

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 $[H^+] = \frac{n}{V_d} = \frac{0.001n}{V} = \frac{1000n}{V_c}$ 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 , V_c is the volume in cm^3 , 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 $pH = ph - 3$.

We define the relative activity $\bar{a}(T, P) = \frac{a(T, P)}{a(T, P^\circ)}$ for a choice of initial conditions at (T, P°) , and similarly the relative activity with respect to a base pressure (T, P_b) . We let $\bar{Q}_b(T, P)$ to be the activity coefficient with relative activities with respect to a base pressure.

Lemma 3.2. *For potentials $\{V, V_b\}$, with $\min(V, V_b) > V^\circ$, we have that;*

$$V(T, P) - V_b = -\frac{RT}{4F} \log(\bar{Q}_b(T, P))$$

If $V_1 - V_b = -(V_2 - V_b)$, then;

$$\bar{Q}_b(T, P_1) = \frac{1}{\bar{Q}_b(T, P_2)}$$

Proof. By the Nernst equation, which doesn't include error terms, for the first part;

$$\begin{aligned} V - V_b &= (V - V^\circ) - (V_b - V^\circ) \\ &= \frac{-RT}{4F} \log\left(\frac{Q(T, P)}{Q(T, P^\circ)}\right) + \frac{RT}{4F} \log\left(\frac{Q(T, P_b)}{Q(T, P^\circ)}\right) \\ &= \frac{-RT}{4F} \log\left(\frac{Q(T, P)}{Q(T, P_b)}\right) \\ &= \frac{-RT}{4F} \log\left(\frac{\prod_{i=1}^p a_i^{\nu_i}(T, P)}{\prod_{i=1}^p a_i^{\nu_i}(T, P_b)}\right) \\ &= \frac{-RT}{4F} \log\left(\prod_{i=1}^p \bar{a}_i^{\nu_i}(T, P)\right) \\ &= \frac{-RT}{4F} \log(\bar{Q}_b(T, P)) \end{aligned}$$

For the second claim;

$$\begin{aligned} V_1 - V_b &= -\frac{RT}{4F} \log(\bar{Q}_b(T, P_1)) \\ &= -(V_2 - V_b) \\ &= \frac{RT}{4F} \log(\bar{Q}_b(T, P_2)) \end{aligned}$$

so that $\bar{Q}_b(T, P_1) = \frac{1}{\bar{Q}_b(T, P_2)}$

as required. □

Lemma 3.3. *For two fuel cells connected in opposition, with voltage between anode and cathode increasing on the left and voltage between anode and cathode increasing in the same proportion on the right, from a base voltage, the two anodes being at the same potential, (platinum*

wire connects the two anodes), the two cathodes being at the same potential, (circuit shorted), with the order cathode, anode, anode, cathode being read from left to right, and with hydrogen at the same pressure for both anodes, we have that, for relative activities;

$$Ph - Ph^b(\text{left}) = Ph - Ph^b(\text{right})$$

$$a(O_2)_l \simeq a(O_2)_r$$

Proof. As the anodes are at the same potential, we have by the Nernst equation for the respective half cells, that;

$$\frac{a(H^+)_l^4}{a(H_2)_l^2} = \frac{a(H^+)_r^4}{a(H_2)_r^2} \quad (*)$$

so that as hydrogen is at the same pressure in both anodes, $a(H_2)_l = a(H_2)_r$ and we obtain that, from (*);

$$a(H^+)_l = a(H^+)_r \quad (**)$$

and;

$$Ph - Ph^b(\text{left}) = -\log_{10}(a(H^+)_l) = -\log_{10}(a(H^+)_r) = Ph - Ph^b(\text{right})$$

as claimed. By the Nernst equation for the half cell at the cathode, we obtain, by symmetry;

$$\frac{a(H_2O)_l^2}{a(O_2)_l a(H^+)_l^4} = \frac{a(H_2O)_r^2}{a(O_2)_r a(H^+)_r^4}$$

so that, with $a(H_2O)_l \simeq a(H_2O)_r \simeq 1$ and using (**), we obtain;

$$a(O_2)_l \simeq a(O_2)_r$$

giving the second claim. □

Lemma 3.4. *For two fuel cells connected in opposition, with voltage between anode and cathode increasing on the left and voltage between anode and cathode decreasing in the same proportion on the right, from a base voltage, the two anodes being at the same potential, (connected with a platinum wire), with the order cathode, anode, anode, cathode*

being read from left to right, we have that, for relative activities;

$$Ph - Ph^b(\text{left}) = -\frac{1}{2}\log_{10}(a_l(H_2))$$

$$Ph - Ph^b(\text{right}) = -\frac{1}{2}\log_{10}(a_r(H_2))$$

In particular, $Ph - Ph^b$ decreases in the left cell, and increases in the right cell.

Proof. Using the Nernst equations for the left and right cells, and lemma 3.2, $a(H_2O) \simeq 1$, we have that;

$$\frac{1}{a(H_2)_l^2 a(O_2)_l} \simeq a(H_2)_r^2 a(O_2)_r \quad (A)$$

Using the fact that, without loss of generality, the potentials at the cathodes are $\{-(E_b + \epsilon), -(E_b - \epsilon)\}$, using the Nernst equation for the left and right *half* cells (cathodes), and lemma 3.2 again, we have that;

$$\frac{1}{a(H^+)_l^4 a(O_2)_l} \simeq a(H^+)_r^4 a(O_2)_r \quad (B)$$

Combining (A), (B), we obtain that;

$$\begin{aligned} \frac{\frac{1}{a(H_2)_l^2 a(O_2)_l}}{\frac{1}{a(H^+)_l^4 a(O_2)_l}} &\simeq \frac{a(H_2)_r^2 a(O_2)_r}{a(H^+)_r^4 a(O_2)_r} \\ \frac{a(H^+)_l^4}{a(H_2)_l^2} &= \frac{a(H_2)_r^2}{a(H^+)_r^4} \quad (C) \end{aligned}$$

As the anodes are at the same potential, we also have by the Nernst equation for the left and right half cells (anodes), that;

$$\frac{a(H^+)_l^4}{a(H_2)_l^2} = \frac{a(H^+)_r^4}{a(H_2)_r^2} \quad (D)$$

Combining (C), (D), we obtain that;

$$\frac{a(H^+)_r^4}{a(H_2)_r^2} = \frac{a(H_2)_r^2}{a(H^+)_r^4}$$

$$\text{so that } a(H^+)_r = a(H_2)_r^{\frac{1}{2}}$$

and taking logarithms, using the definition of relative potentials;

$$Ph - Ph^b(\text{right}) = -\frac{1}{2}\log_{10}(a_r(H_2))$$

The same considerations apply on the left. For the final claim, observe that electrolysis is encouraged by increasing voltage on the left, and the fuel cell reaction by decreasing voltage on the right. For the electrolysis reaction, the relative activity $a_l(H_2)$ increases and for the fuel cell reaction, the relative activity $a_r(H_2)$ decreases. \square

Lemma 3.5. *For two fuel cells connected in series, with voltage between anode and cathode increasing on the left and voltage between cathode and anode decreasing in the same proportion on the right, from a base voltage, the cathode on the left and the anode on the right being at the same potential, (connected with a platinum wire), with the order cathode, anode, cathode, anode being read from left to right, we have that, for relative activities;*

$$Ph - Ph^b(\text{left}) = -\frac{1}{2}\log_{10}(a_l(H_2))$$

$$Ph - Ph^b(\text{right}) = -\frac{1}{2}\log_{10}(a_r(H_2))$$

as in Lemma 3.4.

