NOTE: for this problem set, unless stated otherwise, all standard cell potentials and other standard thermodynamic values are assumed to be reported at 298 K.

1. Consider the demonstration where a piece of copper wire is being immersed in a solution of $AgNO_3$.

   a) What is the sign of $\Delta G°$ for the demonstration you are observing? Explain.

   <p style="color:red; text-align:center;">**Negative.   Reaction is spontaneous.**</p>

   b) Write out a balanced overall reaction for the demonstration, including all phases and stoichiometric coefficients:

   <p style="color:red; text-align:center;">**2 Ag⁺(aq) + Cu(s) → 2 Ag(s) + Cu²⁺(aq)**</p>

   $$2\ Ag^+(aq) + Cu(s) \rightarrow 2\ Ag(s) + Cu^{2+}(aq)$$

   c) In your engineering reference manual you find the following half-reactions:

   $$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \qquad E° = +0.34\ V$$

   $$Ag^+(aq) + e^- \rightarrow Ag(s) \qquad E° = +0.80\ V$$
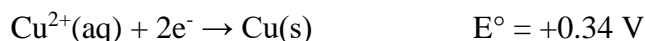
   Determine the standard cell potential associated ($E°cell$) associated with this reaction.

   $$E^0_{cell} = E^0_{red} - E^0_{ox} = 0.80 - 0.34 = 0.46\ V$$

   d) Calculate the value of $\Delta G°$ and K for the demonstration reaction at 298 K.

   $$\Delta G° = -n\,F\,E^0_{cell} = -2 \times 96485\ C\ mol^{-1} \times 0.460\ V = -88766\ J = -89\ kJ$$

   $$\ln K = -\frac{\Delta G°}{RT} = \frac{88766\ J}{1\ mol \times 8.3145\ J\ mol^{-1}K^{-1} \times 298\ K} = 35.83$$

   $$K = e^{35.83} = 3.62 \times 10^{15}$$

   e) Use your knowledge of thermodynamics to predict what would happen if we were to carry out the opposite experiment – a piece of silver in $Cu(NO_3)_2$.

   <p style="color:red;">**Because dipping Cu in $AgNO_3$ was a spontaneous process, that means the opposite process should be non-spontaneous.**</p>

   <p style="color:red;">**Note: both this answer and that for part a) make a subtle assumption. Can you see what it is?**</p>

2. Suppose you cannot find a table of standard reduction potentials. You remember the standard reduction potential of $Cu^{2+} + 2\ e^- \rightarrow Cu(s)$ is 0.337 V. Given $\Delta G°_f(Cu^{2+}) = 65.62$ kJ mol^{-1} and $\Delta G°_f(Ag^+) = 77.20$ kJ mol^{-1}, determine the standard reduction potential of Ag | Ag$^+$ from these data.

There are two methods for solving this problem:
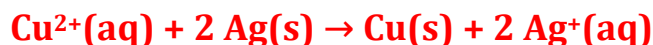
Method 1 (using only the half-cell of the reaction):

$$Ag^+(aq) + e^- \rightarrow Ag(s)$$

$$\Delta G° = \Delta G_f^0(Ag(s)) - \Delta G_f^0(Ag^+(aq)) = 0 - 1\ mol \times \left(77.20\frac{kJ}{mol}\right) = -77.20\ kJ$$

$$\Delta G° = -nFE_{half-cell}^0 \quad \rightarrow \quad -77200\ J = -1\ mol \times 96485\ C\ mol^{-1} \times E_{half-cell}^0$$

$$E_{half-cell}^0 = 0.80\ V$$

Method 2 (using the complete cell reaction):

$$Cu^{2+}(aq) + 2\ Ag(s) \rightarrow Cu(s) + 2\ Ag^+(aq)$$

$$\begin{aligned}\Delta G^0 &= \left[2\ mol \times \Delta G_f^0(Ag^+) + 1\ mol \times \Delta G_f^0(Cu)\right]\\ &\quad - \left[2\ mol \times \Delta G_f^0(Ag) + 1\ mol \times \Delta G_f^0(Cu^{2+})\right]\\ &= 154.40\ k\ J - 65.62\ kJ = 88.78\ kJ\end{aligned}$$

$$E_{cell}^0 = \frac{-\Delta G^0}{n\ F} = \frac{-(88.78\ kJ)\left(\frac{1000\ J}{1\ kJ}\right)}{2\ mol \times 96485\ C\ mol^{-1}} = -0.46\ V$$

