by 0.1 volt when the nickel is the cathode, whereas the value is nearly constant when the nickel is the anode until the current passing is one thousand times as great as this. It should be emphasized that no current is passing during the actual measurement of the above potentials. The constancy of the values under anodic treatment appears to be due to the slow continuous removal of the surface of the nickel leaving a clean surface always exposed to the electrolyte. Only under these conditions are the rapid fluctuations of single potential suppressed and constant reproducible values obtained.

Deductions from the Experimental Results.—The cell Ni | $NiSO_4$ $M/2$ | Hg_2SO_4 | Hg shows three distinct values under different conditions, two limiting values of approximately 0.25 and 0.65 volt and one somewhat persistent intermediate value of 0.53 volt at 25°.

Assuming the nickel salt to be 25% dissociated, the single potential of the mercury electrode is 0.96 volt referred to the normal calomel electrode as 0.56 volt. Hence the single potential of nickel in contact with a normal solution of nickel ions will be 0.73, 0.33 or 0.45 volt referred to normal calomel electrode = 0.56 volt, and 0.45, 0.05 or 0.17 volt referred to normal hydrogen electrode = 0.00 volt. In order to explain the existence of three values for one metal it is necessary first to note that the variability of the results obtained when nickel amalgam is used in a dropping electrode indicates that the variations are inherent in the nickel itself and are not due solely to interaction between electrode and electrolyte. Again, the extreme values are obtained at will by extreme polish or extreme roughness. It is well known that in polishing a metal the crystals are pressed down and the amorphous binding material is smoothed over the top of them. The obvious conclusion to draw, therefore, is that amorphous and crystalline nickel have different solution pressures and therefore different normal single potentials. These are 0.73 and 0.33 volt, respectively, whereas the intermediate value of 0.45 volt represents that of the equilibrium mixture normally present throughout the mass of the nickel. An objection to this theory may be made that in the amalgam it is not possible to have amorphous and crystalline nickel present at the same time. If, however, we call the two allotropes α-nickel and β-nickel, respectively, it is not necessary to postulate that these are identical with the amorphous and crystalline phases, but merely that the concentration of the α-nickel is higher in the amorphous phase and that of β-nickel in the crystalline. Both types may therefore retain their identity even when dissolved in mercury.

The extreme values found for the single potential will therefore still represent those of mixtures and not of pure α- and β-nickel. Since the experimental values are 0.45 and 0.05 volt, respectively, referred to the hydrogen electrode, we may safely put down the single potential of α-nickel as at least 0.5 volt and that of β-nickel as approximately equal to that of hydrogen.

In the solution the existence of α-nickel is doubtful. If present at all it must be in very small proportions since no appreciable quantities of nickel are deposited in a nickel-plating cell until the applied e.m.f. greatly exceeds that theoretically needed for a metal with a single potential of 0.5 volt. β-Nickel and hydrogen are then deposited together; the hydrogen escapes and the β-nickel reverts to the equilibrium mixture of α- and β- by a comparatively slow change. These processes greatly hinder the formation of large crystals and thus produce a marked tendency to the production of smooth polished deposits. In addition, the escape of hydrogen, together with the rearrangement of the deposited metal, results in a contraction of the metal with consequent tendency to strip off the base metal, especially if the deposit is thick.

The suggestion that nickel contains two allotropic forms is not new. Others have used it in attempts to explain the passivity and the overvoltage of nickel and Glasstone[3] has used it to explain the retardation phenomena shown during electrolytic deposition of the iron group metals. If a current of about 0.02 amp. be passed between two nickel electrodes each of 1 sq. cm. surface in a neutral solution of nickel sulfate, hydrogen is liberated at one electrode, which then exhibits overvoltage, and oxygen at the other, which becomes passive. The back e.m.f. of this cell then exceeds 2.2 volts, the single potential of the cathode being at least 0.7 volt below that ascribed to β-nickel and that of the anode 1.0 volt above that ascribed to α-nickel. As an explanation of overvoltage or passivity, therefore, such a theory is untenable. As an explanation of the retardation phenomena along the lines suggested by Glasstone it is equally untenable. If β-nickel in solution requires the application of an e.m.f. similar to that needed for zinc to deposit it on a cathode, then in a solution containing zinc and nickel in equal proportions, a high current density should deposit the two metals in approximately equal quantity and the relative proportions should not vary greatly with change of current density. Such is far from being the case. It is found in practice that at the cathode of such a cell the proportion of nickel and of hydrogen relative to zinc becomes rapidly less as the current density increases and at a very high current density (200 to 600 amps. per sq. ft.) nearly pure zinc is deposited with high current efficiency. This shows that both nickel and hydrogen are subject to some powerful retarding force which increases with current density and which does not affect zinc. The hydrogen ion is almost certainly hydrated. When deposited on the cathode it must lose its water of hydration before it can form gaseous hydrogen—a process requiring time. If a part of the current is being carried by a non-hydrated ion at the same time, it is evident that at higher current densities a greater proportion of the current will be carried by the non-hydrated ion. Zinc appears to be such a non-hydrated ion, whereas nickel appears to be hydrated in a similar way to hydrogen.[4] The retardation phenomena observed with hydrogen and all the iron group metals are therefore to be explained on the basis of hydration of the ions. At higher temperatures the velocity of dehydration of the ions will increase and therefore the retarding forces will decrease, as has been observed by Glasstone.[3]

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[3] Glasstone, *J. Chem. Soc.*, **129**, 2896 (1926).

