

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 , (\dagger). The Nernst equation in a generalised form, without error terms, see [3], Lemma 8.4, states that;

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

(**)

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 stoichiometric 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 stoichiometric coefficients is equivalent to changing $\left(\frac{\partial G}{\partial \xi}\right)_{T,P}$ 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;

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

and, if $x_0 \simeq 1$, where substance 0 is the solvent H_2O , we can obtain Q^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;

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

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.

2. ACIDS AND BASES

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

$$\begin{aligned} \text{ph}(X) &= -\log_{10}([H^+]) \\ &= -\log_{10}\left(\frac{n}{V_d}\right) \\ &= -\log_{10}(0.001) - \log_{10}\left(\frac{n}{V}\right) \\ &= 3 - \log_{10}\left(\frac{n}{V}\right) \end{aligned}$$

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 $\text{ph}(H_2O) = 7$. We call substance X an acid if $\text{ph}(X) < 7$, an alkali if $\text{ph}(X) > 7$ and neutral if $\text{ph}(X) = 7$. 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 $\text{ph}(X) = x$ is added to water, to form substance Y , with $\text{ph}(Y) = y$, then;

$$x < y < 7$$

In particular, Y is an acid. If an alkali X with $\text{ph}(X) = x$ is added to water, to form substance Y , with $\text{ph}(Y) = y$, then;

$$7 < y < x$$

If a neutral X with $\text{ph}(X) = 7$ is added to water, to form substance Y , then $\text{ph}(Y) = 7$. 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;

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

We have that;

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

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

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

We have that;

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

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 $\log_{10}\left(\frac{1+\frac{n_2}{V_2}}{1+\frac{n_1}{V_1}}\right) = 0$ 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 particular, 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;

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

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;

$$\begin{aligned}
& -\log_{10}\left(\frac{n_{X'}+n_Y}{V_{X'}+V_Y}\right) = 7 \\
& \text{iff } -\log_{10}\left(\frac{n_{X'}+10^{-y}V_Y}{V_{X'}+V_Y}\right) = 7 \\
& \text{iff } n_{X'} + 10^{-y}V_Y = 10^{-7}(V_{X'} + V_Y) \\
& \text{iff } V_Y = \frac{n_{X'}-10^{-7}V_{X'}}{10^{-7}-10^{-y}} \\
& = V_{X'}\left(\frac{\frac{n_{X'}}{V_{X'}}-10^{-7}}{10^{-7}-10^{-y}}\right) \\
& = V_{X'}\left(\frac{10^{\epsilon-7}-10^{-7}}{10^{-7}-10^{-y}}\right) \\
& = cV_{X'} > 0
\end{aligned}$$

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 $ph(\text{water}) = 7$ but it disassociates in the neutral substance water to form H^+ ions. □

3. PH AND ELECTROLYSIS

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

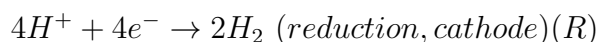
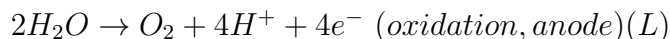
where a is activity. Assuming we have a solute in a dilute solution, so we can ignore activity coefficients, we have that $a(H^+) = [H^+]$, so that $pH = ph - 3$.

Lemma 3.2. pH

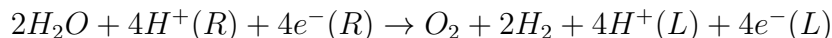
$$\begin{aligned}
& \simeq -\frac{1}{2\ln(10)}\left(\frac{2F(E-E^\circ)}{RT} + \ln\left(\frac{P(H_2)}{P^\circ(H_2)}\right)\right) \\
& \simeq \frac{1}{4\ln(10)}\ln\left(\frac{P(O_2)}{P^\circ(O_2)}\right)
\end{aligned}$$

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) .