$E_{cell}^0 = E^0{}_{red} - E^0{}_{ox}$ **(Cu^{2+} being reduced and Ag being oxidized. Solve for oxidation.)**

$E_{ox} = E_{red} - E_{cell}^0 = 0.34\ V - (-0.46\ V) = 0.80\ V$

3. **Good question.** A Proton Exchange Membrane Fuel Cell (PEMFC) uses hydrogen and oxygen to produce electricity by the following reactions:

   Anode (Oxidation): $H_2(g) \rightarrow 2\ H^+(aq) + 2\ e^-$
   Cathode (Reduction): $O_2(g) + 4\ H^+(aq) + 4\ e^- \rightarrow 2\ H_2O(l)$
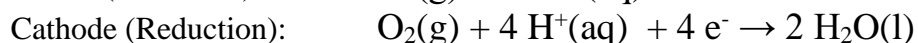
   a) Determine the overall, balanced electrochemical reaction in the PEMFC:

$$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l)$$
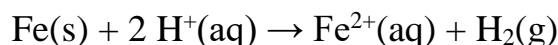
b) In the *CRC handbook of chemistry and physics* you look up the Gibbs energy of formation of water – $\Delta G°_f(H_2O) = -236.81$ kJ mol^{-1}. Determine the cell potential for the PEMFC operating under standard conditions.

$$\Delta G^0 = 2 \text{ mol} \times \Delta G_f^0(H_2O) - \left[2 \text{ mol} \times \Delta G_f^0(H_2) + 1 \text{ mol} \times \Delta G_f^0(O_2)\right]$$
$$= 2 \text{ mol} \times (-236.81 \text{ kJ mol}^{-1}) = -473.62 \text{ kJ}$$

$$E^0_{cell} = \frac{-\Delta G^0}{n \text{ F}} = \frac{-(-473.62 \text{ kJ})\left(\frac{1000 \text{ J}}{1 \text{ kJ}}\right)}{4 \text{ mol} \times 96485 \text{ C mol}^{-1}} = 1.23 \text{ V}$$

4. Iron metal reacts with 1 M acidic solutions to form Fe(II) salts according to

$$\text{Fe(s)} + 2 \text{ H}^+\text{(aq)} \rightarrow \text{Fe}^{2+}\text{(aq)} + \text{H}_2\text{(g)}$$

Standard Reduction Potentials	
$Fe^{2+} + 2e^- \rightarrow Fe$	-0.44 V
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.77 V

Explain why Fe(II) salts, instead of Fe(III) salts, are produced.

Since the concentrations are at 1 M, the reactions are at standard state so the standard cell potential is

$$\textbf{E}^0_{\textbf{cell}} = \textbf{E}^0_{\textbf{red}} - \textbf{E}^0_{\textbf{ox}} = \textbf{0} - \textbf{(-0.44)} = \textbf{0.44 V}$$

and the reaction proceeds spontaneously for form Fe(II) salts. To form Fe(III) salts, consider the reaction

$$\textbf{Fe(s)} + \textbf{3 H}^+\textbf{(aq)} \rightarrow \textbf{Fe}^{3+}\textbf{(aq)} + \textbf{3/2 H}_2\textbf{(g)}$$

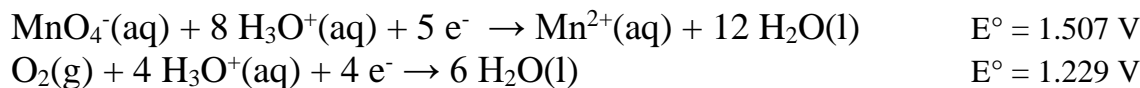**for which E^0_{cell} = 0.44 - 0.77 = -0.33 V. Since the cell potential is negative, this reaction will not proceed spontaneously, meaning Fe(II) salts are preferred to Fe(III) ones if iron reacts with acid.**