[4] The term "hydration" here implies true chemical hydration and not mere surface adsorption. The hydration of the ions of the alkali metals, halogens, etc., which is assumed in order to explain anomalies in ionic velocities must be of an entirely different nature.

The variations of single potential of a nickel electrode in a solution of a nickel salt appear to be due to a variety of causes. If the surface is highly polished, the surface film contains excess of α-nickel and the potential first observed will be too high. This film is extremely thin and very slight attack by the electrolyte will be sufficient to expose the underlying β-nickel, with consequent fall of single potential. If the electrode is at rest, an interchange of ions with the solution occurs, but the ions received will be hydrated while those expelled will be non-hydrated. There will therefore be an accumulation of non-hydrated ions in the solution and an accumulation of water in contact with the electrode. At the same time a film of basic salt may form around the electrode and thus change the ionic concentration of the solution. Hence motion of the electrode with respect to the electrolyte may produce large changes of single potential, and the equilibrium potential of a stationary electrode will be very different from that of a rotating electrode.

Iwaŝe and Miyazaki[5] have recently found that the single potential of an iron single crystal is much greater and more constant than that of polycrystalline iron. Hence the above theory will also apply to iron and probably to cobalt.

It appears probable that the true reversible single potential of a metal cannot be determined directly if that metal gives rise to hydrated ions.

Summary

The single potential of nickel in a solution of nickel sulfate has been measured by three distinct methods under very varied conditions. The values obtained vary greatly with the condition of the electrode surface, with time and with relative motion between electrode and electrolyte.

Constant and reproducible values are obtained when the nickel is treated anodically with a small current density insufficient to produce passivity, the potential being measured when the current is not passing. Whether these values represent true reversible potentials or not is open to question. Nickel amalgam is even more erratic than massive nickel when used for single potential measurements.

It is suggested that solid nickel contains two allotropes having normal single potentials of approximately + 0.5 and 0.0 volt, respectively, referred to the normal hydrogen electrode. The equilibrium mixture of the two allotropes normally present in massive nickel has a corresponding potential of 0.17 volt.

On the basis of the above theory, together with that of the hydration of nickel ions, an explanation is offered (1) of the observed variations of single potential, (2) of the retardation phenomena observed during elec-

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[5] Iwaŝe and Miyazaki, *Science Repts. Tôhoku Imp. Univ.*, **17**, 163 (1928).

trolytic deposition of nickel and (3) of the electrodeposition of nickel in a polished condition.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

AN ISOTOPE OF OXYGEN, MASS 18. INTERPRETATION OF THE ATMOSPHERIC ABSORPTION BANDS

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RECEIVED JANUARY 14, 1929 PUBLISHED MAY 6, 1929

In connection with our study of the entropies of gases we have recently considered the available spectroscopic data for oxygen. The atmospheric absorption bands of oxygen contain the necessary information concerning the rotation levels of the oxygen molecule but we found that no completely satisfactory interpretation of these bands has been given, although Mulliken[1] has recently arrived at a partial solution. However, he expresses the opinion that a revised interpretation will probably be necessary in order to include a weak band for which no explanation has been offered by any previous worker.

We can have little confidence in an entropy calculation based on uncertain interpretation since a misunderstood multiplicity would introduce a serious error in our result. We were thus led to a further study of the data.

We may say at once that, in view of our result, no revision of Mulliken's interpretation is necessary.

The most accurate data are those of Dieke and Babcock[2] so they alone have been considered.

The absorption bands are due to a 1.6-volt excitation from the various rotation levels of the normal oxygen molecule, to the various rotation levels of several vibration states of the 1.6-volt level. Only the alternate rotation levels are present, as would be expected for a non-polar molecule with two non-spinning nuclei. All of the lines of the bands, which are of the P and R types, appear as doublets and in addition a weak band is present, the "A' band," which appears to be an exact duplication of the A band except that the rotation lines have a different spacing.

Our principal problem was to decide whether the A and the A' bands originated from a common source or not. We tried many ways of combining the lines both within the strong A and the weak A' bands, respectively, and also combining weak with strong but could find no scheme that would account for the bands arising from a single molecular form. Mulliken considers that the normal oxygen molecule must be a triplet

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[1] Mulliken, *Phys. Rev.*, **32**, 880 (1928).

[2] Dieke and Babcock, *Proc. Nat. Acad. Sci.*, **13**, 670 (1927).