ELECTROLYSIS, ACIDS AND PH

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

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 electricity 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 ρ ;

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

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 ρ by a factor of λ , then, according to the formula $\rho = CE$, treating the electrode/cathode assembly as a capacitor, we change the potential E by a factor of λ as well. We can also multiply the equation (*) by a factor of λ , changing the stochiometric coefficients by a factor of λ , without changing (**). We have that;

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

see Lemma 2.5 of [3], so that the change in stochiometric coefficients is equivalent to changing $(\frac{\partial G}{\partial \xi})_{T,P}$ by a factor of λ as well, if the chemical potentials μ_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 λ , and Q changes to Q^{λ} . We have that;

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

and, if $x_0 \simeq 1$, where substance 0 is the solvent H_2O , we can obtain Q^{λ} , by altering x_0 to x_0^{λ} , n_0 to n_0^{λ} , with a small alteration in the other substances $i, 1 \leq i \leq c$, and n changed roughly to n^{λ} . 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 λ . If we assume that $\lambda \simeq 1$, so *n* is roughly unchanged, we obtain that, n'_0 changes roughly by a factor of λ as well, giving (†).

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;

$$\frac{\Delta n_{0,2}}{\Delta n_{0,1}} = \frac{n'_{0,2}t}{n'_{0,1}t} = \frac{I_2t}{I_1t} = \frac{\rho_2}{\rho_1}$$

so that the amount of substance formed ξ , 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.

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2. Acids and Bases

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

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

= $-log_{10}(\frac{n}{V_d})$
= $-log_{10}(0.001) - log_{10}(\frac{n}{V})$
= $3 - log_{10}(\frac{n}{V})$

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 m³ 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) > 7and 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;

$$x = -\log_{10}\left(\frac{n_1}{V_1}\right) < 7$$
$$-\log_{10}\left(\frac{n_2}{V_2}\right) = 7$$

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;

$$\begin{split} y &= -\log_{10}\left(\frac{n_1 + n_2}{V_1 + V_2}\right) \\ &= -\log_{10}\left(\frac{n_1}{V_1}\right) - \log_{10}\left(\frac{1 + \frac{n_2}{n_1}}{1 + \frac{V_2}{V_1}}\right) \\ &= x - \log_{10}\left(\frac{1 + \frac{n_2}{n_1}}{1 + \frac{V_2}{V_1}}\right) \end{split}$$

We have that:

$$\begin{split} -log_{10} \big(\frac{1+\frac{n_2}{n_1}}{1+\frac{V_2}{V_1}}\big) &> 0\\ \text{iff } log_{10} \big(\frac{1+\frac{n_2}{n_1}}{1+\frac{V_2}{V_1}}\big) &< 0\\ \text{iff } \frac{1+\frac{n_2}{n_1}}{1+\frac{V_2}{V_1}} &< 1\\ \text{iff } \frac{1+\frac{n_2}{n_1}}{1+\frac{V_2}{V_1}} &< 1\\ \text{iff } \frac{n_2}{n_1} &< \frac{V_2}{V_1}\\ \text{iff } \frac{n_2}{V_2} &< \frac{n_1}{V_1}\\ \text{iff } log_{10} \big(\frac{n_2}{V_2}\big) &< log_{10} \big(\frac{n_1}{V_1}\big)\\ \text{iff } -log_{10} \big(\frac{n_2}{V_2}\big) &> -log_{10} \big(\frac{n_1}{V_1}\big)\\ \text{iff } 7 > x \end{split}$$

