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The Electrodeposition Behavior of a Simple Ion

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\* \* \* \* \*

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### Abstract

The electrodeposition behavior of a trace on an inert electrode can be described by the unabridged form of the Nernst equation after it has been modified by the addition of a term to account for energy differences at the deposit-electrode interface. Both the original and the modified Nernst equations predict that in dealing with amounts of depositable element insufficient to cover completely the inert electrode, the percentage of an ion deposited at any specific potential is independent of the amount of element present but is dependent upon the area of the electrode and the volume of the solution.

### Introduction

Successful electrolytic separations of some of the radioactive elements found in nature (Bi, Pb, Po) have been possible for many years (4). The method has, however, been applied to very few artificially-produced radioactive elements despite the fact that many elements can be electrodeposited easily.

The reluctance of investigators to exploit this method of separation appears to have been due to their concern as to whether or not the Nernst equation, or some comparable expression, could be used to describe the behavior of traces. Haissinsky (4) has discussed the results of many potentiometric and electrolytic studies in which the Nernst equation was tested with very dilute solutions, and he has found statements in support of both sides of the question. However, the conclusions of some of the authors are not valid because the authors overlooked the fact that two predictions can be made from the Nernst equation depending upon whether the usual "active" electrode, one whose entire surface is composed of the material being deposited, or a partially covered "inert" electrode is in equilibrium with the solution. The chief difficulty appears to

be that some investigators, who concluded that the Nernst equation did not apply, tested the abbreviated form of the equation, which applies only to a covered electrode, in a situation where they were actually dealing with an incompletely covered inert electrode. This error has appeared quite frequently despite the fact that Hevesy (6), in 1912, pointed out that the complete Nernst equation should be used in such a situation. The basis of Hevesy's argument was that if the Nernst relation defined the equilibrium potential of a completely covered electrode under a condition such that the rate of deposition equalled the rate of dissolution, the rate of dissolution for an incompletely covered electrode having fewer atoms of deposit per unit of surface area should be smaller. In order for an incompletely covered electrode to be in equilibrium with a particular concentration of ion, its potential would have to differ from that of a covered electrode in the same solution.

The present paper is an extension of Hevesy's concept. It points out that the Nernst equation predicts that the position of the deposition curve, where one plots "percentage of element deposited" versus "potential", should be independent of the amount of reducible element involved providing: (a) the "inert" electrode is incompletely covered with deposit, and (b) all other experimental factors are held constant. Furthermore, the equation predicts that the deposition curves should shift with changes in electrode area, volume of solution and size of the deposited atom (or aggregate). Any factor involving changes in the number of deposited atoms on the surface at the solution-electrode surface will also produce a shift. In conclusion, the paper points out that another term must be added to the Nernst equation to account for energy changes originating at the deposit-electrode interface.

Discussion

Deposition of a Single Simple Ionic Species According to Nernst

The Nernst equation ((using the Lewis and Randall (8) convention for signs)) has been found to describe the potential on an inert electrode

$$E = E^{\circ} - \frac{RT}{nF} \ln \frac{a_{ox}}{a_{red}} \quad (1)$$

for a reversible reaction involving only soluble ions where  $a_{ox}$  is the activity of the oxidant and  $a_{red}$  the activity of the reductant. One example is the reaction



If one of the species is deposited, the electrode can no longer be considered "inert" but instead is termed "active". In the usual case where one is dealing with relatively large amounts of material, an inert electrode is almost instantaneously covered with deposit by the passage of current following which the electrode potential for a simple reaction such as



can be described adequately by an abbreviated form of the Nernst equation

$$E = E^{\circ} - \frac{RT}{nF} \ln a_{ox} \quad (4)$$

in which the activity of the deposit is assumed to be constant and is defined as unity.

If only trace amounts of deposit are involved and the inert electrode is not completely covered by the deposit, the activity of the deposit, should, according to Hevesy (6), vary with the fraction of the surface covered. By making an assumption, which will be discussed more fully in a later section, that the free energy required to deposit an atom is independent of the electrode material, one can write equation 1 in the form

$$E = E^{\circ} - \frac{RT}{nF} \ln \frac{C_{ox} f_1}{f_r f_2} \quad (5)$$

where  $f_r$  is the fraction of the surface covered by the deposit and  $f_1$  and  $f_2$  are the activity coefficients of the ion and the deposited atom respectively. In an experiment, appropriate values can easily be determined for  $f_1$  whereas  $f_2$  is indeterminate, at least for the present, and will be considered to be unity.