5. The permanganate ion is a powerful oxidizing agent that oxidizes water to oxygen under standard conditions. The notation describing the electrochemical cell consists of:

$$\text{Pt(s)} \mid \text{O}_2\text{(g)} \mid \text{H}_3\text{O}^+\text{(aq)} \parallel \text{MnO}_4^-\text{(aq)}, \text{H}_3\text{O}^+\text{(aq)}, \text{Mn}^{2+}\text{(aq)} \mid \text{Pt(s)}$$
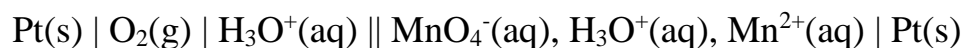
The relevant half-reactions are:

$$\text{MnO}_4^-\text{(aq)} + 8 \text{ H}_3\text{O}^+\text{(aq)} + 5 \text{ e}^- \rightarrow \text{Mn}^{2+}\text{(aq)} + 12 \text{ H}_2\text{O(l)} \qquad E° = 1.507 \text{ V}$$
$$\text{O}_2\text{(g)} + 4 \text{ H}_3\text{O}^+\text{(aq)} + 4 \text{ e}^- \rightarrow 6 \text{ H}_2\text{O(l)} \qquad E° = 1.229 \text{ V}$$

a) Write the overall balanced electrochemical equation. Include phases and stoichiometric coefficients. Calculate $E°_{cell}$.

$$4\ MnO_4^-(aq) + 12\ H_3O^+(aq) \rightarrow 4\ Mn^{2+}(aq) + 5\ O_2(g) + 18\ H_2O(l)$$

$$E°_{cell} = 1.507\ V - 1.229\ V = 0.278\ V$$

b) Write the reaction quotient (Q) that describes the electrochemical cell in terms of activities:

$$Q = \frac{(a[Mn^{2+}])^4 (a[O_2])^5 (a[H_2O])^{18}}{(a[MnO_4^-])^4 (a[H_3O^+])^{12}} \quad \textit{NOTE: Activity of H₂O = 1.}$$

c) What is the cell potential of the permanganate-oxygen cell operating at 25 °C, pH = 6.50, P_{O2} = 0.135 bar, $[MnO^{4-}]$ = $[Mn^{2+}]$ = 0.150 M. (Recall that pH = -log[H+])

$$Q = \frac{(P_{O_2})^5 [Mn^{2+}]^4}{[MnO_4^-]^4 [H_3O^+]^{12}} = \frac{(0.135)^5 [0.150]^4}{[0.150]^4 [1.00 \times 10^{-6.5}]^{12}} = 4.48 \times 10^{73}$$

$$E = E° - \frac{RT}{nF}\ln Q = 0.278\ V - \frac{8.3145\ J\ mol^{-1}K^{-1} \times 298\ K}{20 \times 96485\ C\ mol^{-1}} \times \ln(4.48 \times 10^{73})$$
$$= 0.060\ V$$

6. **Good question.** If the permanganate cell from Question 5 is operated at 25 °C, pH = 4.00, $[MnO_4^-]$ = 0.300 M and $[Mn^{2+}]$ = 0.0450 M and the cell potential is measured to be 0.200 V, what must be the pressure of $O_2(g)$ within the cell? (Recall that pH = -log[H⁺])

$$E = E° - \frac{RT}{nF}\ln Q \text{ (solve for } Q)$$
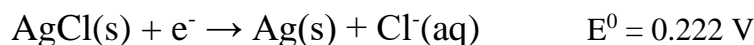
$$\ln Q = \frac{-nF(E - E°)}{RT} = \frac{-20 \times 96485\ C\ mol^{-1} \times (0.200\ V - 0.278\ V)}{8.3145\ J\ mol^{-1}K^{-1} \times 298\ K} = 60.757$$

$$Q = e^{60.757} = 2.4357 \times 10^{26} = \frac{(P_{O_2})^5 [Mn^{2+}]^4}{[MnO_4^-]^4 [H_3O^+]^{12}}$$

(solve for P_{O2})

$$P_{O_2} = \left(\frac{Q\ [MnO_4^-]^4\ [H_3O^+]^{12}}{[Mn^{2+}]^4} \right)^{\frac{1}{5}} = 0.000217\ bar$$

7. **Good question.** Use the standard reduction potentials for the reactions:

$$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq) \qquad E^0 = 0.222 \text{ V}$$
$$Ag^+(aq) + e^- \rightarrow Ag(s) \qquad E^0 = 0.799 \text{ V}$$

to calculate the value of K_{sp} for silver chloride at 298 K.