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

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

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

We have that;

$$\begin{split} -log_{10} (\frac{1+\frac{n_1}{n_2}}{1+\frac{V_1}{V_2}}) &< 0\\ \text{iff } log_{10} (\frac{1+\frac{n_1}{n_2}}{1+\frac{V_1}{V_2}}) &> 0\\ \text{iff } \frac{1+\frac{n_1}{n_2}}{1+\frac{V_1}{V_2}} &> 1\\ \text{iff } \frac{1+\frac{n_1}{n_2}}{1+\frac{V_1}{V_2}} &> 1+\frac{V_1}{V_2}\\ \text{iff } \frac{n_1}{n_2} &> \frac{V_1}{V_2}\\ \text{iff } \frac{n_1}{n_2} &> \frac{V_2}{V_2}\\ \text{iff } log_{10} (\frac{n_1}{V_1}) &> log_{10} (\frac{n_2}{V_2})\\ \text{iff } -log_{10} (\frac{n_1}{V_1}) &< -log_{10} (\frac{n_2}{V_2})\\ \text{iff } x < 7 \end{split}$$

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 $ph(X) = x \ge 7$, then, by the previous results, ph(Y) = y > 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;

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

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;

$$-log_{10}(\frac{n_{X'}+n_{Y}}{V_{X'}+V_{Y}}) = 7$$

iff $-log_{10}(\frac{n_{X'}+10^{-y}V_{Y}}{V_{X'}+V_{Y}}) = 7$
iff $n_{X'} + 10^{-y}V_{Y} = 10^{-7}(V_{X'} + V_{Y})$
iff $V_{Y} = \frac{n_{X'}-10^{-7}V_{X'}}{10^{-7}-10^{-y}}$
 $= V_{X'}(\frac{\frac{n_{X'}}{V_{X'}}-10^{-7}}{10^{-7}-10^{-y}})$
 $= V_{X'}(\frac{10^{\epsilon-7}-10^{-7}}{10^{-7}-10^{-y}})$
 $= cV_{X'} > 0$

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 δ_1 moles of H^+ ions with corresponding volume δ_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.

3. PH AND ELECTROLYSIS

Definition 3.1. We define $pH(T, P) = -log_{10}(a(H^+))$

where a is activity. Assuming we have a solute in a dilute solution, so we can ignore activity coefficients, we have that $a(H^+) = [H^+]$, so that pH = ph - 3.

Lemma 3.2. *pH*

$$\simeq -\frac{Flog_{10}(e)}{RT}(E - E^{\circ}) - \frac{log_{10}(e)ln(\frac{P(H_2)}{P^{\circ}})}{2}$$
$$\simeq -log_{10}(e)ln(\frac{P(H_2)}{P^{\circ}}) - \frac{log_{10}(e)ln(\frac{P(O_2)}{P^{\circ}})}{4}$$

where pH(T, P) is the pH at the potential difference E(T, P), $P(H_2)$ is the hydrogen pressure at (T, P), $P(O_2)$ is the oxygen pressure at (T, P).

Proof. We consider the equations for electrolysis of pure water, with platinum anode and cathode, and a DC power supply;

$$2H_2 \rightarrow 4H^+ + 4e^- \ (oxidation, anode)(L)$$

 $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \ (reduction, cathode)(R)$

which combine to give;

$$2H_2 + O_2 + 4H^+(R) + 4e^-(R) \to 2H_2O + 4H^+(L) + 4e^-(L)$$

simplifying to;

 $2H_2 + O_2 \rightarrow 2H_2O$

and the equations for the standard electrochemical cell, consisting of the hydrogen anode and a silver-silver chloride cathode, immersed in a solution of saturated KCl;

$$H_2 \rightarrow 2H^+ + 2e^- (oxidation, anode)(L)$$

 $AgCl + e^- \rightarrow Ag + Cl^- (reduction, cathode)(R)$

which combine to give;

$$H_2 + 2AgCl + 2e^{-}(R) \rightarrow 2H^{+}(R) + 2Ag + 2Cl^{-}(L) + 2e^{-}(L)$$

simplifying to;

$$H_2 + 2AgCl \rightarrow 2HCl + 2Ag$$

We assume the two cells are contained in separate flasks, with water on the left and the standard electrochemical cell on the right, but connected with a porous plug. The porous plug, allowing only transfer of H^+ and Cl^- ions, should establish an equilibrium between H^+ ions in both flasks, with no liquid potential. There will be an imbalance of Cl^- ions on both sides of the junction, which creates a potential,