Proof. The proof is similar to Lemma 3.4. Using the Nernst equations for the left and right cells, and lemma 3.2, $a(H_2O) \simeq 1$, with the convention on negative voltages, see [3], we have that;

$$a(H_2)_l^2 a(O_2)_l \simeq \frac{1}{a(H_2)_r^2 a(O_2)_r} \quad (A)$$

Using the fact that, without loss of generality, the potentials at the left cathode and right anode are $\{-(E_b + \epsilon), -(E_b - \epsilon)\}$, using the Nernst equation for the left and right *half* cells (cathode and anode), and lemma 3.2 again, we have that;

$$\frac{1}{a(H^+)_l^4 a(O_2)_l} \simeq \frac{a(H_2)_r^2}{a(H^+)_r^4} \quad (B)$$

Multiplying both sides of (A), (B), we obtain that;

$$\frac{a(H_2)_l^2}{a(H^+)_l^4} \simeq \frac{1}{a(H^+)_r^4 a(O_2)_r} \quad (C)$$

As the anode on the left and the cathode on the right are at the same potential, we also have by the Nernst equation for the left and right half cells (anode and cathode), that;

$$\frac{a(H^+)_l^4}{a(H_2)_l^2} = \frac{1}{a(H^+)_r^4 a(O_2)_r} \quad (D)$$

Combining (C), (D), we obtain that;

$$\frac{a(H^+)_l^4}{a(H_2)_l^2} = \frac{a(H_2)_l^2}{a(H^+)_l^4}$$

$$\text{so that } a(H^+)_l = a(H_2)_l^{\frac{1}{2}}$$

and taking logarithms, using the definition of relative potentials;

$$Ph - Ph^b(\text{left}) = -\frac{1}{2} \log_{10}(a_l(H_2))$$

The same considerations apply on the right. For the final claim, observe that electrolysis is encouraged by increasing voltage on the left, and the fuel cell reaction by decreasing voltage on the right. For the electrolysis reaction, the relative activity $a_l(H_2)$ increases and for the fuel cell reaction, the relative activity $a_r(H_2)$ decreases. \square

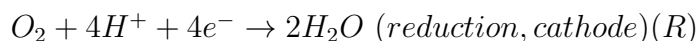
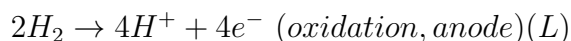
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Lemma 3.6. *For a hydrogen fuel cell connected in opposition to the standard electrochemical cell;*

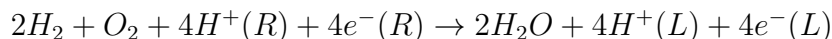
$$\begin{aligned} pH - pH^\circ & \\ & \simeq -\frac{F \log_{10}(e)}{RT} (E - E^\circ) - \frac{\log_{10}(e) \ln\left(\frac{P(H_2)}{P^\circ}\right)}{2} \\ & \simeq -\log_{10}(e) \ln\left(\frac{P(H_2)}{P^\circ}\right) - \frac{\log_{10}(e) \ln\left(\frac{P(O_2)}{P^\circ}\right)}{4} \end{aligned}$$

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) , $pH^\circ(T, P^\circ)$ is pH at standard pressure.

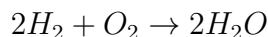
Proof. We consider the equations for electrolysis of pure water, with platinum anode and cathode, and a DC power supply;



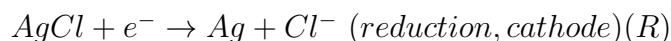
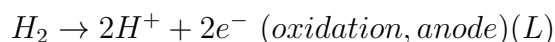
which combine to give;



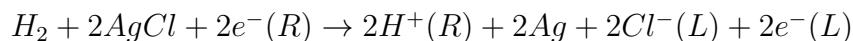
simplifying to;



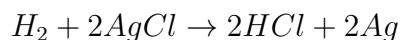
and the equations for the standard electrochemical cell, consisting of the hydrogen anode and a silver-silver chloride cathode, immersed in a solution of saturated KCl ;



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. There will be a large concentration of Cl^- ions in the standard electrochemical cell, but this will not change much at different temperatures and pressures due to the saturation of HCl on one side. We put the hydrogen anode for water electrolysis on the right and the hydrogen anode for the standard electrochemical cell on the left and measure cell potential from right to left. We can ensure the potential of the anode for water electrolysis is the same as the potential of the anode in the electrochemical cell, (*), by attaching them with a piece of platinum wire, and we assume hydrogen gas at the same pressure is fed into both anodes, see [2] (p363) for a similar set up. Let E denote the potential difference of the DC power supply, between the anode and the cathode for water electrolysis, and let V denote the potential difference between the cathode and the anode of the electrochemical cell, both are measured from right to left. We short the circuit by attaching a platinum wire between the two cathodes. Then we have, by Kirchoff's voltage law and (*), that;

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

so that $V = -E$. We assume the temperature T of the water and HCl are the same, but not the pressure P .

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

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

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. We can assume that the concentrations of the H^+ ions are the same in both cells;

As by the Nernst equation, using the fact that the anodes are at the same potential, the relative hydrogen activities are the same, with forward reactions in both cells, which we can assume by decreasing the potential in both cells between the anode and the cathode, we have that;

$$\begin{aligned}
-\frac{RT \ln(Q_{water,ox})}{4F} &= -\frac{RT \ln(Q_{standard,ox})}{2F} \\
\frac{\ln\left(\frac{a(H^+,l)^4}{a(H_2)^2}\right)}{4} &= \frac{\ln\left(\frac{a(H^+,r)^2}{a(H_2)}\right)}{2} \\
\frac{a(H^+,l)^4}{a(H_2)^2} &= \left(\frac{a(H^+,r)^2}{a(H_2)}\right)^2 \\
\frac{a(H^+,l)^4}{a(H_2)^2} &= \frac{a(H^+,r)^4}{a(H_2)^2}
\end{aligned}$$

so that $a(H^{+,l}) = a(H^{+,r})$, for the relative activities of H^+ ions.

We also have that $a(H^+)(T, P^\circ) = a(H_2)(T, P^\circ) = 1$, as we are using relative activities, so we have that;

$$\begin{aligned}
V(T, P') - V'(T, P'') &= (V - V^\circ)(T, P') - (V' - V'^\circ)(T, P'') \\
&= -\frac{RT}{2F} \ln(Q')(T, P') + \frac{RT}{2F} \ln(Q')(T, P'') \\
&= -\frac{RT}{2F} \ln\left(\frac{a(H^+)^2 a(\text{Ag})^2 a(\text{Cl}^-)^2}{a(\text{H}_2) a(\text{AgCl})^2}\right)(T, P') + \frac{RT}{2F} \ln\left(\frac{a(H^+)^2 a(\text{Ag})^2 a(\text{Cl}^-)^2}{a(\text{H}_2) a(\text{AgCl})^2}\right)(T, P'') \\
&\simeq -\frac{RT}{2F} \ln\left(\frac{a(H^+)^2 a(\text{Cl}^-)^2}{a(\text{H}_2)}\right)(T, P') + \frac{RT}{2F} \ln\left(\frac{a(H^+)^2 a(\text{Cl}^-)^2}{a(\text{H}_2)}\right)(T, P'') \\
&= -\frac{RT}{2F} \ln\left(\frac{a(H^+)^2}{a(\text{H}_2)}\right)(T, P') + \frac{RT}{2F} \ln\left(\frac{a(H^+)^2}{a(\text{H}_2)}\right)(T, P'') \\
&= -\frac{RT}{2F} \ln\left(\frac{a(H^+)^2}{a(\text{H}_2)}\right)(T, P) + \frac{RT}{2F} \ln\left(\frac{a(H^+)^2}{a(\text{H}_2)}\right)(T, P^\circ) \\
&= -\frac{RT}{2F} \ln\left(\frac{a(H^+)^2}{a(\text{H}_2)}\right)(T, P)
\end{aligned}$$

so that;

$$\begin{aligned}
\ln(a(H^+)) &= -\frac{F}{RT}(V - V') + \frac{\ln(a(\text{H}_2))}{2} \\
&= \frac{F}{RT}(E - E^\circ) + \frac{\ln(a(\text{H}_2))}{2} \\
&\simeq \frac{F}{RT}(E - E^\circ) + \frac{\ln\left(\frac{P(\text{H}_2)}{P^\circ}\right)}{2} \\
&\simeq \frac{F}{RT}\left(\frac{RT}{4F} \ln(a(\text{H}_2)^2 a(\text{O}_2))\right) + \frac{\ln(a(\text{H}_2))}{2} \\
&= \frac{\ln(a(\text{H}_2))}{2} + \frac{\ln(a(\text{O}_2))}{4} + \frac{\ln(a(\text{H}_2))}{2} \\
&= \ln\left(\frac{P(\text{H}_2)}{P^\circ}\right) + \frac{\ln\left(\frac{P(\text{O}_2)}{4}\right)}{4}
\end{aligned}$$

and;

$$\begin{aligned}
pH - pH_0 &= -\log_{10}(a(H^+)) = -\log_{10}(e) \ln(a(H^+)) \\
&\simeq -\frac{F \log_{10}(e)}{RT}(E - E^\circ) - \frac{\log_{10}(e) \ln\left(\frac{P(\text{H}_2)}{P^\circ}\right)}{2} \\
&\simeq -\log_{10}(e) \ln\left(\frac{P(\text{H}_2)}{P^\circ}\right) - \frac{\log_{10}(e) \ln\left(\frac{P(\text{O}_2)}{4}\right)}{4}
\end{aligned}$$

□

Lemma 3.7. *In water electrolysis;*

$$\begin{aligned} pH(T, P) &\simeq -\frac{4.91\log_{10}(e)(P-P^\circ)}{4RT} - \frac{\log_{10}(e)\ln\left(\frac{P(H_2)}{P^\circ}\right)}{2} \\ &\simeq -\frac{4.91\log_{10}(e)(P-P^\circ)}{4RT} - \frac{\log_{10}(e)\ln\left(\frac{kx_{H_2}(T, P)}{P^\circ}\right)}{2} \end{aligned}$$

k is the constant for H_2 in Raoult's law, $x_{H_2}(T, P)$ is the concentration of H_2 dissolved in H_2O .

