

Derivation of the Nernst Equation from the Butler-Volmer Equation

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Abstract: The Butler -Volmer equation plays an important role in electrochemical kinetics. In this article we find a new way of deriving the Nernst equation from the Butler-Volmer equation.

Keywords: electrochemistry, oxidation, reduction,

1. Introduction

Electrochemical kinetics deals with the theoretical aspects that mainly relates with the processes, methodologies, reactions and transformations. The butler-volmer equation is considered as the most fundamental relationship in electrochemical kinetics. It explains how the electrical current on an electrode depends on its potential by considering that the same electrode conducts the both cathodic and anodic reaction. The Nernst equation relates the reduction potential of an electrochemical reaction to the standard electrode potential, temperature and activities of the chemical species which is undergoing reduction and oxidation. In this article we derive the Nernst equation by using the chemical reaction of Butler-Volmer equation.

2. Preliminaries

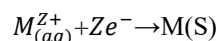
A. Definition 1

It is the branch of chemistry the studies the relationship between electricity, as a measurable and quantitative phenomenon, and identifiable chemical change, with either electricity considered on outcome of a particular chemical change a vice versa. The Nernst equation enables the determination of all potential under non-standard conditions. It relates the measured cell potential to the reaction quotient and allow the accurate determination of equilibrium constants including solubility constants.

B. Definition 2

Electrochemical kinetics is the field of electrochemistry that studies the rate of electrochemical processes. This includes the study of how process conditions such as concentration and electric potential influence the rate of oxidation and reduction reactions that occur at the surface of an electrode, as well as an investigation into electrochemical reaction mechanism. Due to electrochemical phenomena unfolding at the interface between an electrode and an electrolyte, there are accompanying Phenomena to electrochemical reaction which contribute to the overall reaction rate.

3. Derivation of Nernst equation from Butler-Volmer equation



M^{Z+} - Reactant

Chemical reaction

$$K_2 = B \exp\left(\frac{-\Delta G^\#}{RT}\right)$$

$\Delta G^\#$ - Gibbs free energy of activation

B - Constant

K_2 - Rate constant

Rate of the process

$$K_c[Ox] \text{ and } K_a[Red]$$

Apply F (faradays) the cathodic current density i_c arises from reduction is given by,

$$i_c = F K_c[Ox]$$

The anodic current density i_a arises from oxidation is

$$i_a = F K_a[Red]$$

Net current density at the electrode

$$i = i_a - i_c$$

$$i = F K_a[Red] - F K_c[Ox]$$

chemical reaction is apply by the net current density

$$I = F[Red] \exp\left(\frac{-\Delta G_a^\#}{RT}\right) - F B_c[Ox] \exp\left(\frac{-\Delta G_c^\#}{RT}\right)$$

Gibbs free energy of activation is different for anodic and cathodic process

$$i_a > i_c \text{ so } i > 0 \text{ current is anodic}$$

$i_a < i_c$ so $i < 0$ current is cathodic

Electrical work done is $e \Delta\phi$
 e- electrical change

$\Delta\phi$ -different between the electrode

A. Reduction

Gibbs free energy of activation is changed $\Delta G^\#$ to $\Delta G^\# + nF\Delta\phi$

$\Delta G^\#$ is independent of $\Delta\phi$

Gibbs free energy of activation for reduction $\Delta G^\# + nF\Delta\phi$

α -transfer coefficient

B. Oxidation

Gibbs free energy of activation is changed $\Delta G^\#$ to $\Delta G^\# - nF\Delta\phi$

Gibbs free energy of activation for oxidation $\Delta G^\# - (1 - \alpha)nF\Delta\phi$

In current density

$$i_a = \{ FB_a[\text{Red}] \exp\left(\frac{-\Delta G_a^\#}{RT}\right) - e^{(1-\alpha)nF\Delta\phi/RT} \}$$

$$i_c = \{ FB_c[\text{Ox}] \exp\left(\frac{-\Delta G_c^\#}{RT}\right) - e^{-\alpha nF\Delta\phi/RT} \}$$