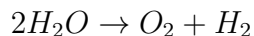
Proof. We consider the equations for electrolysis of pure water, with platinum anode and cathode, and a DC power supply;



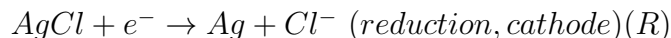
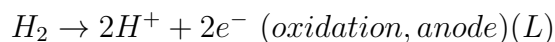
which combine to give;



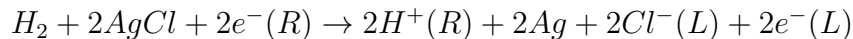
simplifying to;



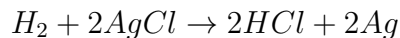
and the equations for the standard electrochemical cell, consisting of the hydrogen anode and a silver-silver chloride cathode, immersed in a solution of saturated KCl ;



which combine to give;



simplifying to;



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;

$$\begin{aligned} 0 &= \phi(R, rightcell) - \phi(L, leftcell) \\ &= \phi(R, rightcell) - \phi(L, rightcell) + \phi(R, leftcell) + E_{LJ} - \phi(L, leftcell) \\ &= V + E + E_{LJ} \end{aligned}$$

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;

$$\begin{aligned} E - E^\circ &= -\frac{RT}{4F} \ln(Q) \\ &= -\frac{RT}{4F} \ln\left(\frac{a(H_2)^2 a(O_2)}{a(H_2O)^2}\right) \\ &\simeq -\frac{RT}{4F} \ln(a(H_2)^2 a(O_2)) \end{aligned}$$

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;

$$\begin{aligned} V(T, P') - V'(T, P'') &= (V - V^\circ)(T, P') - (V' - V'^\circ)(T, P'') \\ &= -\frac{RT}{2F} \ln(Q')(T, P') + \frac{RT}{2F} \ln(Q')(T, P'') \\ &= -\frac{RT}{2F} \ln\left(\frac{a(H^+)^2 a(Ag)^2 a(Cl^-)^2}{a(H_2) a(AgCl)^2}\right)(T, P') + \frac{RT}{2F} \ln\left(\frac{a(H^+)^2 a(Ag)^2 a(Cl^-)^2}{a(H_2) a(AgCl)^2}\right)(T, P'') \end{aligned}$$

$$\begin{aligned}
&\simeq -\frac{RT}{2F} \ln\left(\frac{a(H^+)^2 a(Cl^-)^2}{a(H_2)}\right)(T, P') + \frac{RT}{2F} \ln\left(\frac{a(H^+)^2 a(Cl^-)^2}{a(H_2)}\right)(T, P'') \\
&= -\frac{RT}{2F} \ln\left(\frac{a(H^+)^2}{a(H_2)}\right)(T, P') + \frac{RT}{2F} \ln\left(\frac{a(H^+)^2}{a(H_2)}\right)(T, P'') \\
&= -\frac{RT}{2F} \ln\left(\frac{a(H^+)^2}{a(H_2)}\right)(T, P) + \frac{RT}{2F} \ln\left(\frac{a(H^+)^2}{a(H_2)}\right)(T, P^\circ) \\
&= -\frac{RT}{2F} \ln\left(\frac{a(H^+)^2}{a(H_2)}\right)(T, P)
\end{aligned}$$

so that;

$$\begin{aligned}
\ln(a(H^+)) &= -\frac{F}{RT}(V - V') + \frac{\ln(a(H_2))}{2} \\
&= \frac{F}{RT}(E - E^\circ) + \frac{\ln(a(H_2))}{2} \\
&\simeq \frac{F}{RT}(E - E^\circ) + \frac{\ln\left(\frac{P(H_2)}{P^\circ}\right)}{2} \\
&\simeq \frac{F}{RT}\left(-\frac{RT}{4F} \ln(a(H_2)^2 a(O_2))\right) + \frac{\ln(a(H_2))}{2} \\
&= -\frac{\ln(a(H_2))}{2} - \frac{\ln(a(O_2))}{4} + \frac{\ln(a(H_2))}{2} \\
&= -\frac{\ln\left(\frac{P(O_2)}{P^\circ}\right)}{4}
\end{aligned}$$

and;

$$\begin{aligned}
pH &= -\log_{10}(a(H^+)) = -\log_{10}(e) \ln(a(H^+)) \\
&\simeq -\frac{F \log_{10}(e)}{RT}(E - E^\circ) - \frac{\log_{10}(e) \ln\left(\frac{P(H_2)}{P^\circ}\right)}{2} \\
&\simeq \frac{\log_{10}(e) \ln\left(\frac{P(O_2)}{P^\circ}\right)}{4}
\end{aligned}$$