In particular, as $E(T, P) \rightarrow \infty$, if we encourage the electrolysis reaction;

$$P \rightarrow \infty, P(H_2) \text{ remains bounded and } pH(T, P) \rightarrow -\infty.$$

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 7.3 of [3], we use the approximation;

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

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

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

where $\epsilon = \sum_{i=1}^c \nu_i \bar{V}_{m,i}(T, P)$, from [3]. Calculating ϵ for water electrolysis, in Lemma 7.3 of [3];

$$\epsilon = -4.7 \times 10^{-5}$$

Then from (C), we have;

$$E - E^\circ(T, P) = \frac{(4.7 \times 10^{-5})(P - P^\circ)}{4F} \quad (D)$$

Substituting (D) into the penultimate equation of Lemma 3.6;

$$\begin{aligned} pH &\simeq -\frac{F \log_{10}(e)}{RT} \left(\frac{(4.7 \times 10^{-5})(P - P^\circ)}{4F} \right) - \frac{\log_{10}(e) \ln\left(\frac{P(H_2)}{P^\circ}\right)}{2} \\ &= -\frac{(4.7 \times 10^{-5}) \log_{10}(e)(P - P^\circ)}{4RT} - \frac{\log_{10}(e) \ln\left(\frac{P(H_2)}{P^\circ}\right)}{2} \quad (F) \end{aligned}$$

Using Henry's law for the solute H_2 in H_2O , $P(H_2)(T, P) = k(T, P)x(T, P)$, where $x(T, P)$ is the mole fraction of H_2 dissolved in the solvent H_2O , we then obtain, from (F);

$$pH \simeq -\frac{(4.7 \times 10^{-5}) \log_{10}(e)(P - P^\circ)}{4RT} - \frac{\log_{10}(e) \ln\left(\frac{k(T, P)x(T, P)}{P^\circ}\right)}{2} \quad (G)$$

so that assuming we keep $x(T, P)$ away from 0, (RB), which is equivalent to encouraging the electrolysis reaction, the term $-\frac{\log_{10}(e) \ln\left(\frac{k(T, P)x(T, P)}{P^\circ}\right)}{2}$ remains bounded. For the final claim, by (D), increasing the potential $E \rightarrow \infty$ forces $P \rightarrow \infty$, and by (G), together with the remark (RB), $pH(T, P) \rightarrow -\infty$.

□

Lemma 3.8. *Maximising the concentration of H^+ ions is compatible with maximising the rate of the electrolysis reaction and converting water into steam if we proceed along a vertical zig-zag path in the (T, P) plane, above $P = P^\circ$. We can maximise 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 3.7, maximising the concentration of H^+ ions is equivalent to lowering pH is equivalent to increasing pressure, while favouring the electrolysis reaction, is equivalent to increasing the potential between the cathode and the anode while favouring water electrolysis. The relationship between temperature T and pressure P along a maximal reaction path for water electrolysis or a fuel cell, from Lemma 8.7 of [3], is given by;

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

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

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

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;

$$(P - P^\circ)^2 = -T^2 + c \text{ (circles centred at the point } (0, P^\circ))$$

where $c \in \mathcal{R}$, we obtain as an approximation that $P = f + eT$, with $e < 0$, (**), provided $P > P^\circ$. 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, for $P > P^\circ$, see [4]. If we substitute (**) into (D) of the previous lemma, we obtain;

$$E - E^\circ(T, P) = \frac{(4.7 \times 10^{-5})(f + eT - P^\circ)}{4F}$$

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

$$E(T, P) = d + rT \text{ (} r < 0)$$

so the potential is increasing, with decreasing temperature, so encourages the production of H^+ ions. If we proceed along a vertical zig-zag path, in the (T, P) plane, above $P = P^\circ$, we encourage electrolysis on the left moving diagonals, and equilibrium on the right moving diagonals, by the classification of the dynamic equilibrium paths;

$$P = P^\circ + \frac{R \ln(c) T}{\epsilon}$$

where $c \in \mathcal{R}$, see Lemma 3.5 of [3]. This maintains the mole fraction of H_2 away from zero, and encourages the electrolysis reaction overall. As the potential is increasing, using the result of Lemma 3.7, we also encourage the production of H^+ ions. It also allows us to convert water into steam during the reaction. If we proceed along a horizontally inclined zig-zag path to the right, above $P = P^\circ$, we have equilibrium on the upward slopes, and encourage the fuel cell reaction on the downward paths, with a decreasing potential, as the reverse direction

to maximising water electrolysis, see [3]. Clearly, the mole fraction of H_2 will approach 0 and the pH increases. \square

Lemma 3.9. *Given a feasible path γ in the temperature pressure plane, if PW is the power;*

$$PW(t) = (-(\lambda + \beta T(t)) - \epsilon P(t)) \left(\frac{1}{3} (\nabla(\ln(Q))) \cdot \gamma'_{12}(t) \right) n(t)$$

where $\lambda = \Delta H^\circ - \epsilon P^\circ$

$$\beta = \frac{\Delta G^\circ(T) - \Delta H^\circ}{T}$$

Proof. We can calculate the energy used to achieve this amount of substance formation along the reaction path. We have that the energy $E(t_0)$ is given by;

$$\int_0^{t_0} \frac{dE}{dt} dt$$

where $\frac{dE}{dt} = PW$ is the power given by the formula $PW(t) = V(t)I(t)$, $V(t)$ is the potential between the anode and the cathode, and $I(t)$ is the current. We have that;

$$I(t) = \frac{dQ(t)}{dt}$$

where the total charge passed;

$$Q(t) = 4F\xi(t)$$

so that, see [3];

$$\begin{aligned} I(t) &= 4F \frac{d\xi}{dt} \\ &= \frac{4F}{3} (\nabla(Q)) \cdot \gamma'_{12}(t) x_1^2 x_2 n \end{aligned}$$

and $x_1(t) = \frac{n_1(t)}{n(t)} = \frac{n_{10} - 2\xi(t)}{n_0 - \xi(t)}$, $x_2(t) = \frac{n_2(t)}{n(t)} = \frac{n_{20} - \xi(t)}{n_0 - \xi(t)}$, $n(t) = n_0 - \xi(t)$, where $\{n_{10}, n_{20}\}$ are the initial molar amounts of hydrogen and oxygen.