 E_{LJ} , but this potential will not change much at different temperatures and pressures due to the saturation of KCl on one side. We can ensure the potential of the anode for water electrolysis is the same as the potential of the cathode in the electrochemical cell, by attaching them with a piece of platinum wire. Let E denote the potential difference of the DC power supply, between the cathode and the anode for water electrolysis, and let V denote the potential difference between the cathode and the anode of the electrochemical cell. Then we have, by construction, that;

$$0 = \phi(R, rightcell) - \phi(L, leftcell)$$

= $\phi(R, rightcell) - \phi(L, rightcell) + \phi(R, leftcell) + E_{LJ} - \phi(L, leftcell)$
= $V + E + E_{LJ}$

so that $V = -E - E_{LJ}$. We assume the temperature T of the water and KCl are the same, but not the pressure P.

By the Nernst equation for electrolysis of water, we have that;

$$E - E^{\circ} = -\frac{RT}{4F} ln(Q)$$
$$= -\frac{RT}{4F} ln(\frac{a(H_2O)^2}{a(H_2)^2 a(O_2)})$$
$$\simeq \frac{RT}{4F} ln(a(H_2)^2 a(O_2))$$

Assuming thermal equilibrium between the two flasks, but allowing for different pressures. Let V(T, P') correspond to E(T, P) and V'(T, P'') correspond to $E^{\circ}(T)$. As $E = -V - E_{LJ}$, $E^{\circ} = -V' - E_{LJ}$, E_{LJ} doesn't vary, we obtain that, $E - E^{\circ} = -(V' - V)$. By the Nernst equation for the electrochemical cell, assuming that $a(Cl^{-})$ doesn't vary by the saturation of the KCl solution, that the H_2 gas is at the same pressure in the two cells, and the concentrations of the H^+ ions are the same, $a(H^+)(T, P^{\circ}) = a(H_2)(T, P^{\circ}) = 1$, we have that;

$$V(T, P') - V'(T, P'') = (V - V^{\circ})(T, P') - (V' - V'^{\circ})(T, P'')$$

= $-\frac{RT}{2F}ln(Q')(T, P') + \frac{RT}{2F}ln(Q')(T, P'')$
= $-\frac{RT}{2F}ln(\frac{a(H^+)^2a(Ag)^2a(Cl^-)^2}{a(H_2)a(AgCl)^2})(T, P') + \frac{RT}{2F}ln(\frac{a(H^+)^2a(Ag)^2a(Cl^-)^2}{a(H_2)a(AgCl)^2})(T, P'')$

$$\simeq -\frac{RT}{2F} ln(\frac{a(H^{+})^2 a(Cl^{-})^2}{a(H_2)})(T, P') + \frac{RT}{2F} ln(\frac{a(H^{+})^2 a(Cl^{-})^2}{a(H_2)})(T, P'')$$

$$= -\frac{RT}{2F} ln(\frac{a(H^{+})^2}{a(H_2)})(T, P') + \frac{RT}{2F} ln(\frac{a(H^{+})^2}{a(H_2)})(T, P'')$$

$$= -\frac{RT}{2F} ln(\frac{a(H^{+})^2}{a(H_2)})(T, P) + \frac{RT}{2F} ln(\frac{a(H^{+})^2}{a(H_2)})(T, P^{\circ})$$

$$= -\frac{RT}{2F} ln(\frac{a(H^{+})^2}{a(H_2)})(T, P)$$

so that;

$$ln(a(H^{+})) = -\frac{F}{RT}(V - V') + \frac{ln(a(H_{2}))}{2}$$

$$= \frac{F}{RT}(E - E^{\circ}) + \frac{ln(a(H_{2}))}{2}$$

$$\simeq \frac{F}{RT}(E - E^{\circ}) + \frac{ln(\frac{P(H_{2})}{P^{\circ}})}{2}$$