□

Lemma 3.3. *In water electrolysis;*

$$\begin{aligned}
pH(T, P) &\simeq \frac{4.84 \log_{10}(e) \ln\left(\frac{P}{P^\circ}\right)}{4RT} - \frac{\log_{10}(e) \ln\left(\frac{P(H_2)}{P^\circ}\right)}{2} \\
&\simeq \frac{4.84 \log_{10}(e) \ln\left(\frac{34722RT \ln\left(\frac{P(H_2)}{A}\right)}{P^\circ}\right)}{4RT} - \frac{\log_{10}(e) \ln\left(\frac{P(H_2)}{P^\circ}\right)}{2}
\end{aligned}$$

where A is an undetermined constant.

In particular, as $E(T, P) \rightarrow \infty$;

$P \rightarrow 0$, $P(H_2) \rightarrow A$, $pH(T, P) \rightarrow -\infty$.

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°) ;

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

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

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

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

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

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;

$P^\circ = 101325$, $\nu_1 = 2, \nu_2 = 1, \nu_3 = -2$, $N_A = 6 \times 10^{23}$, $m_1 = 2 \times 1.67 \times 10^{-27}$, $m_2 = 32 \times 1.67 \times 10^{-27}$, $m_3 = 18 \times 1.67 \times 10^{-27}$, $\kappa_1 = 70.9$, $\kappa_2 = 1141$, $\kappa_3 = 997$ (liquid densities), we obtain that;

$$\epsilon = 4.84$$

Then from (C), we have;

$$E - E^\circ(T, P) = \frac{-4.84 \ln(\frac{P}{P^\circ})}{4F} \quad (D)$$

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

$$\begin{aligned} pH &\simeq -\frac{F \log_{10}(e)}{RT} \left(\frac{-4.84 \ln(\frac{P}{P^\circ})}{4F} \right) - \frac{\log_{10}(e) \ln(\frac{P(H_2)}{P^\circ})}{2} \\ &= \frac{4.84 \log_{10}(e) \ln(\frac{P}{P^\circ})}{4RT} - \frac{\log_{10}(e) \ln(\frac{P(H_2)}{P^\circ})}{2} \quad (F) \end{aligned}$$

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;

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

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;

$$P = 34722RT \ln\left(\frac{P(H_2)}{A}\right)$$

and, substituting into (F), we obtain;

$$pH \simeq \frac{4.84 \log_{10}(e) \ln\left(\frac{34722RT \ln\left(\frac{P(H_2)}{A}\right)}{P^\circ}\right)}{4RT} - \frac{\log_{10}(e) \ln\left(\frac{P(H_2)}{P^\circ}\right)}{2} \quad (G)$$

For the final claim, by (D), increasing the potential $E \rightarrow \infty$ forces $P \rightarrow 0$, and by (H), $P(H_2) \rightarrow A$. Then, by (G), $pH(T, P) \rightarrow -\infty$, noting the right hand term is finite in the limit.

□

..... (iv). Relation between temperature T and pressure P along maximal reaction path, from Lemma 7.7 of [?];

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

(v). With invariance assumptions for the error term, that fugacities don't vary significantly with T and P ;

$$\epsilon(T, P) = \alpha T + \beta P + \gamma$$

where $\{\alpha, \beta, \gamma\}$ are constants. Substituting into (iv);

$$\frac{dP}{dT} = \frac{\epsilon TP^\circ - \beta PT}{(-\epsilon P \ln\left(\frac{P}{P^\circ}\right) + P(\alpha T + \beta P + \gamma) - \alpha PT)}$$

Using Matlab step by step solution to differential equation with error term, got $P = c + eT$, see plots.

(vi). Substitute into (iii);

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

Keeping pressure constant gives chemical equilibrium, see plots, so $E^\circ(T, P)$ is constant f , by assumption of electrical and chemical equilibrium;

$$E(T, P) = d + \ln(c + eT)$$

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