We use the fact that, $Q = \left(\frac{P^\circ}{k_1}\right)^2 \left(\frac{P^\circ}{k_2}\right) e^{\frac{\epsilon(P-P^\circ)}{RT}} = A e^{\frac{\epsilon(P-P^\circ)}{RT}}$, with error terms and $Q_0 = e^{\frac{\epsilon(P-P^\circ)}{RT}}$ without. Using the Nernst equation;

$$\begin{aligned}
V(t) &= V^\circ(t) - \frac{RT \ln(Q_0(t))}{4F} \\
&= V^\circ(t) - \frac{RT(t)}{4F} \left[\frac{\epsilon(P(t) - P^\circ)}{RT(t)} \right] \\
&= -\frac{1}{4F} \left(\frac{\partial G}{\partial \xi} \right)_{(T, P^\circ)} - \frac{RT(t)}{4F} \left[\frac{\epsilon(P(t) - P^\circ)}{RT(t)} \right] \\
&= -\frac{1}{4F} (\lambda + \epsilon P^\circ + \beta T(t)) - \frac{\epsilon}{4F} (P(t) - P^\circ) \\
&= -\frac{1}{4F} (\lambda + \beta T(t)) - \frac{\epsilon P(t)}{4F}
\end{aligned}$$

so that;

$$\begin{aligned}
PW(t) &= \left(-\frac{1}{4F} (\lambda + \beta T(t)) - \frac{\epsilon P(t)}{4F} \right) \left(\frac{4F}{3} (\nabla(Q) \cdot \gamma'_{12}(t)) x_1(t)^2 x_2(t) n(t) \right) \\
&= \left(-(\lambda + \beta T(t)) - \epsilon P(t) \right) \left(\frac{1}{3} (\nabla(Q) \cdot \gamma'_{12}(t)) x_1(t)^2 x_2(t) n(t) \right) \\
&\simeq \left(-(\lambda + \beta T(t)) - \epsilon P(t) \right) \left(\frac{1}{3} (\nabla(Q) \cdot \gamma'_{12}(t)) \frac{n(t)}{Q} \right) \\
&= \left(-(\lambda + \beta T(t)) - \epsilon P(t) \right) \left(\frac{1}{3} (\nabla(\ln(Q)) \cdot \gamma'_{12}(t)) n(t) \right)
\end{aligned}$$

where $\lambda = \Delta H^\circ - \epsilon P^\circ$

$$\beta = \frac{\Delta G^\circ(T) - \Delta H^\circ}{T}$$

see [3].

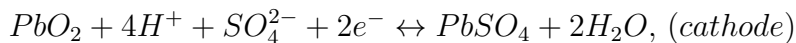
□

Lemma 3.10. *Temperature characteristic of a thermistor in an alternator for maximal reaction*

$$R(T) \simeq -\frac{11T^2}{6T_0T'}$$

where temperature T is measured in kelvin, T_0 is the starting temperature of the battery, $R(T)$ is the resistance of the thermistor, T' is the rate of change of temperature. Observe that at room temperature of 293K, with $T' = -0.53$, $R(T) \simeq 1k\Omega$, which is close to the value of a conventional thermistor in a car alternator at room temperature.

Proof. We consider the lead acid battery reaction;



and an alternator connected to the battery in series with a thermistor having resistance $R(T)$. We assume the voltage output from the alternator is a constant V , so that by Kirchoff's law;

$$E - IR - V = 0$$

the voltage E across the battery is given by;

$$E = V + IR$$

and rearranging;

$$R = \frac{E-V}{I}$$

where I is the current through the circuit, with the convention that a positive current corresponds to a positive rate of reaction. The current is determined by the rate of reaction in the battery, and we have that, see above;

$$I = 2F \frac{d\xi}{dt}$$

where ξ is the substance formed in the battery, Q is the relative activity quotient for a feasible path γ_{12} in the temperature pressure plane. As lead, lead oxide and lead sulphate are solids, we can treat their activities as 1 in the activity quotient, and we obtain that;

$$\begin{aligned} & \frac{\frac{(x-2\xi)^{-2}(y+2\xi)^2}{n^{-2}n^2}}{\frac{x^{-2}y^2}{n_0^{-2}n_0^2}} \\ &= \frac{(x-2\xi)^{-2}(y+2\xi)^2}{x^{-2}y^2} \\ &= Q(T, P) \end{aligned}$$

where $Q(T, P)$ is the relative activity quotient without error terms, $\{x, y\}$ are the initial molar amounts of sulphuric acid and water respectively, n is the total number of moles during the reaction, n_0 is the

initial total number of moles, and we assume that $\{x, y\}$ don't change significantly during the reaction. Rearranging, we obtain;

$$x^{-2}y^2Q(T, P)(x - 2\xi)^2 = (y + 2\xi)^2$$

and taking the derivative with respect to time along a feasible path γ , we have;

$$y^2 \nabla(Q) \cdot \gamma' + x^{-2}y^2Q(-4x\xi') = 4y\xi'$$

so that;

$$\xi' = \frac{y\nabla(Q) \cdot \gamma'}{4(1 + \frac{y}{x}Q)}$$

and;

$$I = \frac{2Fy\nabla(Q) \cdot \gamma'}{4(1 + \frac{y}{x}Q)}$$

We approximate the lead acid battery as a dilute solution and use;

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

where $\epsilon = \sum_{i=1}^c \nu_i V_{m,i}$ and $V_{m,i}$ are the molar volumes, ν_i are the stoichiometric coefficients. Then, by the Nernst equation;

$$E - E^\circ = -\frac{RT \log(Q)}{2F}$$

$$= -\frac{\epsilon(P-P^\circ)}{2F}$$

$$E = 12 - \frac{\epsilon(P-P^\circ)}{2F}$$

where Q is without error terms. Then we can approximate a maximal reaction path for the reverse reaction of charging up the battery as $P = c - T$, passing through (T_0, P°) , so that $c = P^\circ + T_0$, $P - P^\circ = -(T - T_0)$, T_0 is the starting temperature of the battery. Then $P' = -T'$ and;

$$\nabla(Q) \cdot \gamma' = \left(\frac{\partial Q}{\partial T}, \frac{\partial Q}{\partial P} \right) \cdot (1, -1)T'$$

$$= Q \left(-\frac{\epsilon(P-P^\circ)}{RT^2}, \frac{\epsilon}{RT} \right) \cdot (1, -1)T'$$

$$= Q\left(-\frac{\epsilon(P-P^\circ)}{RT^2} - \frac{\epsilon}{RT}\right)T'$$

Then along the maximal reaction path;

$$\begin{aligned} R &= \frac{E-V}{I} \\ &= \frac{-V+12-\frac{\epsilon(P-P^\circ)}{2F}}{\frac{2Fy\nabla(Q)\cdot\gamma'}{4(1+\frac{y}{x}Q)}} \\ &= \frac{-V+12+\frac{\epsilon(T-T_0)}{2F}}{\frac{2FyQ\left(-\frac{\epsilon(P-P^\circ)}{RT^2} - \frac{\epsilon}{RT}\right)T'}{4(1+\frac{y}{x}Q)}} \\ &= \frac{-V+12+\frac{\epsilon(T-T_0)}{2F}}{\frac{2FyQ\left(\frac{\epsilon(T-T_0)}{RT^2} - \frac{\epsilon}{RT}\right)T'}{4(1+\frac{y}{x}Q)}} \end{aligned}$$

We have that;

$$\text{molarvolumeoflead} = 1.826 \times 10^{-5} \text{m}^3/\text{mol}$$

$$\text{molarvolumeofleadoxide} = 2.34 \times 10^{-5} \text{m}^3/\text{mol}$$

$$\text{molarvolumeofsulphuricacid} = 5.33 \times 10^{-5} \text{m}^3/\text{mol}$$

$$\text{molarvolumeofleadsulphate} = 4.86 \times 10^{-5} \text{m}^3/\text{mol}$$

$$\text{molarvolumeofwater} = 1.8 \times 10^{-5} \text{m}^3/\text{mol}$$

$$\frac{y}{x} = \frac{7}{3}$$

$$y = 40$$

$$R = 8.31$$

$$V = 14$$

so that;

$$\epsilon = (-1.826 - 2.34 - 2 \times 5.33 + 2 \times 4.86 + 2 \times 1.8) \times 10^{-5}$$

$$= -1.506 \times 10^{-5}$$

Faraday's constant;

$$F = 96485$$

$$\epsilon F = -1.453$$

$$R \simeq \frac{2(12-V)(1+\frac{y}{x}Q)}{-1.5yQ(\frac{T-T_0}{RT^2}-\frac{1}{RT})T'}$$

and with $Q \simeq 1$ along the reaction path;

$$\begin{aligned} R &\simeq \frac{2(12-V)(1+\frac{7}{3})}{-1.5 \times 40(\frac{T-T_0}{RT^2}-\frac{1}{RT})T'} \\ &\simeq \frac{2(12-V)(\frac{10}{3})8.31T^2}{-60((T-T_0)-T)T'} \\ &\simeq \frac{55(12-V)T^2}{60T_0T'} \\ &\simeq \frac{-11T^2}{6T_0T'} \end{aligned}$$

