

BUTLER VOLMER EQUATION - Electro-chemical kinetics

B.Viswanathan

May 9, 2013

It is possibly appropriate to state why do we need to look into these text book material again. It is known that the two pillars of processes are the thermodynamics and kinetics. The one of the connection points of these two branches is the chemical equilibrium, a state where the two rates (not rate constants) that of forward and back ward are equal. If one were to convert these concentration terms involved in these discussions to electrical quantities (for example for electro-chemical processes)then the parameter of relevance is the current densities which possibly reflect the rate of the reaction taking place. Butler Volmer equation possibly deals with the anodic and cathodic currents and the net current that is responsible for the overall reaction observed. In this sense, Bultler Volmer equation possibly provides opportunities to learn on the nature of the electrochemical reactions that is if it is reversible equilibrium reactions or if it were to be a irreversible process, the extent of ir-reversibility. From this point of view, it was considered worthwhile to write this short presentation on Butler Volmer equation.

In dealing with electro-chemical kinetics one has to learn more equations one of which goes with the name Butler-Volmer equation. Generally, the generalized form of electro-chemical reaction is written as $R \rightarrow O + ne^-$ Where R stands for the reduced state and is given by $\sum s_{iR} R_i^{Z_i R}$ where s is the stoichiometric coefficient of species i (positive for the reduced state and negative for the oxidized state by convention) and O stands for the oxidized state and is equal to $\sum s_{iO} O_i^{Z_i O}$, R_i (O_i) stand for the symbol for the chemical formula and Z_i stands for the charge on the species. This notation may appear cumbersome but it is simply for a single species s takes value one and one charge species z takes the value one and the equation written above simply represent a reduced species goes to the oxidized species with one electron like $M \rightarrow M^+ + e^-$. The reaction rate R (not to be confused with the Reduced species indicated above) for a generalized Faradaic half-cell reaction is given by $(R = k_a C_R \exp(1-\alpha)ne\Delta \phi/kT - k_c C_o \exp(-\alpha ne\Delta \phi/kT) = R_a - R_c)$ Where C_R and C_O stand for the concentration terms and the powers to which the concentration terms will be raised in a kinetic expression. For example $C_R = \prod C_{iR}^{S_i R}$ denoting the concentration of the i reduced species to the power of s. $\Delta \phi = \phi_C - \phi =$ electrode potential – solution potential and α is the so called symmetry factor usually termed as transfer coefficient. It has to be realized that the ratio of the rate of anode reaction rate to that of the cathode reaction rate does not depend on , transfer coefficient or any of the properties of the transition state and it is given as

$$(R_a/R_c) = (k_a C_R/k_c C_0)\exp(ne\Delta \phi/kT)$$
 Under the equilibrium conditions,

the net reaction rate R is zero. That is $R_c = R_a$ $\Delta \phi_{eq} = (kT/ne) \ln (k_c C_0/k_a C_R) = V^0 - (kT/ne) \ln (\Pi C_{iR}^s / \Pi C_{iO}^s)$ where $V^0 = (kT/ne) \ln (k_c/k_a)$ This is the Nernst equation and V^0 is the kinetic description of the standard potential related to the microscopic reaction rates. It is necessary that one learns the significance of the term Activation over-potential which is a major contributor in many of the practical electro-chemical processes. Though one can determine the potential between the two electrodes in an electro-chemical cell, herein referred as $\Delta \phi$ but over-potential appears to be the general term commonly employed in electro-chemistry. It is defined as $\eta = (\Delta \phi - \Delta \phi_{eq})$ This denotes the additional voltage that drives the Faradaic current. In terms of over potential the reaction rate is

$$R = k_a C_R \exp(((1 - \alpha)ne(\eta + \Delta \phi_{eq}))/kT) - (k_c C_0 \exp((- \alpha ne(\eta + \Delta \phi_{eq}))/kT))$$

However,

$$\Delta \phi_{eq} = (kT/ne) \ln((k_c C_0)/(k_a C_R))$$

Therefore,

$$R = (k_c C_0)^{(1-\alpha)} (k_a C_R)^\alpha (\exp(1 - \alpha)ne\eta/kT) - \exp(-\alpha ne\eta/kT)$$

where $I = neAR$ where A is the area of the electrode.

