# ELECTROLYSIS AND ACIDS

TRISTRAM DE PIRO

ABSTRACT. We makes some observations about Faraday's First Law of Electrolysis, different definitions of acids and applications to biochemistry.

## 1. FARADAY'S LAW OF ELECTROLYSIS

In [1], Faraday makes three claims;

(704) The chemical decomposing action of current is constant for a constant quantity of electricity.

(783) The chemical power of a current of electricity is in direct proportion to the absolute quantity of electricity which passes.

(732) With regard to water. The quantity of it decomposed is exactly proportional to the quantity of electricty which has passed.

The last claim has become the basis for Faraday's first law of electrolysis which is now interpreted as saying that the mass $m$ of elements deposited at an electrode is directly proportional to the charge $\rho$;

$\frac{m}{\rho} = Z$

where $Z$ is the electro-chemical equivalent of the substance.

However, the claims $(704), (783)$ seem to make a stronger statement, which implies the claim $(732)$, namely that the rate of chemical reaction is proportional to the electricity passed or $\rho = It$, for a direct current $I$, (†). The Nernst equation in a generalised form, without error terms, see [3], Lemma 8.4, states that;

$4F(E(T_1, P_1) - E^\circ(T_1)) = (\frac{\partial G}{\partial \xi})_{T,P}(T_1, P_1) - (\frac{\partial G}{\partial \xi})_{T,P}(T_1, P_1^\circ) - RT_1 ln(Q(T_1, P_1))$
$(**)$

for the reaction $2H_2O + 4e^-(R) \rightarrow 2H_2 + O_2 + 4e^-(L)$, $(*)$. If we multiply the charge $\rho$ by a factor of $\lambda$, then, according to the formula $\rho = CE$, treating the electrode/cathode assembly as a capacitor, we change the potential $E$ by a factor of $\lambda$ as well. We can also multiply the equation $(*)$ by a factor of $\lambda$, changing the stochiometric coefficients by a factor of $\lambda$, without changing $(**)$. We have that;

$$(\tfrac{\partial G}{\partial \xi})_{T,P} = \sum_{i=0}^{c} \nu_i \mu_i$$

see Lemma 2.5 of [3], so that the change in stochiometric coefficients is equivalent to changing $(\tfrac{\partial G}{\partial \xi})_{T,P}$ by a factor of $\lambda$ as well, if the chemical potentials $\mu_i$, $0 \leq i \leq c$, are unchanged. It follows that, for the equation $(**)$ to balance, $ln(Q(T_1, P_1))$ must be changed by a factor $\lambda$, and $Q$ changes to $Q^\lambda$. We have that;

$$Q = \prod_{0 \leq i \leq c} x_i^{\nu_i}$$

and, if $x_0 \simeq 1$, where substance 0 is the solvent $H_2O$, we can obtain $Q^\lambda$, by altering $x_0$ to $x_0^\lambda$, $n_0$ to $n_0^\lambda$, with a small alteration in the other substances $i$, $1 \leq i \leq c$, and $n$ changed roughly to $n^\lambda$. It follows that the rate of change of concentration;

$$(x_0^\lambda)' = \lambda x_0^{\lambda-1} x_0' \simeq \lambda x_0'$$

changes roughly by a factor of $\lambda$. If we assume that $\lambda \simeq 1$, so $n$ is roughly unchanged, we obtain that, $n_0'$ changes roughly by a factor of $\lambda$ as well, giving $(\dagger)$.

We then have that, for 2 different quantities $\{\rho_1, \rho_2\}$, that;

$$\frac{\rho_2}{\rho_1} = \frac{n_{0,2}'}{n_{0,1}'} = \frac{\frac{\rho_2}{t}}{\frac{\rho_1}{t}} = \frac{I_2}{I_1}$$

so that, observing the rates $\{n_{0,2}', n_{0,1}'\}$ are constant;

$$\frac{\Delta n_{0,2}}{\Delta n_{0,1}} = \frac{n_{0,2}' t}{n_{0,1}' t} = \frac{I_2 t}{I_1 t} = \frac{\rho_2}{\rho_1}$$

so that the amount of substance formed $\xi$, proportional to the mass $m$ formed at the electrodes, is proportional to the amount of electricity passed, which is $(732)$. Faraday makes no claim about the electrochemical equivalent $Z$ as the constant of proportionality.