$$\simeq \frac{F}{RT}(\frac{RT}{4F}ln(a(H_{2})^{2}a(O_{2}))) + \frac{ln(a(H_{2}))}{2}$$

$$= \frac{ln(a(H_{2}))}{2} + \frac{ln(a(O_{2}))}{4} + \frac{ln(a(H_{2}))}{2}$$

$$= ln(\frac{P(H_{2})}{P^{\circ}}) + \frac{ln(\frac{P(O_{2})}{P^{\circ}})}{4}$$

and;

$$pH = -log_{10}(a(H^+)) = -log_{10}(e)ln(a(H^+))$$
$$\simeq -\frac{Flog_{10}(e)}{RT}(E - E^\circ) - \frac{log_{10}(e)ln(\frac{P(H_2)}{P^\circ})}{2}$$
$$\simeq -log_{10}(e)ln(\frac{P(H_2)}{P^\circ}) - \frac{log_{10}(e)ln(\frac{P(O_2)}{P^\circ})}{4}$$

Lemma 3.3. In water electrolysis;

$$pH(T,P) \simeq \frac{4.84 \log_{10}(e) ln(\frac{P}{P^{\circ}})}{4RT} - \frac{\log_{10}(e) ln(\frac{P(H_2)}{P^{\circ}})}{2}$$
$$\simeq \frac{4.84 \log_{10}(e) ln(\frac{34722RT ln(\frac{P(H_2)}{P^{\circ}})}{4RT})}{4RT} - \frac{\log_{10}(e) ln(\frac{P(H_2)}{P^{\circ}})}{2}$$

where A is an undetermined constant.

In particularly, as $E(T, P) \to \infty$;

$$P \to \infty, \ P(H_2) \to \infty, \ pH(T, P) \to -\infty.$$

Proof. By the Nernst Equation for electrolysis of water, Lemma 8.1 of [3], we have that at electrical chemical equilibrium (T, P) and (T, P°) ;

$$E - E^{\circ}(T, P) = -\frac{RTln(Z(T, P))}{4F} - \frac{\epsilon(T, P)}{4F} (A)$$

where Z(T, P) is the activity coefficient. The activity coefficient is determined in Lemma 7.6 of [3];

$$Z(T,P) = e^{\frac{\epsilon \ln(\frac{P}{P^{\circ}}) - \epsilon(T,P)}{RT}} (B)$$

(*iii*) Substituting Z from (B) into (A), the error term cancels and we have that;

$$E - E^{\circ}(T, P) = \frac{-\epsilon ln(\frac{P}{P^{\circ}}) + \epsilon(T, P)}{4F} - \frac{\epsilon(T, P)}{4F}$$
$$= \frac{-\epsilon ln(\frac{P}{P^{\circ}})}{4F} (C)$$

where $\epsilon = P^{\circ}(\sum_{i=1}^{c} \frac{\nu_i N_A m_i}{\kappa_i(T, P^{\circ})})$, from [3]. Calculating ϵ for water electrolysis, with;

 $P^{\circ} = 101325, \nu_1 = 2, \nu_2 = -2, \nu_3 = -1, N_A = 6 \times 10^{23}, m_1 = 18 \times 1.67 \times 10^{-27}, m_2 = 2 \times 1.67 \times 10^{-27}, m_3 = 32 \times 1.67 \times 10^{-27}, \kappa_1 = 998.21, \kappa_2 = 70.9, \kappa_3 = 1141$ (liquid densities), we obtain that;

 $\epsilon = -4.91$

(matlab: -4.91)

Then from (C), we have;

$$E - E^{\circ}(T, P) = \frac{4.91\ln(\frac{P}{P^{\circ}})}{4F} (D)$$

Substituting (D) into the penultimate equation of Lemma 3.2;

$$pH \simeq -\frac{Flog_{10}(e)}{RT} \left(\frac{4.91ln(\frac{P}{P^{\diamond}})}{4F}\right) - \frac{log_{10}(e)ln(\frac{P(H_2)}{P^{\diamond}})}{2}$$

$$= -\frac{4.91 log_{10}(e) ln(\frac{P}{P^{\circ}})}{4RT} - \frac{log_{10}(e) ln(\frac{P(H_2)}{P^{\circ}})}{2} \ (F)$$

We have that, by a further result in [3], the equilibrium vapour pressure P'' at pressure P and temperature T in the liquid phase is given by;

$$P''(P) = Ae^{\frac{V_m(I)P}{RT}} (H)$$

where $V_m(I)$ is the molar volume of the liquid phase, A > 0 is an undetermined constant.