□

Remarks 3.11. *What happens with other temperature gradients?*

The natural question to ask is what happens in the above lemma if $T' > 0$. We can follow through the above calculation with the requirement that $P' = \lambda T'$, $(P - P^\circ) = \lambda(T - T_0)$ and obtain;

$$R(T) \simeq -\frac{11T^2}{-6\lambda T_0 T'}$$

where we obtain the result of the above lemma when $\lambda = -1$. Then if we set $R(T)$ to the physically reasonable value of a thermistor;

$$\frac{11T^2}{6T_0}$$

we obtain the equation;

$$-\frac{11T^2}{-6\lambda T_0 T'} = \frac{11T^2}{6T_0}$$

so that;

$$\frac{1}{\lambda T'} = 1$$

and rearranging;

$$\lambda = \frac{1}{T'}$$

Then $P' = \lambda T' = 1$, so that with T' set by the external environment, the choice of thermistor forces the reaction path in the battery to be approximately given by $(T(t), P(t))$, with $P' = 1$. The subsidiary question is then, does this always charge up the battery? The answer appears to be yes, as;

$$I < 0 \text{ iff } \nabla \cdot \gamma' < 0$$

$$\text{iff } \left(-\frac{\epsilon(P-P^\circ)}{RT^2}, \frac{\epsilon}{RT}\right) \cdot (T', 1) < 0$$

$$\text{iff } -\frac{(P-P^\circ)T'}{RT^2} + \frac{1}{RT} > 0$$

$$\text{iff } -(P - P^\circ)T' > -T$$

$$\text{iff } (P - P^\circ)T' < T$$

$$\text{iff } \lambda(T - T_0)T' < T$$

$$\text{iff } T - T_0 < T$$

which is true.

So we can conclude that adding a thermistor with $R(T) = \frac{11T^2}{6T_0}$ in series with an alternator connected in opposition to the car battery should always charge the battery with the temperature generated by the environment, and with a very effective charging rate occurring when $T' = -1$.

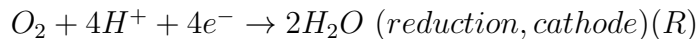
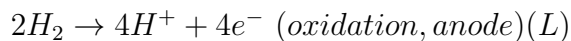
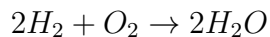
We can apply the same argument to the electrolysis of water;

Lemma 3.12. *Temperature characteristic of a thermistor in a maximal reaction for water electrolysis*

$$R(T) \simeq \frac{-1.38VT^2}{T_0nT'}$$

where temperature T is measured in kelvin, T_0 is the starting temperature of the fuel cell, $R(T)$ is the resistance of the thermistor, T' is the rate of change of temperature, V is the electrolysis voltage and n is the number of moles of water.

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



and a DC power supply connected to the fuel cell battery in series with a thermistor having resistance $R(T)$. We assume the voltage output from the DC power supply is a constant V , so that by Kirchoff's law;

$$E - IR - V = 0$$

and the voltage E across the fuel cell is given by;

$$E = V + IR$$

and rearranging;

$$R = \frac{E-V}{I}$$

where I is the current through the circuit, with the convention that a positive current corresponds to a positive rate of reaction. The current is determined by the rate of reaction in the fuel cell, and we have that, see above;

$$I = 4F \frac{d\xi}{dt}$$

where ξ is the substance formed in the fuel cell, Q is the relative activity quotient for a feasible path γ_{12} in the temperature pressure plane. As we are dealing with a dilute solution, we can treat the activity of water as 1 in the activity quotient, and we obtain, as above, that;

$$I = \frac{4F}{3} (\nabla(Q) \cdot \gamma'_{12}(t)) x_1^2 x_2 n, \quad (*)$$

and $x_1(t) = \frac{n_1(t)}{n(t)} = \frac{n_{10} - 2\xi(t)}{n_0 - \xi(t)}$, $x_2(t) = \frac{n_2(t)}{n(t)} = \frac{n_{20} - \xi(t)}{n_0 - \xi(t)}$, $n(t) = n_0 - \xi(t)$, where $\{n_{10}, n_{20}\}$ are the initial molar amounts of hydrogen and oxygen.

We approximate water electrolysis as a dilute solution and again use;

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

where $\epsilon = \sum_{i=1}^c \nu_i V_{m,i}$ and $V_{m,i}$ are the molar volumes, ν_i are the stoichiometric coefficients. As $Q(T, P)$ doesn't include error terms, if we make the assumption that $\{x_1, x_2\}$ do not vary considerably during the reaction, and multiply by $Q_0 = x_1^{-2}x_2^{-1}$, we obtain, from (*);

$$\begin{aligned} I &= \frac{4F}{3} x_1^{-2} x_2^{-1} (\nabla(Q) \cdot \gamma'_{12}(t)) x_1^2 x_2 n, (*) \\ &= \frac{4F}{3} (\nabla(Q) \cdot \gamma'_{12}(t)) n, (*) \end{aligned}$$

Then, by the Nernst equation, taking $E^\circ \simeq 0.03V$ at room temperature;

$$\begin{aligned} E - E^\circ &= -\frac{RT \log(Q)}{4F} \\ &= -\frac{\epsilon(P-P^\circ)}{4F} \\ E &= 0.03 - \frac{\epsilon(P-P^\circ)}{4F} \end{aligned}$$

where Q is without error terms. Then we can approximate a maximal reaction path for the reverse reaction of electrolysing water as $P = c - T$, passing through (T_0, P°) , so that $c = P^\circ + T_0$, $P - P^\circ = -(T - T_0)$, T_0 is the starting temperature of the battery. Then $P' = -T'$ and;

$$\begin{aligned} \nabla(Q) \cdot \gamma' &= \left(\frac{\partial Q}{\partial T}, \frac{\partial Q}{\partial P} \right) \cdot (1, -1) T' \\ &= Q \left(-\frac{\epsilon(P-P^\circ)}{RT^2}, \frac{\epsilon}{RT} \right) \cdot (1, -1) T' \\ &= Q \left(-\frac{\epsilon(P-P^\circ)}{RT^2} - \frac{\epsilon}{RT} \right) T' \end{aligned}$$

Then along the maximal reaction path;

$$\begin{aligned} R &= \frac{E-V}{I} \\ &= \frac{-V + 0.03 - \frac{\epsilon(P-P^\circ)}{4F}}{\frac{4F}{3} (\nabla(Q) \cdot \gamma'_{12}(t)) n} \\ &= \frac{-V + 0.03 + \frac{\epsilon(T-T_0)}{4F}}{\frac{4F}{3} Q \left(-\frac{\epsilon(P-P^\circ)}{RT^2} - \frac{\epsilon}{RT} \right) n T'} \end{aligned}$$

$$= \frac{-V+0.03+\frac{\epsilon(T-T_0)}{4F}}{\frac{4F}{3}Q\left(\frac{\epsilon(T-T_0)}{RT^2}-\frac{\epsilon}{RT}\right)nT'}$$

We have that;

$$\epsilon = -4.7 \times 10^{-5}$$

Gas constant;

$$R = 8.31$$

Faraday's constant;

$$F = 96485$$

$$\epsilon F = -4.53$$

$$R(T) \simeq \frac{(0.03-V)}{\frac{-4 \times 4.53}{3}Q\left(\frac{(T-T_0)}{RT^2}-\frac{1}{RT}\right)nT'}$$

and with $Q \simeq 1$ along the reaction path;

$$\begin{aligned} R(T) &\simeq \frac{(0.03-V)}{\frac{-4 \times 4.53}{3}\left(\frac{(T-T_0)}{RT^2}-\frac{1}{RT}\right)nT'} \\ &\simeq \frac{(0.03-V)8.31T^2}{-6.04((T-T_0)-T)nT'} \\ &\simeq \frac{1.38(0.03-V)T^2}{T_0nT'} \\ &\simeq \frac{-1.38VT^2}{T_0nT'} \end{aligned}$$

□

Lemma 3.13. *Application to Hydrox Scuba Diving*

A thermistor with resistance;

$$R(T) = \frac{0.5T^2}{T_0}$$

with a linear rating of $0.5\Omega/K$ and a base resistance of 149Ω at room temperature, forces hydrox production along a maximal reaction path, $P' = -T' = 0.12$, where $T' = -0.12$ is achievable in a lake or quarry environment up to a depth of 20m with a descent time of 150s.