Thus one gets

$$I = I_0 [\exp((1 - \alpha)ne\eta/kT) - \exp((- \alpha ne\eta)/kT)]$$

$$\text{where } I_0 = neA(k_c C_0)^{(1-\alpha)} (k_a C_R)^\alpha$$

is the exchange current in dilute solution. This is the Butler Volmer equation.

Limiting cases of Butler-Volmer equation

For small over potentials that is

($\eta \ll (kT/ne)$), one can linearize the Butler-Volmer equation

$$I = I_0 (ne\eta/kT) + [(1 - 2\alpha)/2][ne\eta/kT]^2 + \dots$$

Approximating to

$$I \sim I_0 [ne\eta/kT]$$

$$\eta_{act} \sim [I/R_{act}]; R_{act} = [kT/neI_0]$$

R_{act} (greater than 0) is the constant resistance of the Faradaic reaction. Activation over potential is positive at anode and negative at cathode for a galvanic cell (I is greater than 0) and electron flows from anode to cathode.

The next condition is when the over potential is large that is (when $|\eta| \gg (kT/ne)$) that is

$$I \sim (I_0 \exp((1 - \alpha)ne\eta/kT)), \eta \gg (kT/ne)$$

$$\text{or } I \sim (-I_0 \exp(-\alpha ne\eta/kT)), \eta \ll -(kT/ne)$$

Tafel plot of $\ln|I|$ versus η has a slope of $((1-\alpha)ne/kT)$ for anodic current and $(\alpha ne/kT)$ for cathodic current and Y intercept is $\ln I_0$.

Symmetric electron transfer when α takes the value of 0.5

It is common to assume symmetric electron transfer in the Butler Volmer equation and this often agrees well with experimental Tafel plots. As one will see this assumption is also mathematically convenient, since the Butler Volmer equation can be expressed as a hyperbolic sine dependence, which can be inverted in terms of inverse hyperbolic sine $\eta = (2kT/ne) \sinh^{-1}(I/2I_0)$ It is seen that the activation over potential is mainly important at small currents and has roughly the magnitude of the thermal voltage (kT/e). At large currents, the activation over potential grows slowly as a logarithm of the applied current (relative to the exchange current)

Asymmetric electron Transfer (when alpha is lower or higher than 0.5)

If the interfacial voltage only biases one direction of a Faradaic reaction, say the positive reaction (anode) and not the other, then the Butler Volmer equation

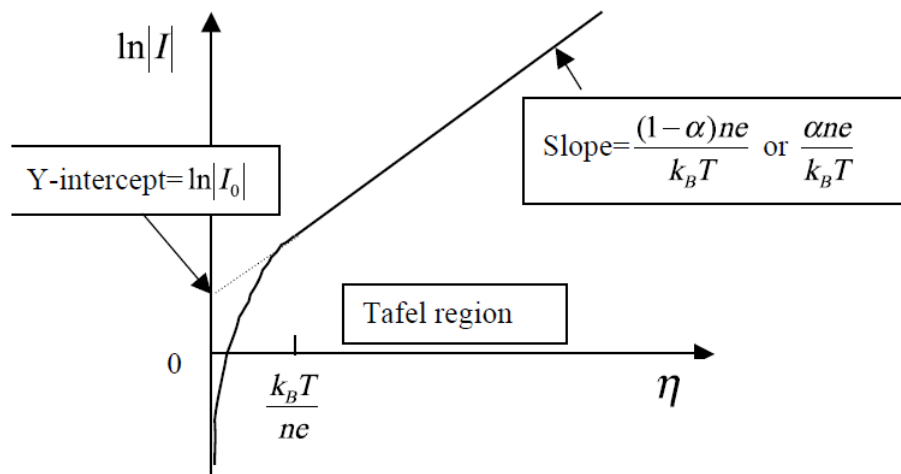


Figure 1: Typical Tafel plot of log(current) versus over potential. The Butler-Volmer equation predicts an asymptotic linear dependence for large over potentials, where the slope is related to the transfer coefficient and the y-intercept gives the exchange current.