## 2. Acids and Bases

**Definition 2.1.** *We define the ph of a substance $X$ by;*

$$ph(X) = -log_{10}([H^+])$$

$$= -log_{10}(\tfrac{n}{V_d})$$

$$= -log_{10}(0.001) - log_{10}(\tfrac{n}{V})$$

$$= 3 - log_{10}(\tfrac{n}{V})$$

*where $[H^+] = \frac{n}{V_d} = \frac{0.001n}{V}$ is the concentration of hydrogen ions in moles/litre, $n$ is the number of moles of hydrogen ions, $V$ is the volume in $m^3$ and $V_d$ is the volume in litres. We have that $ph(H_2O) = 7$. We call substance $X$ an acid if $ph(X) < 7$, an alkali if $ph(X) > 7$ and neutral if $ph(X) = 7$. We call substance $X$ a Bronsted acid if it disassociates in a neutral substance $Y$ to form $H^+$ ions, and an Arrhenius acid if it increases the concentration of $H^+$ ions, when added to water.*

**Lemma 2.2.** *If an acid $X$ with $ph(X) = x$ is added to water, to form substance $Y$, with $ph(Y) = y$, then;*

$$x < y < 7$$

*In particularly, $Y$ is an acid. If an alkali $X$ with $ph(X) = x$ is added to water, to form substance $Y$, with $ph(Y) = y$, then;*

$$7 < y < x$$

*If a neutral $X$ with $ph(X) = 7$ is added to water, to form substance $Y$, then $ph(Y) = 7$. A substance $X$ is an acid iff it is an Arrhenius acid. An acid or an Arrhenius acid is a Bronsted acid. Water is a Bronsted acid but not an acid or an Arrhenius acid.*

*Proof.* If $X$ is an acid, we have that;

$$x = -log_{10}(\tfrac{n_1}{V_1}) < 7$$

$$-log_{10}(\tfrac{n_2}{V_2}) = 7$$

where $\{n_1, n_2\}$ are the number of moles of hydrogen ions in the alkali $X$ and water, $\{V_1, V_2\}$ are the volumes of the alkali and water respectively, measured in litres. Then;

$$y = -log_{10}(\tfrac{n_1+n_2}{V_1+V_2})$$

$$= -log_{10}(\tfrac{n_1}{V_1}) - log_{10}(\tfrac{1+\frac{n_2}{n_1}}{1+\frac{V_2}{V_1}})$$

$$= x - log_{10}(\tfrac{1+\frac{n_2}{n_1}}{1+\frac{V_2}{V_1}})$$

We have that;

$$-log_{10}(\tfrac{1+\frac{n_2}{n_1}}{1+\frac{V_2}{V_1}}) > 0$$

iff $log_{10}(\tfrac{1+\frac{n_2}{n_1}}{1+\frac{V_2}{V_1}}) < 0$

iff $\tfrac{1+\frac{n_2}{n_1}}{1+\frac{V_2}{V_1}} < 1$

iff $1 + \frac{n_2}{n_1} < 1 + \frac{V_2}{V_1}$

iff $\frac{n_2}{n_1} < \frac{V_2}{V_1}$

iff $\frac{n_2}{V_2} < \frac{n_1}{V_1}$

iff $log_{10}(\frac{n_2}{V_2}) < log_{10}(\frac{n_1}{V_1})$

iff $-log_{10}(\frac{n_2}{V_2}) > -log_{10}(\frac{n_1}{V_1})$

iff $7 > x$

which is true by the definition of an acid, so that $x < y$. Similarly;

$$y = -log_{10}(\tfrac{n_1+n_2}{V_1+V_2})$$

$$= -log_{10}(\tfrac{n_2}{V_2}) - log_{10}(\tfrac{1+\frac{n_1}{n_2}}{1+\frac{V_1}{V_2}})$$

$$= 7 - log_{10}(\tfrac{1+\frac{n_1}{n_2}}{1+\frac{V_1}{V_2}})$$

We have that;