Proof. We have that for a light lithium iron phosphate battery, $V = 12.8$, and for a single cylinder, half full of water, we have the value;

$$n = \frac{11.1 \times 0.5 \times 10^{-3}}{1.8 \times 10^{-5}} = 308$$

$$\frac{V}{n} = \frac{12.8}{308} = 0.04$$

$$R(T) \simeq \frac{-1.38VT^2}{T_0nT'} = -\frac{0.06T^2}{T_0T'}$$

For a lake or quarry;

$$T' = -\frac{18}{150} = -0.12$$

$$R(T) \simeq \frac{-0.06 \times 298}{-0.12}$$

$$= 149$$

at room temperature, so that if we set $R(T) = \frac{0.06T^2}{0.12T_0}$

$$= \frac{0.5T^2}{T_0}$$

with a linear rating of $0.5\Omega/K$ and a base resistance of 149Ω at room temperature, we can force hydrox production along a maximal reaction path, $P' = -T' = 0.12$.

□

Lemma 3.14. *Further calculation for hydrox scuba diving*

A 12.8V lithium phosphate battery with a rating of 200Ah, will provide breathable oxygen for at least 4 hours by electrolysis of water, and proceed on an effective reaction path, if connected to a thermistor of base resistance = 0.27Ω and a linear rating of $9 \times 10^{-4}\Omega/K$.

Proof. We consume oxygen at a rate of about $1.3 \times 10^{-4}mol/s$, so we need $\xi' \leq -1.3 \times 10^{-4}$, Using the fact above that;

$$\xi' = \frac{1}{3}(\nabla(Q) \cdot \gamma'_{12}(t))n$$

and;

$$\nabla(Q) \cdot \gamma'_{12}(t) = Q\left(-\frac{\epsilon(P-P^0)}{RT^2}, \frac{\epsilon}{RT}\right) \cdot (T', P')$$

with $T' < 0$, $\epsilon = -4.7 \times 10^{-5}$, $P' > 0$;

$$\xi' \leq \frac{n}{3} \frac{Q\epsilon P'}{RT}$$

$$\simeq \frac{n\epsilon P'}{3RT}$$

so we require;

$$\frac{n\epsilon P'}{3RT} \leq -1.3 \times 10^{-4}$$

$$P' \geq \frac{3RT \times -1.3 \times 10^{-4}}{n\epsilon}$$

$$\simeq \frac{3 \times 8.31 \times 298 \times -1.3 \times 10^{-4}}{308 \times -4.7 \times 10^{-5}}$$

$$\simeq 66.71$$

Then with $T' = -0.12$, and $P' = \lambda T'$, $\lambda = \frac{66.71}{-0.12} = -556$

$$R(T) = -\frac{0.06T^2}{-\lambda T_0 T'}$$

which has a base resistance at room temperature of;

$$-\frac{0.06 \times 298}{556 \times -0.12}$$

$$= 0.27\Omega$$

and a linear rating of;

$$\frac{0.06}{556 \times 0.12} \Omega/K$$

$$\simeq 9 \times 10^{-4} \Omega/K$$

We have that;

$$I = 4F\xi'$$

$$\simeq -4 \times 96485 \times 1.3 \times 10^{-4} A$$

$\simeq 50A$

so a 12.8V lithium phosphate battery with a rating of 200Ah, will provide breathable oxygen for about 4 hours by electrolysis of water. \square

4. ERROR TERMS

Lemma 4.1. *The equilibrium vapor pressure curve for water is given by;*

$$P(T) \simeq (5.1 \times 10^{10})e^{-\frac{4898}{T}}$$

where pressure is measured in pascals, temperature in kelvin.

Proof. By the Clausius-Clapeyron relation, we have that for pressures $\{P_1, P_2\}$ on the equilibrium curve, with corresponding temperatures $\{T_1, T_2\}$;

$$\ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta H_m}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

where ΔH_m is the molar enthalpy change of vaporisation, and $\Delta H_m \simeq 40.65 \times 10^3$ for water, R is the gas constant, $R \simeq 8.3$. At The boiling point of water $T_1 = 373$ in kelvin, we have that $P_1 = P^\circ = 101325$ in pascals, so that;

$$\begin{aligned} \ln\left(\frac{P_2}{101325}\right) &= -\frac{\Delta H_m}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \\ &= -\frac{40.65 \times 10^3}{8.3}\left(\frac{1}{T_2} - \frac{1}{373}\right) \\ P_2 &= 101325e^{-\frac{40.65 \times 10^3}{8.3}\left(\frac{1}{T_2} - \frac{1}{373}\right)} \\ &\simeq 101325e^{-4898\left(\frac{1}{T_2} - \frac{1}{373}\right)} \\ &\simeq (5.1 \times 10^{10})e^{-\frac{4898}{T_2}} \end{aligned}$$

\square

Remarks 4.2. *We have, using the phase rule for an ideal solution in equilibrium with its vapour, and using the ideal gas law, see [2], that;*

$$\mu_i^{(sol)}(T, P) = \mu_i^{(g)}(T, P_i) = \mu_i^{\circ(g)}(T) + RT\ln\left(\frac{P_i}{P^\circ}\right)$$

$$\begin{aligned}\mu_i^{\circ(sol)}(T) &= \mu_i^{(g)}(T, P_{i,\circ}) = \mu_i^{\circ(g)}(T) + RT\ln\left(\frac{P_{i,\circ}}{P^\circ}\right) \\ \mu_i^{(sol)}(T, P) &= \mu_i^{\circ(sol)}(T) - RT\ln\left(\frac{P_{i,\circ}}{P^\circ}\right) + RT\ln\left(\frac{P_i}{P^\circ}\right) \\ &= \mu_i^{\circ(sol)}(T) + RT\ln\left(\frac{P_i}{P_{i,\circ}}\right) \quad (*)\end{aligned}$$

where P_i is the equilibrium partial vapour pressure for the mixture at temperature and pressure (T, P) , $P_{i,\circ}$ is the equilibrium partial vapour pressure for the mixture at temperature and pressure (T, P°) .

By the definition of an ideal solution, we have that;

$$\mu_i = \mu_i^* + RT\ln(x_i) \quad (**)$$

where, by $\mu_i^*(T, P)$, we mean the chemical potential of substance i on its own, at temperature and pressure (T, P) . By Raoult's law $P_i = x_i P_i^*$, see [2], where P_i^* is the equilibrium vapor pressure of substance i on its own at temperature T , combined with (**), we obtain;

$$\begin{aligned}\mu_i &= \mu_i^* + RT\ln(x_i) \\ &= \mu_i^* + RT\ln\left(\frac{P_i}{P_i^*}\right) \\ &= \mu_i^* + RT\ln\left(\frac{P_i}{P_{i,\circ}}\right) - RT\ln\left(\frac{P_i^*}{P_{i,\circ}}\right) \quad (***)\end{aligned}$$

Combining (*), (**), we obtain that;

$$\begin{aligned}\mu_i^* &= \mu_i - RT\ln\left(\frac{P_i}{P_{i,\circ}}\right) + RT\ln\left(\frac{P_i^*}{P_{i,\circ}}\right) \\ &= (\mu_i^\circ + RT\ln\left(\frac{P_i}{P_{i,\circ}}\right)) - RT\ln\left(\frac{P_i}{P_{i,\circ}}\right) + RT\ln\left(\frac{P_i^*}{P_{i,\circ}}\right) \\ &= \mu_i^\circ + RT\ln\left(\frac{P_i^*}{P_{i,\circ}}\right) \quad (\dagger)\end{aligned}$$

Letting $P_i^* = P_{i,\circ}$, we obtain that $\mu_i^*(T, P') = \mu_i^\circ$, (** **), where (T, P') is the temperature and pressure at which the equilibrium pressure $P_i^* = P_{i,\circ}$. From (**), the fact that $\mu_i^*(T, P) \simeq \mu_i^*(T, P')$ and (** **), we obtain that;

$$\mu_i \simeq \mu_i^\circ + RT\ln(x_i), \quad (** ** *)$$

as a very good approximation. This avoids the contradiction that $x_i = 1$ for a solution involving more than one component, at $P = P^\circ$. To make the results here more precise, we need to compute the error term, but the proof is still consistent if we allow that $n_i(T, P) \rightarrow 0$ as $P \rightarrow P^\circ$, so that $x_i = \frac{n_i}{n} \rightarrow 1$, and x_i is not defined at $P = P^\circ$.