Equation 5 can be extended by using the following terms:

- $A_a$  = cross-sectional area, in  $\text{cm}^2$ , of an atom of deposit
- $A_e$  = area of the electrode in  $\text{cm}^2$
- $V$  = volume, in liters, of the solution in equilibrium with the electrode
- $C^0$  = molar concentration of a solution of volume  $V$  which, if completely deposited on an electrode of area  $A_e$ , would be just sufficient to form a monolayer
- $C$  = initial molar concentration of reducible (or oxidizable) ions
- $C_{\text{ox}}$  = equilibrium concentration of reducible ion
- $(C - C_{\text{ox}}) V$  = total moles of atoms on the electrode surface at equilibrium
- $N_a$  = Avogadro's number
- $N^0$  = total number of reducible ions and atoms involved
- $N_{\text{ox}}$  = number of reducible ions in solution at equilibrium
- $N_{\text{red}}$  = number of atoms deposited at equilibrium
- $x$  = fraction of element deposited at equilibrium
- $E_{50\%}$  = potential at which  $C_{\text{ox}} = \frac{C}{2}$  and therefore  $N_{\text{ox}} = N_{\text{red}}$

The discussion can be simplified by making the following assumptions:

- (1) The area of the electrode is equal to the area of a monolayer of deposit which, to a first approximation, can be expressed as a mathematical product of the cross-sectional area of the deposited atom and the number of such atoms.
- (2) A second layer of atoms is not formed until the surface of the electrode has been completely covered with a monolayer.

- (3) A simple reaction is considered which involves only electron transfer without any change in complexity in going from ion to deposit, i.e.



It is then possible to express the activity of a deposit on an incompletely covered electrode of "inert" material as

$$a_{red} = f_1 f_2 = \frac{N_{red} A_e f_2}{A_e} = \frac{(C - C_{ox}) V N_a A_e f_2}{A_e} \quad (6)$$

Whenever  $(C - C_{ox})$  is equal to (or greater than)  $C^{\circ}$ , a monolayer (or more) can be formed thereby producing a deposit with an activity which, by definition, has the limiting maximum value of unity

$$(a_{red})_{max} = \frac{C^{\circ} V N_a A_e f_2}{A_e} = 1 \quad (7)$$

In these terms, the potential of a completely covered electrode dipping into a solution of unit activity would be  $E^{\circ}$  expressed as

$$E^{\circ} = \frac{RT}{nF} \ln \frac{A_e}{C^{\circ} V N_a A_e f_2} \quad (8)$$

For the general case, the equilibrium potential of an incompletely covered electrode dipping into a solution having the concentration  $C_{ox}$  can be obtained by substituting equation 6 into equation 5.

$$E = E^{\circ} - \frac{RT}{nF} \ln \frac{A_e}{V N_a A_e} - \frac{RT}{nF} \ln \frac{f_1}{f_2} - \frac{RT}{nF} \ln \frac{C_{ox}}{C - C_{ox}} \quad (9)$$

Recalling that  $E_{50\%}$  was defined as the potential at which  $N_{ox} = N_{red}$  and  $C_{ox} = C - C_{ox}$ , one can write

$$E = E_{50\%} - \frac{RT}{nF} \ln \frac{C_{ox}}{C - C_{ox}} \quad (10)$$

or

$$E = E_{50\%} - \frac{RT}{nF} \ln \frac{1 - x}{x} \quad (11)$$

where

$$E_{50\%} = E^{\circ} - \frac{RT}{nF} \ln \frac{A_e f_1}{V N_a A_e f_2} \quad (12)$$

Equation 12 is equivalent to

$$E_{50\%} = E^{\circ} - \frac{RT}{nF} \ln \frac{C^{\circ} f_1}{f_2} \quad (13)$$

Because equation 11 has a constant point of inflection at  $E_{50\%}$ , the potential at which a specific percentage of a trace will deposit on an incompletely covered electrode should, in a series of similar electrolyses, be independent of the initial concentration of reducible ion.