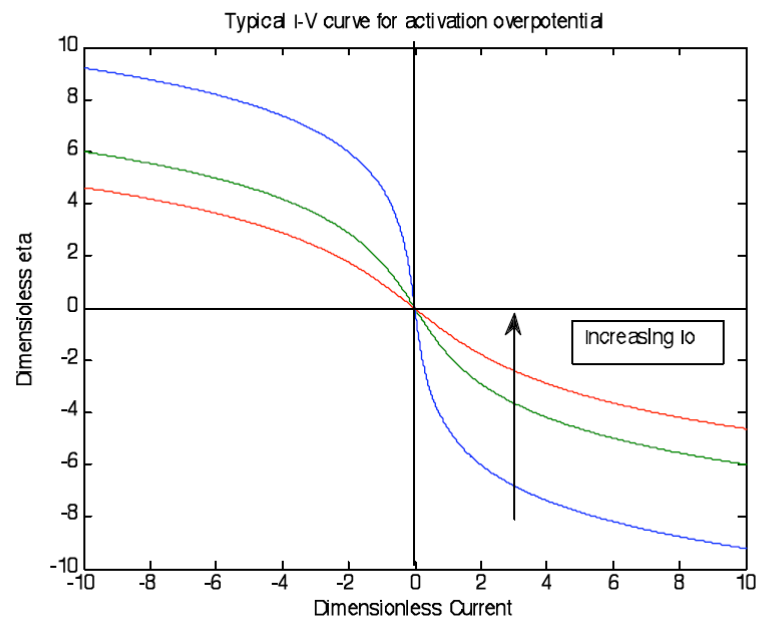


Figure 2: Typical I-V curve for activation over potential for symmetric electron transfer (that is alpha is 0.5)

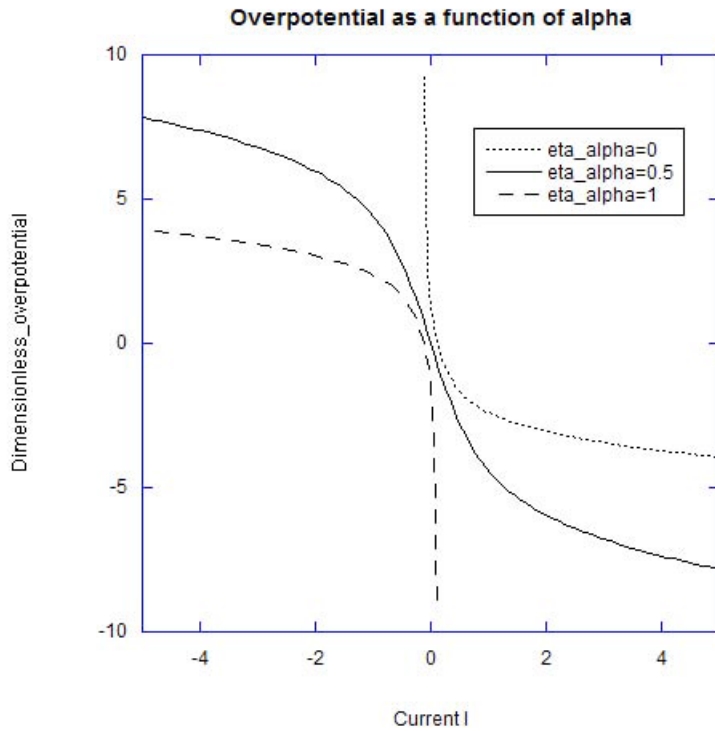


Figure 3: Dimensionless over-potential versus current for different values of Butler-Volmer transfer coefficient. In the limits $\alpha = 0$ the interface acts like an ideal semiconductor diode, which passes current preferentially in one direction (Forward bias) with only a small saturation current in the opposite direction (reverse bias)

is given as $I = I_0[\exp[n\eta/kT] - 1]$ This expression is identical to the non-linear I-V response of a semiconductor diode. In this case, for a positive over potential, (so called forward bias) which enhances the oxidation reaction, the current grows exponentially with voltage, while the current saturates to a constant for large negative over potentials set by the reduction reaction rate. (see Fig.3)