More specifically, we have that;

$$\mu_i^*(T, P) = \mu_i^*(T, P') + \delta$$

where $\delta = \mu_i^*(T, P) - \mu_i^*(T, P')$, so that;

$$\mu_i = \mu_i^\circ + RT \ln(x_i) + \delta$$

For Raoult's law, see [2], we also need an approximation. We have that, by the definition of an ideal solution, the phase rule, Dalton's law that each gas in a mixture of ideal gases behaves as if it were alone in the container at the equilibrium pressures $\{P_i, P_i^*\}$, see [2], that;

$$\begin{aligned} \mu_i &= \mu_i^* + RT \ln(x_i) \\ &= \mu_i^*(T, P_i^*) + RT \ln(x_i) + \epsilon \\ &= \mu_i^{\circ(g)} + RT \ln\left(\frac{P_i^*}{P^\circ}\right) + RT \ln(x_i) + \epsilon \\ &= \mu_i^{\circ(g)} + RT \ln\left(\frac{P_i}{P^\circ}\right) \end{aligned}$$

so that;

$$\begin{aligned} RT \ln(x_i) &= RT \ln\left(\frac{P_i}{P^\circ}\right) - RT \ln\left(\frac{P_i^*}{P^\circ}\right) - \epsilon \\ &= RT \ln\left(\frac{P_i}{P_{i,\circ}}\right) - RT \ln\left(\frac{P_i^*}{P_{i,\circ}}\right) - \epsilon \end{aligned}$$

where $\epsilon = \mu_i^*(T, P) - \mu_i^*(T, P_i^*)$, so that $(***)$ becomes;

$$\begin{aligned} \mu_i &= \mu_i^* + RT \ln(x_i) \\ &= \mu_i^* + RT \ln\left(\frac{P_i}{P_{i,\circ}}\right) - RT \ln\left(\frac{P_i^*}{P_{i,\circ}}\right) - \epsilon (***)' \end{aligned}$$

Combining $(*)$, $(***)'$, we obtain that;

$$\begin{aligned}
\mu_i^* &= \mu_i - RT \ln\left(\frac{P_i}{P_{i,o}}\right) + RT \ln\left(\frac{P_i^*}{P_{i,o}}\right) + \epsilon \\
&= (\mu_i^\circ + RT \ln\left(\frac{P_i}{P_{i,o}}\right)) - RT \ln\left(\frac{P_i}{P_{i,o}}\right) + RT \ln\left(\frac{P_i^*}{P_{i,o}}\right) + \epsilon \\
&= \mu_i^\circ + RT \ln\left(\frac{P_i^*}{P_{i,o}}\right) + \epsilon \quad (\dagger)'
\end{aligned}$$

Letting $P_i^* = P_{i,o}$ again, we obtain that $\mu_i^*(T, P') = \mu_i^\circ + \epsilon, (***)'$

From (**), (***)', we obtain that;

$$\begin{aligned}
\mu_i &= \mu_i^* + RT \ln(x_i) \\
&= \mu_i^*(T, P') + \delta + RT \ln(x_i) \\
&= \mu_i^\circ + \epsilon + \delta + RT \ln(x_i) \\
&= \mu_i^\circ + RT \ln(x_i) + \gamma_i
\end{aligned}$$

$$\begin{aligned}
\text{where } \gamma_i &= \epsilon + \delta = \mu_i^*(T, P) - \mu_i^*(T, P_i^*) + \mu_i^*(T, P) - \mu_i^*(T, P') \\
&= 2\mu_i^*(T, P) - \mu_i^*(T, P_i^*) - \mu_i^*(T, P') \simeq 0
\end{aligned}$$

We have that $dG = -SdT + VdP$, so that, if temperature is fixed, $dG = VdP$, then, for the Gibbs energy function of substance i on it own, in the liquid phase;

$$\begin{aligned}
\mu_i^*(T, P) - \mu_i^*(T, P_i^*) &= \frac{G(T, P, n) - G(T, P_i^*, n)}{n} \\
&= \frac{1}{n} \int_{P_i^*}^P dG \\
&= \frac{1}{n} \int_{P_i^*}^P V dP \\
&= \frac{1}{n} \int_{P_i^*}^P \frac{n N_A m_i}{\kappa_i(T, P)} dP \\
&\simeq \frac{N_A m_i (P - P_i^*)}{\kappa} \\
&= V_{m,i} (P - P_i^*)
\end{aligned}$$

where $\kappa(T, P)$ is the density of substance i in the liquid phase, and which we assume to be approximately constant, and $V_{m,i}$ is the molar

volume. Similarly;

$$\begin{aligned}\mu_i^*(T, P) - \mu_i^*(T, P') &\simeq \frac{N_A m_i (P - P')}{\kappa} \\ &= V_{m,i} (P - P')\end{aligned}$$

so that;

$$\gamma_i(P, T) \simeq V_{m,i} (2P - P_i^* - P') \simeq 0$$

We have that the equilibrium vapour pressure P'' at (T, P) for substance i on its own, is given by;

$$P'' = \bar{P} e^{\frac{V_{m,i}(P - \bar{P})}{RT}}$$

where $\bar{P}(T)$ is the equilibrium vapour pressure of substance i on its own, at temperature T , described by the Clausius-Clapeyron equation, so that;

$$P_i^* = \bar{P} e^{\frac{V_{m,i}(\bar{P} - \bar{P})}{RT}}$$

$$= \bar{P}$$

$$P' = \frac{RT}{V_{m,i}} \log\left(\frac{P_{i,\circ}}{\bar{P}}\right) + \bar{P}$$

$$\gamma_i(P, T) \simeq V_{m,i} \left(2P - \bar{P} - \frac{RT}{V_{m,i}} \log\left(\frac{P_{i,\circ}}{\bar{P}}\right) - \bar{P}\right)$$

$$= 2V_{m,i}P - 2V_{m,i}\bar{P} - RT \log\left(\frac{P_{i,\circ}}{\bar{P}}\right)$$

Using Raoult's law, $P_{i,\circ} \simeq P_{i,\circ}^* x_i(T, P^\circ)$, $P_{i,\circ} = \bar{P} x_i(T, P^\circ) e^{\frac{V_{m,i}(P^\circ - \bar{P})}{RT}}$, so that;

$$RT \log\left(\frac{P_{i,\circ}}{\bar{P}}\right) = RT \log\left(\frac{\bar{P} x_i e^{\frac{V_{m,i}(P^\circ - \bar{P})}{RT}}}{\bar{P}}\right)$$

$$= RT \log\left(\frac{\bar{P} e^{\frac{V_{m,i}(P^\circ - \bar{P})}{RT}} x_i}{\bar{P}}\right)$$

$$= RT V_{m,i} \frac{(P^\circ - \bar{P})}{RT} + RT \log(x_i)$$

$$= V_{m,i} (P^\circ - \bar{P}) + RT \log(x_i)$$

and then;

$$\begin{aligned}
 \gamma_i(P, T) &\simeq 2PV_{m,i} - 2\bar{P}V_{m,i} - V_{m,i}(P^\circ - \bar{P}) - RT\log(x_i) \\
 &\simeq 2PV_{m,i} - \bar{P}V_{m,i} - P^\circ V_{m,i} - RT\log(x_i)(T, P^\circ) \\
 &= V_{m,i}(2P - \bar{P} - P^\circ) - RT\log(x_i)(T, P^\circ) \\
 &\simeq -RT\log(x_i)(T, P^\circ)
 \end{aligned}$$

We can do the same calculation, this time taking P_i^* to be the equilibrium vapour pressure of substance i on its own at the pressure and temperature of the solution (T, P) , in which case we do not need an approximation for Raoult's law.