Since equation 11 applies only when the inert electrode surface is incompletely covered, equation 11 will describe the complete deposition curve only when the total amount of depositable element is smaller than  $C^{\circ}$ . For amounts larger than  $C^{\circ}$ , equation 11 will describe the deposition only until an amount equal to  $C^{\circ}$  has deposited following which, because equation 9 reduces to equation 4, the deposition will be described by equation 4.

If the deposition takes place from a solution having the reducible element in the form of a complex ion, it is necessary to take into consideration the activity of the complex-forming ion or molecule if it differs from unity. An ion or molecule,  $g$ , having  $b$  groups coordinated with the reducible ion introduces an additional term.

$$E = E_{50\%} - \frac{RT}{nF} \ln \frac{1-x}{x} - \frac{bRT}{nF} \ln C_g f_g \quad (14)$$

where  $C_g$  is the molar concentration and  $f_g$  the activity coefficient of the complexing ion. The complex-forming ion will usually be present in large excess, and will, therefore, be the chief factor influencing the activity coefficient of the reducible ion.

If precipitation occurs as a result of anodic oxidation the following set of equations can be written:

$$E = E^{\circ} - \frac{RT}{nF} \ln \frac{V N_a A_a}{A_e} - \frac{RT}{nF} \ln \frac{f_2}{f_1} - \frac{RT}{nF} \ln \frac{C - C_{red}}{C_{red}} \quad (15)$$

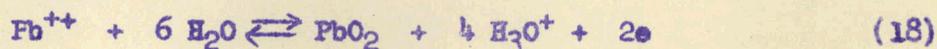
$$E = E_{50\%} - \frac{RT}{nF} \ln \frac{C - C_{red}}{C_{red}} \quad (16)$$

and

$$E = E_{50\%} - \frac{RT}{nF} \ln \frac{x}{1-x} \quad (17)$$

where  $C_{red}$  is the concentration of the oxidizable ion. If the oxidation involves a complex ion, a term must be introduced in the same way that it was done for a reduction except that its sign should be reversed.

An additional consideration is introduced by the fact that anodic reactions often deposit an oxide rather than the free element. In such cases,  $A_a$  will be the area of the oxide molecule and the scope of  $E_{50\%}$  must be expanded to include a consideration of the activity of the hydronium ion. A complete equation can be developed for every reaction in a way similar to that for the following example:



and

$$E = E_{50\%} - \frac{RT}{nF} (a_{H_3O^+})^4 - \frac{RT}{nF} \ln \frac{C - C_{red}}{C_{red}} \quad (19)$$

At a constant pH,

$$E = E'_{50\%} - \frac{RT}{nF} \ln \frac{x}{1-x} \quad (20)$$

where

$$E'_{50\%} = E_{50\%} - \frac{RT}{nF} \ln (a_{H_3O^+})^4 \quad (21)$$

Any factor which affects the assumption that the rate of dissolution of the deposit is proportional to the number of deposited atoms will produce change in the observed activity of the deposit and consequently a change in the value of  $E_{50\%}$ . One mechanism by which atoms can be removed from the surface of the electrode is by diffusion of the deposit into the body of the electrode material. Another mechanism involves the formation of aggregates or multilayers of deposit. In both cases, the observed activity of the deposit would be lowered and the overall behavior of the trace changed to more "noble". In actual practice

it might be possible to ignore these considerations providing that short periods of electrolysis and amounts of deposit covering only a small fraction of the electrode surface were involved.

#### Interfacial Considerations Not Included in the Nernst Equation

All of the preceding discussion has been based upon the assumption that the energy required to deposit an element is independent of the surface upon which it is deposited. That is to say, it has been assumed that the energy involved in depositing a silver atom on a silver surface is the same as for a silver atom on a platinum ("inert") surface. The literature contains much evidence which, if not in direct support of this postulate, at least indicates that the deposition behavior of a trace element on a number of different "inert" elements is the same (1, 2). However, a number of exceptions have been reported by the same and other authors (4).