We have that $V_m(H_2) = 2.88 \times 10^{-5}$, $V_m(O_2) = 2.8 \times 10^{-5}$, so that; $P = 34722RTln(\frac{P(H_2)}{A})$

and, substituting into (F), we obtain;

$$pH \simeq -\frac{4.91 \log_{10}(e) ln(\frac{34722 RT ln(\frac{P(H_2)}{A})}{P^{\circ}})}{4 RT} - \frac{log_{10}(e) ln(\frac{P(H_2)}{P^{\circ}})}{2} (G)$$

For the final claim, by (D), increasing the potential $E \to \infty$ forces $P \to \infty$, and by (H), $P(H_2) \to \infty$. Then, by (G), $pH(T, P) \to -\infty$.

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Lemma 3.4. Maximising the concentration of H^+ ions is compatible with maximising the rate of the electrolysis reaction if we proceed along an upward sloping diagonal in the (T, P) plane and with maximising the rate of the fuel cell reaction if we proceed right along a horizontally inclined zig-zag path in the (T, P) plane.

Proof. By the definition of pH and Lemma 3.3, maximising the concentration of H^+ ions is equivalent to lowering pH is equivalent to increasing pressure, is equivalent to increasing the potential between the cathode and the anode which favours water electrolysis. The relationship between temperature T and pressure P along a maximal reaction path for water electrolysis or a fuel cell, from Lemma 7.7 of [3], is given by;

$$\frac{dP}{dT} = \frac{\epsilon T - PT \frac{\partial \epsilon}{\partial P}(T,P)}{(-\epsilon P \ln(\frac{P}{P^{\circ}}) + P\epsilon(T,P) - PT \frac{\partial \epsilon}{\partial T}(T,P))} (*)$$

Assuming the error term $\epsilon(T, P) = 0$ as a first approximation, and substituting into (*), we obtain that;

$$\frac{dP}{dT} = \frac{\epsilon T}{-\epsilon P ln(\frac{P}{P^{\diamond}})} = -\frac{T}{P ln(\frac{P}{P^{\diamond}})}$$

Using a Matlab step by step solution to differential equation, or using the theoretical result in [3], that the maximal reaction paths are given by;

$$P^{2}\left(\frac{\ln(P)}{2} - \frac{\ln(P^{\circ})}{2} - \frac{1}{4}\right) + \frac{T^{2}}{2} = c$$

where $c \in \mathcal{R}$, we obtain that P = f + eT, with e < 0, (**). The direction along the path for maximising water electrolysis is given by increasing pressure and lowering temperature, provided it is done sufficiently slowly, as can be verified experimentally and theoretically, see [4]. If we substitute (**) into (D) of the previous lemma, we obtain;

$$E - E^{\circ}(T, P) = \frac{4.91(ln(f+eT) - ln(P^{\circ}))}{4F}$$

Keeping pressure constant gives chemical equilibrium, see [4], so $E^{\circ}(T, P)$ is constant g, by assumption of electrical and chemical equilibrium;

$$E(T,P) = d + rln(f + eT) \ (r > 0)$$

so the potential is log increasing, with decreasing temperature, so encourages the production of H^+ ions. If we proceed along a horiontally inclined zig-zag path to the right, we increase pressure and the production of H^+ on the upward paths, while encouraging the fuel cell reaction on the downward paths, with a log decreasing potential, as the reverse direction to maximising water electrolysis, see [3]

References

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