This time, we have that, using the same notation as above, except for P_i^* ;

$$\mu_i^*(T, P) = \mu_i^*(T, P') + \delta$$

where $\delta = \mu_i^*(T, P) - \mu_i^*(T, P')$, so that;

$$\mu_i = \mu_i^\circ + RT\ln(x_i) + \delta$$

For Raoult's law, we don't need an approximation. We have that, by the definition of an ideal solution, the phase rule, Dalton's law that each gas in a mixture of ideal gases behaves as if it were alone in the container at the equilibrium pressures $\{P_i, P_i^*\}$, that;

$$\begin{aligned}
 \mu_i &= \mu_i^* + RT\ln(x_i) \\
 &= \mu_i^{*(g)}(T, P_i^*) + RT\ln(x_i) \\
 &= \mu_i^{\circ(g)} + RT\ln\left(\frac{P_i^*}{P^\circ}\right) + RT\ln(x_i) \\
 &= \mu_i^{\circ(g)} + RT\ln\left(\frac{P_i}{P^\circ}\right)
 \end{aligned}$$

so that;

$$\begin{aligned}
 RT\ln(x_i) &= RT\ln\left(\frac{P_i}{P^\circ}\right) - RT\ln\left(\frac{P_i^*}{P^\circ}\right) \\
 &= RT\ln\left(\frac{P_i}{P_{i,\circ}}\right) - RT\ln\left(\frac{P_i^*}{P_{i,\circ}}\right)
 \end{aligned}$$

and taking exponentials, we obtain Raoult's law. Then $(***)$ above becomes;

$$\begin{aligned}\mu_i &= \mu_i^* + RT \ln(x_i) \\ &= \mu_i^* + RT \ln\left(\frac{P_i}{P_{i,o}}\right) - RT \ln\left(\frac{P_i^*}{P_{i,o}}\right) \quad (***)'\end{aligned}$$

Combining $(*)$ above and $(***)'$, we obtain that;

$$\begin{aligned}\mu_i^* &= \mu_i - RT \ln\left(\frac{P_i}{P_{i,o}}\right) + RT \ln\left(\frac{P_i^*}{P_{i,o}}\right) \\ &= (\mu_i^\circ + RT \ln\left(\frac{P_i}{P_{i,o}}\right)) - RT \ln\left(\frac{P_i}{P_{i,o}}\right) + RT \ln\left(\frac{P_i^*}{P_{i,o}}\right) \\ &= \mu_i^\circ + RT \ln\left(\frac{P_i^*}{P_{i,o}}\right) \quad (\dagger)'\end{aligned}$$

Letting $P_i^* = P_{i,o}$ again, we obtain that $\mu_i^*(T, P') = \mu_i^\circ$, $(***)'$

From $(**)$ above, $(***)'$, we obtain that;

$$\begin{aligned}\mu_i &= \mu_i^* + RT \ln(x_i) \\ &= \mu_i^*(T, P') + \delta + RT \ln(x_i) \\ &= \mu_i^\circ + \delta + RT \ln(x_i) \\ &= \mu_i^\circ + RT \ln(x_i) + \gamma_i\end{aligned}$$

where $\gamma_i(T, P) = \delta = \mu_i^*(T, P) - \mu_i^*(T, P') \simeq V_{m,i}(P - P')$

We have that the equilibrium vapour pressure P'' at (T, P) for substance i on its own, is given by;

$$P'' = \bar{P} e^{\frac{V_{m,i}(P - \bar{P})}{RT}}$$

where $\bar{P}(T)$ is the equilibrium vapour pressure of substance i on its own, at temperature T , described by the Clausius-Clapeyron equation, so that;

$$P_i^* = \bar{P} e^{\frac{V_{m,i}(\bar{P} - P)}{RT}}$$

$$\begin{aligned}
P' &= \frac{RT}{V_{m,i}} \log\left(\frac{P_{i,\circ}}{\bar{P}}\right) + \bar{P} \\
\gamma_i(P, T) &\simeq V_{m,i}\left(P - \bar{P} - \frac{RT}{V_{m,i}} \log\left(\frac{P_{i,\circ}}{\bar{P}}\right)\right) \\
&= V_{m,i}P - V_{m,i}\bar{P} - RT \log\left(\frac{P_{i,\circ}}{\bar{P}}\right)
\end{aligned}$$

Using Raoult's law, $P_{i,\circ} = P_{i,\circ}^* x_i(T, P^\circ)$, $P_{i,\circ} = \bar{P} x_i(T, P^\circ) e^{\frac{V_{m,i}(P^\circ - \bar{P})}{RT}}$, so that;

$$\begin{aligned}
RT \log\left(\frac{P_{i,\circ}}{\bar{P}}\right) &= RT \log\left(\frac{\bar{P} x_i e^{\frac{V_{m,i}(P^\circ - \bar{P})}{RT}}}{\bar{P}}\right) \\
&= RT \log\left(\bar{P} e^{\frac{V_{m,i}(P^\circ - \bar{P})}{RT}} x_i\right) \\
&= RT V_{m,i} \frac{(P^\circ - \bar{P})}{RT} + RT \log(x_i) \\
&= V_{m,i}(P^\circ - \bar{P}) + RT \log(x_i)
\end{aligned}$$

and then;

$$\begin{aligned}
\gamma_i(P, T) &\simeq PV_{m,i} - \bar{P}V_{m,i} - V_{m,i}(P^\circ - \bar{P}) - RT \log(x_i) \\
&= V_{m,i}(P - P^\circ) - RT \log(x_i) \\
&\simeq -RT \log(x_i)(T, P^\circ)
\end{aligned}$$

In either case, we obtain an error term which avoids the contradiction that in an ideal solution, if exactly $\mu_i = \mu_i^\circ + RT \log(x_i)(T, P)$, then $x_i(T, P^\circ) = 1$, $1 \leq i \leq c$, $c > 1$, whereas $\sum_{1 \leq i \leq c} x_i = 1$.

We can perform the same calculation, taking into account fugacity δ_i of the gas mixture in equilibrium with the liquid solution, and a deviation from Raoult's law, $P_i = P_i^* \gamma_i x_i$. We have that;

$$\begin{aligned}
\mu_i^{(sol)} &= \mu_i^{(g)\circ} + RT \ln\left(\frac{\delta_i(T, P_i) P_i}{P^\circ}\right) \\
\mu_i^{(sol)*} &= \mu_i^{(g)\circ*}(T, P_i^*) = \mu_i^{(g)\circ} + RT \ln\left(\frac{\delta_i(T, P_i^*) P_i^*}{P^\circ}\right) \\
\mu_i - \mu_i^* &= RT \ln\left(\frac{\delta_i(T, P_i) P_i}{P^\circ}\right) - RT \ln\left(\frac{\delta_i(T, P_i^*) P_i^*}{P^\circ}\right)
\end{aligned}$$

$$= RT\ln\left(\frac{P_i}{P_i^*}\right) + RT\ln\left(\frac{\delta_i(T, P_i)}{\delta_i(T, P_i^*)}\right)$$

so that;

$$\begin{aligned} \mu_i &= \mu_i^* + RT\ln(\gamma_i x_i) + RT\ln\left(\frac{\delta_i(T, P_i)}{\delta_i(T, P_i^*)}\right) \\ &= \mu_i^* + RT\ln\left(\frac{P_i}{P_{i,\circ}}\right) - RT\ln\left(\frac{P_i^*}{P_{i,\circ}}\right) + RT\ln\left(\frac{\delta_i(T, P_i)}{\delta_i(T, P_i^*)}\right) \\ \mu_i^* &= \mu_i - RT\ln\left(\frac{P_i}{P_{i,\circ}}\right) + RT\ln\left(\frac{P_i^*}{P_{i,\circ}}\right) - RT\ln\left(\frac{\delta_i(T, P_i)}{\delta_i(T, P_i^*)}\right) \\ &= \left(\mu_i^\circ + RT\ln\left(\frac{P_i}{P_{i,\circ}}\right) + RT\ln\left(\frac{\delta_i(T, P_i)}{\delta_i(T, P_{i,\circ})}\right)\right) - RT\ln\left(\frac{P_i}{P_{i,\circ}}\right) + RT\ln\left(\frac{P_i^*}{P_{i,\circ}}\right) \\ &\quad - RT\ln\left(\frac{\delta_i(T, P_i)}{\delta_i(T, P_i^*)}\right) \\ &= \mu_i^\circ + RT\ln\left(\frac{P_i^*}{P_{i,\circ}}\right) + RT\ln\left(\frac{\delta_i(T, P_i^*)}{\delta_i(T, P_{i,\circ})}\right) \quad (AB) \end{aligned}$$

When $P_i^* = P_{i,\circ}$, we have that $P_i^* \delta_i(T, P_i^*) = P_{i,\circ} \delta_i(T, P_{i,\circ})$, so that, by (AB), $\mu_i^*(T, P') = \mu_i^\circ$, and;

$$\mu_i = \mu_i^\circ + RT\ln(\gamma_i x_i) + \epsilon(T, P)$$

where, as in the previous proof, using the approximation to Raoult's law instead, we have that;

$$\epsilon(T, P) = \mu_i^*(T, P) - \mu_i^*(T, P') \simeq -RT\ln(\gamma_i x_i(T, P^\circ))$$

so we are free to choose the molar concentration $x_i(T, P^\circ)$ of the solvent.

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