At equilibrium

$$\Delta\phi = \Delta\phi_{eq}$$

In over potential

$$\eta = \Delta\phi - \Delta\phi_{eq}$$

$\Delta\phi = \eta + \Delta\phi_{eq}$ value apply i_c and i_a equation we gets

$$I = \{ FB_a[\text{Red}] \exp\left(\frac{-\Delta G_a^\#}{RT}\right) e^{(1-\alpha)nF(\eta + \frac{\Delta\phi_{eq}}{RT})} \} \\ \{ FB_c[\text{Ox}] \exp\left(\frac{-\Delta G_c^\#}{RT}\right) e^{-\alpha nF(\eta + \frac{\Delta\phi_{eq}}{RT})} \}$$

we also known

$$I_{a,e} = \{ FB_a[\text{Red}] \exp\left(\frac{-\Delta G_a^\#}{RT}\right) e^{nF\frac{\Delta\phi_{eq}}{RT}} \} -$$

$$I_{c,e} = \{ FB_c[\text{Ox}] \exp\left(\frac{-\Delta G_c^\#}{RT}\right) e^{nF\Delta\phi_{eq}/RT} \}$$

So we get

$$i_a = i_{a,e} \exp^{(1-\alpha)nF\eta/RT}$$

$$i_c = i_{c,e} \exp^{-\alpha nF\eta/RT}$$

$I_{a,e}$ & $I_{c,e}$ is equal

$$I = i_a - i_c$$

$$I = i_{a,e} \exp^{(1-\alpha)nF\eta/RT} - i_{c,e} \exp^{-\alpha nF\eta/RT} \}$$

$$I = i_0 \{ \exp^{(1-\alpha)nF\eta/RT} - \exp^{-\alpha nF\eta/RT} \}$$

i_0 = exchange current density

This is butler-volmer equation

In Nernst equation

taken butler-volmer equation

$$I = B_a[\text{Red}] \exp^{(1-\alpha)nF\eta/RT} - B_c[\text{Ox}] \exp^{-\alpha nF\eta/RT}$$

$$I = i_a - i_c$$

Already known $\Delta\phi = \eta + \Delta\phi_{eq}$

$$\frac{i_a}{i_c} = \frac{B_a[\text{Red}]}{B_c[\text{Ox}]} \exp^{1-\alpha + nF\eta/RT}$$

$$\frac{i_a}{i_c} = \frac{B_a[\text{Red}]}{B_c[\text{Ox}]} \exp^{nF\eta/RT}$$

$$\eta = \Delta\phi - \Delta\phi_{eq}$$

$$\frac{i_a}{i_c} = \frac{B_a[\text{Red}]}{B_c[\text{Ox}]} \exp^{nF(\Delta\phi - \Delta\phi_{eq})/RT}$$

The Ratio of anode reaction rate to cathode reaction rate does not depend on α or any properties of the transition state

In equilibrium the net reaction rate I is zero

This is $i_a = i_c$

$$\Delta\phi_{eq} = -\frac{RT}{nF} \ln \left[\frac{B_c[\text{Ox}]}{B_a[\text{Red}]} \right]$$

$$\Delta\phi_{eq} = \frac{RT}{nF} \ln \frac{B_c}{B_a} + \frac{RT}{nF} \ln \frac{[\text{Ox}]}{[\text{Red}]}$$

Electrolyte potential is constant that means $V_0 = \frac{RT}{nF} \ln \frac{B_c}{B_a}$

$$\Delta\phi_{eq} = V_0 + \frac{RT}{nF} \ln \frac{[\text{Ox}]}{[\text{Red}]}$$

This is the Nernst Equation

4. Conclusion

In this research paper, we have successfully derived the Nernst Equation from the Butler-volmer Equation.

References

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