In order to have an equation which will describe all of the experimental results, it is necessary to introduce a term which will take into consideration any difference in free energy,  $E_a$ , between the deposition of an atom on a surface of similar atoms and on a surface of dissimilar atoms. It is quite likely that deposition onto a dissimilar surface might liberate additional free energy due to alloy formation and possibly sorption. Equation 9 and subsequent equations must therefore be expanded to

$$E_{50\%} = E^{\circ} - E_a - \frac{RT}{nF} \ln \frac{A_a f_1}{V N_a A_a f_3} \quad (22)$$

where  $f_3$  represents the activity coefficient of the deposited atom whose standard state, where  $f_3$  is unity, is the most stable alloy form. If  $E_a$  is positive, the trace should behave more nobly than predicted from the Nernst equation (Eq. 9). If  $E_a$  is negative, one should observe a shift of the deposition curve in the opposite direction thereby leading one to conclude erroneously that the deposition was obeying equation 4. A negative value for  $E_a$  might result in deposition curves which would drift, with longer periods of electrolysis toward more negative potentials (for a reduction) due to the greater stability of aggregates of deposit

compared to a random distribution of atoms over the "inert" surface.

It appears that the deposition curve of a trace might undergo a shift to more positive potentials if the surface of the "inert" electrode were dissolving. In order to gain the same net rate of deposition as that observed for an insoluble (or more slowly soluble) electrode, a more positive potential would be required (for a reduction) in order to decrease the rate of dissolution of the surface and to increase the rate of deposition of the trace. Experiments with silver tracer (3) have indicated that such a process may be an important consideration, but in the face of such a conclusion, one has evidence that chemical replacement is a satisfactory method for the separation of a trace element (11, 12). Reconciliation of these two observations appears to be possible, but no attempt will be made to do it here.

In reconsidering as a whole the question of electrodeposition of a trace by reduction, it is important to note that both the original and the modified forms of the Nernst equation predict that the  $E_{50\%}$  should be independent of the amount of element undergoing reaction providing the amount is insufficient to form a monolayer. For that reason, one must reconsider the conclusions from experiments similar to those recently reported by Heal (5). Heal concluded that the Nernst equation did not describe the deposition of a trace because: (a) his deposition curves did not shift with dilution, and (b) his curves agreed within experimental error with those obtained by another investigator who worked with more concentrated solutions of the same element. Actually, the question which might be raised is why his data for the deposition potential agreed with those of the other investigator if changes in area of the electrode and volume of the solution are important considerations. This agreement could be explained by assuming that the investigators accidentally used  $A_e/v$  ratios which were the same within the limits of experimental error.

#### Complex Electrode Reactions

As long as the assumption is valid that the complexity of the ion and of

the atom is the same, equations 11, 17, and 20 will apply to aggregates of any complexity from simple ions to colloids, providing the aggregates have a uniform charge-to-size ratio. An interesting special case is encountered if  $n$  is smaller than  $y$  because the overall result is the deposition of an atom of  $M$  by a fraction of an electron. As examples of this behavior, one might imagine the deposition of aggregates such as  $Mo_6Cl_8^{4+}$  and  $Ta_6Cl_{12}^{++}$  (10). It is quite possible that the deposition of polonium, which puzzled Haissinsky (4) because it required only  $1/3$  of an electron per atom, falls into this class. In the case of polonium, however, one cannot make a definite statement that a polymeric ion is the source of the anomaly, even though polonium polymers are known, because the conclusions were based upon data obtained by a rate-of-deposition technique (7,9) in which the mechanism of the reaction may play an important role.

If the complexity of the ion differs from that of the deposit, the  $E_{50\%}$  and the subsequent dependent terms are no longer independent of the amount of reducible element. This conclusion can be reached easily by examining values of the logarithmic term (and its derivatives) containing  $x$ .

#### Conclusions

Although the information in most of the papers in the literature is too scanty to allow a definite statement to be made, it appears that some investigators have erroneously reported that the Nernst equation did not describe the deposition of traces because they tested the abridged form rather than the complete reaction. Nevertheless, it appears that the equation may be inadequate because it does not include a term to describe energy differences in the deposit-electrode interface. This energy factor is undoubtedly an important one not only in theoretical studies of trace deposition, but also in commercial electroplating where one is interested in determining how firmly an electrodeposit will adhere to the underlying material.

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