

# The Nernst Equation

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The Nernst equation is well established and supported by an impressive mass of experimental evidence. However, its classical derivation is based on a macroscopic variable, the electrochemical potential, defined as the sum of a chemical potential and a field/molar charge interaction. Both of these concepts are rife with caveats. In this paper we show that the Nernst equation can be derived directly from basic thermodynamic principles, that is, the Boltzmann distribution and a field-charge interaction energy.

## The Chemical and Electrochemical Potential

By definition, the chemical potential of a compound is the differential of a mixture's free energy relative to the amount of the compound in question.

$$\mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{P, T, n_j} \quad (1)$$

This concept presents no problem when dealing with a mixture of ideal, noninteracting gases, where the ideal gas law allows immediate calculation of the free energy change upon addition of an infinitesimal amount of one of the components.

$$\mu_i = \mu_{i,0} + RT \ln \left( \frac{p_i}{p_{i,0}} \right) \quad (2)$$

where  $\mu_{i,0}$  is the molar free energy at temperature  $T$  and pressure  $p_0$ .

However, for real gasses, we must consider fugacity rather than pressure, and this requires a model or approximations to account for the nonideality. Furthermore, if we are dealing with liquids or solutes, it then becomes necessary to consider the gas/liquid equilibrium, which is rarely ideal. Hence we would use, for example, either Raoult's law (low concentration or pressure) or Henry's law (higher concentrations or pressure), or another empirical equation based on  $pvT$  data obtained within a limited  $pvT$  domain extrapolated to the domain of interest. This could mean that we may in fact end up extrapolating low-pressure data to a high-pressure situation, where the same  $pvT$  relationships may not apply. If, in addition, the solute is charged, then further correction is required to account for electrostatic interactions.

The electrochemical potential is then defined as the sum of the chemical potential and a molar-charge/field interaction according to the classical laws of electrostatics.

$$\mu_{ei} = \mu_i + nFE \quad (3)$$

where  $n$  is the number of particle's charge in electron charge units;  $F$  is the Faraday constant; and  $E$  is the potential of the phase in question.

This is a daring hypothesis because it implies that all particles of species  $i$  are under constant electric field. Although the potential in a bulk solution phase is relatively

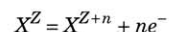
constant, it changes sharply near an interface. If we consider the electrochemical potential to be constant for a system at equilibrium, then the activity of a charged species near an interface must also change sharply. However, the classical derivation of the Nernst equation invokes bulk activities, not those at the reaction site (which is the electrode surface).

Another approach found in the literature relies on the application of kinetic equations to a reversible reaction system, where the direct and indirect reaction rates are described by an Arrhenius-type equation. Although statistical thermodynamics yields this form of expression to describe reaction rates, it requires the determination of a partition function in order to obtain both the preexponential and the transition state free energy terms. Due to the large number of intermolecular interaction modes and the large coupling between molecules in a liquid phase, such a calculation also requires many approximations. Thus, it would not necessarily bring us any closer to a fundamental derivation of a concentration/electrochemical potential relationship.

Interestingly enough, it is possible to derive the same equation from first principles without attempting to bring in complicated concepts such as fugacity, activity, or partition functions. In fact, all that is required are the Boltzmann distribution and the concentration of each charged species in the bulk solution.

## Nernst's Equation from First Principles

Let us consider a solution of a redox couple at redox equilibrium.



From the Boltzmann distribution law, we can state

$$C_i(V_1) = C_i(V_0) e^{\frac{z_i e(V_0 - V_1)}{k_b T}} \quad (4)$$

where  $z_i e$  is the charge on species  $i$ ; and  $C_i$  indicates the concentrations at two points of a system at equilibrium where the potentials are  $V_0$  and  $V_1$ .

The equilibrium constant,

$$K = \frac{[X^{Z+n}]}{[X^Z]}$$

can thus be expressed as

$$K(V_1) = K(V_0) e^{\frac{ne(V_0 - V_1)}{k_b T}} \quad (5)$$

where  $ne$  is the charge exchanged per particle during the course of the reaction.

Equation 5 can be rewritten as

$$\ln K(V_1) = \ln K(V_0) = V_0 \left( \frac{ne}{k_b T} \right) - V_1 \left( \frac{ne}{k_b T} \right) \quad (6)$$

or

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$$\left(\frac{k_b T}{ne}\right) \ln K(V_1) - \left(\frac{k_b T}{ne}\right) \ln K(V_0) + V_0 = V_1 \quad (7)$$

Combining the two last terms of the left-hand side of eq 7 into one reference quantity,  $E_0$ , we obtain

$$E_0 + \left(\frac{k_b T}{e}\right) \ln K = V_1 \quad (8)$$

which is the Nernst equation.  $E_0$  can of course be defined in the classical manner, that is, as the potential of an inert metal electrode immersed in a solution where both forms of the redox couple are present at 1 M concentration.

#### *Caveats Concerning the Nernst Equation from First Principles*

The above derivation considers the ions to be point charges interacting with a field. This is discussed in depth in any basic electrochemistry or physical chemistry text, such as Bockris<sup>2</sup> and Atkins,<sup>3</sup> where quite reasonable first-principle models for nonideality are presented. Hence this does not introduce any need for empirical or number-fitting steps.

It also does not require a constant potential throughout the solution, as the model does not consider the concentrations anywhere except at the surface of the measuring electrode. This points to another caveat: In an electrochemical experiment we can measure only that portion of the solution that lies within the double layer, although the difference in internal solution potential due to a concentration ratio gradient follows the same rule. The potentials therein can be strongly influenced by factors, for example, specific adsorption of either part of the redox pair or competitive adsorption of a supporting electrolyte.

<sup>2</sup>Bockris, J. O'M.; Reddy, K. *Modern Electrochemistry*; Plenum: New York, 1970.

<sup>3</sup>Atkins, P. W. *Physical Chemistry*, Clarendon: Oxford, 1980.

Here lies the danger in extrapolating experimentally determined  $E_0$  data to other solvents or electrode materials, as well as in taking the standard reduction potential as a faithful mirror of reaction energies, via the classically or statistically derived  $\Delta G_r = -RT \ln K$ . This will be even more obvious when surface-located reaction energies are used to predict homogeneous reaction parameters. Here the presence of the experimental probe disturbs the system to a configuration that may be far from the one assumed in its absence.

In addition, although the derivation presented considers only electrostatic point-charge/field interactions, there is no impediment to fine-tuning the model in order to take nonideality effects—normally lumped together under the “activity” heading—into account. In fact, there are quite satisfactory first-principle descriptions of nonideality, such as the ionic atmosphere model, which attributes deviations from ideality to the breakdown of the assumption that the ions are infinitely small, unpolarizable point charges.

Although it is a tedious task, such a model can be integrated into the above derivation without requiring any conceptual compromise. In this way we can derive a self-consistent model, where physical reality is described by successive improvements of a first-principle model, rather than one based on an approximate description that requires experimentally obtained values in order to determine the appropriate correction factors.

#### **Conclusion**

Shedding some light on the approximations and imprecisions involved in the derivation of one of the most-used laws in electrochemistry is of interest as it points out possible causes for discrepancy between theoretical predictions and experimental fact.

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