$$-log_{10}(\frac{1+\frac{n_1}{n_2}}{1+\frac{V_1}{V_2}}) < 0$$

iff $log_{10}(\frac{1+\frac{n_1}{n_2}}{1+\frac{V_1}{V_2}}) > 0$

iff $\frac{1+\frac{n_1}{n_2}}{1+\frac{V_1}{V_2}} > 1$

iff $1 + \frac{n_1}{n_2} > 1 + \frac{V_1}{V_2}$

iff $\frac{n_1}{n_2} > \frac{V_1}{V_2}$

iff $\frac{n_1}{V_1} > \frac{n_2}{V_2}$

iff $log_{10}(\frac{n_1}{V_1}) > log_{10}(\frac{n_2}{V_2})$

iff $-log_{10}(\frac{n_1}{V_1}) < -log_{10}(\frac{n_2}{V_2})$

iff $x < 7$

again, so that $y < 7$. The proof is virtually the same if $X$ is an alkali, reversing the inequalities. If $X$ is neutral, with $ph(X) = x = 7$, then just use the first part of the proof, noting that $log_{10}(\frac{1+\frac{n_2}{n_1}}{1+\frac{V_2}{V_1}}) = 0$ iff $x = 7$. For the next claim, if $X$ is an acid, with $ph(X) = x < 7$, then, by the previous results, if $X$ is added to water to form substance $Y$, then $ph(Y) = y < 7$ as well. In particularly, we must have that $-log_{10}([H^+]_Y) < -log_{10}([H^+]_{water})$, so that $[H^+]_Y > [H^+]_{water}$ and the hydrogen ion concentration is increased, so that $X$ is an Arrhenius acid. Conversely, if $X$ is an Arrhenius acid, then adding water to form substance $Y$, we have that the hydrogen ion concentration is increased relative to water, so that $ph(Y) = y < 7$. If $ph(X) = x \geq 7$, then, by the previous results, $ph(Y) = y \geq 7$, which is a contradiction, so $ph(X) = x < 7$ and $X$ is an acid. For the next claim, if $X$ is an acid with $ph(X) < 7$, then $\frac{n_X}{V_X} > 10^{-7} = [H^+]_{water}$. For fixed $\delta_1 \simeq 0$, $\delta_2 \simeq 0$, corresponding to the removal of some $H^+$ ions and corresponding molecules/ions from $X$, with a corresponding volume, we can assume, for sufficiently large $V_X$ and corresponding $n_X$, obtained by increasing the volume of $X$, that;

$$\frac{n_X - \delta_1}{V_X - \delta_2} = \frac{n_X}{V_X}(\frac{1-\frac{\delta_1}{n_X}}{1-\frac{\delta_2}{V_X}}) \simeq \frac{n_X}{V_X} > 10^{-7} = [H^+]_{water}$$

With the smaller amount of substance $X'$ and $ph(X') < 7$, suppose we have a substance $Y$ with $ph(Y) = y > 7$ that does not react with $X'$, then $n_Y = 10^{-y}V_Y$ and $n_{X'} = 10^{\epsilon - 7}V_{X'}$, with $\epsilon > 0$. We have that;

$$-log_{10}(\tfrac{n_{X'} + n_Y}{V_{X'} + V_Y}) = 7$$

iff $-log_{10}(\tfrac{n_{X'} + 10^{-y}V_Y}{V_{X'} + V_Y}) = 7$

iff $n_{X'} + 10^{-y}V_Y = 10^{-7}(V_{X'} + V_Y)$

iff $V_Y = \tfrac{n_{X'} - 10^{-7}V_{X'}}{10^{-7} - 10^{-y}}$

$= V_{X'}(\tfrac{\frac{n_{X'}}{V_{X'}} - 10^{-7}}{10^{-7} - 10^{-y}})$

$= V_{X'}(\tfrac{10^{\epsilon - 7} - 10^{-7}}{10^{-7} - 10^{-y}})$

$= cV_{X'} > 0$

where $c > 0$. Choosing the volume of $Y$ to be $cV_{X'}$ and adding it to $X'$, we obtain a neutral mixture $Z$ with $ph(Z) = 7$. Adding the $\delta_1$ moles of $H^+$ ions with corresponding volume $\delta_2$ to $Z$, we clearly get a disassociation of $X$ in a neutral substance $Z$, with a formation of $H^+$ ions, so $X$ is a Bronsted acid. For the final claim, we have that $ph(water) = 7$ but it disassociates in the neutral substance water to form $H^+$ ions.

$\square$

## References

[1] Experimental Researches in Electricity, Michael Faraday, Royal Society, (1834).

[2] Physical Chemistry, Third Edition, R. G. Mortimer, (2008).

[3] Equilibria in Electrochemistry and Maximal Rates of Reaction, Tristram de Piro, available at http://www.curvalinea.net (60), (2022)

FLAT 3, REDESDALE HOUSE, 85 THE PARK, CHELTENHAM, GL50 2RP
*E-mail address*: t.depiro@curvalinea.net