K_{sp} describes the following reaction: AgCl(s) → Ag⁺(aq) + Cl⁻(aq)

To obtain this equation add the first given equation to the reverse of the second, giving $E^0 = E_{red} – E_{ox} = 0.222$ V – 0.799 V = -0.577 V
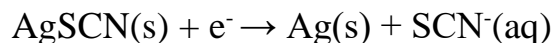
$$E° = \frac{RT}{nF} \ln K \text{ (solve for } \ln K)$$

$$\ln K = \frac{E°nF}{RT} = \frac{-0.577 \text{ V} \times 1 \text{ mol} \times 96485 \text{ C mol}^{-1}}{1 \text{ mol} \times 8.3145 \text{ J mol}^{-1}\text{K}^{-1} \times 298 \text{ K}} = -22.47$$

$$K = e^{-22.47} = 1.74 \times 10^{-10}$$

(actual value of K_{sp} is 1.77 x 10⁻¹⁰ so result is close)

8. **Good question.** The standard potential for the reaction

$$AgSCN(s) + e^- \rightarrow Ag(s) + SCN^-(aq)$$

is +0.0895 V, whereas E^0_{red} for $Ag^+(aq)$ is 0.799 V. Use these values to determine the K_{sp} for AgSCN at 298 K.

K_{sp} describes the following reaction: AgSCN(s) → Ag⁺(aq) + SCN⁻(aq)

To obtain this equation add the given equation to the oxidation reaction for silver

Ag(s) → Ag⁺(aq) + e⁻   E⁰ = -0.799 V

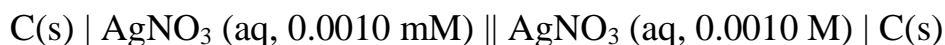**so that $E^0 = E_{red} – E_{ox} = 0.0895$ – 0.799 V = -0.7095 V and following the same procedure used for Question 6 gives**

$$\ln K = \frac{E°nF}{RT} = \frac{-0.7095 \text{ V} \times 1 \text{ mol} \times 96485 \text{ C mol}^{-1}}{1 \text{ mol} \times 8.3145 \text{ J mol}^{-1}\text{K}^{-1} \times 298 \text{ K}} = -27.63$$

$$K = e^{-27.63} = 1.00 \times 10^{-12}$$

9. Consider the following concentration cell:

$$C(s) \mid AgNO_3 \ (aq, 0.0010 \ mM) \parallel AgNO_3 \ (aq, 0.0010 \ M) \mid C(s)$$

a) What will be the measured potential (E_{cell}) for the concentration cell above at 298K?

Ag^+ is the species of interest in the cell (NO_3^- is a counterion.)

$E^o_{cathode} = E^o_{anode}$ because both half-cells are identical, but only differ in concentration (this is a concentration cell, after all) so $E^o_{cell} = 0$ and the overall reaction is: $Ag^+(aq, 0.0010 \ M) \rightarrow Ag^+(aq, 0.001 \ mM)$

Applying the Nernst equation with this overall equation gives (n=1 since one mole of electrons is transferred in the reaction)

$$E_{cell} = E^o_{cell} - \frac{0.0592}{n} \log Q = -\frac{0.0592}{1} \log \left(\frac{[Ag^+]_{anode}}{[Ag^+]_{cathode}} \right)$$

$$E_{cell} = -\frac{0.0592}{1} \log \left(\frac{0.0010 \times 10^{-3} \ M}{0.001 M} \right) = 0.1776 \ V$$

The equation above shows there is a 59.2 mV change in potential for every order of magnitude change in concentration per electron transferred. The difference in concentration between cathode and anode is THREE orders of magnitude (0.001 M vs. 0.001 x 10^{-3} M), therefore the expected change will be 0.0592 V * 3 = 0.1776V

b) Adding 4.0×10^{-4} mol of KCl to one of the half cells (whose volume is 10 mL) precipitates some AgCl resulting in $E_{cell} = 0.317$ V. Using E_{cell}, calculate $[Ag^+]$ in this half-cell. Note that $[Ag^+]$ in the other half-cell does NOT change.

Since the voltage is even greater than in part a), it must be that the concentration of silver ions in the anode is even smaller, that is the KCl must have been added to the anode half-cell. Using the equation from part a) gives

$$E_{cell} = 0.317 = -\frac{0.0592}{1} \log \left(\frac{[Ag^+]_{anode}}{[Ag^+]_{cathode}} \right) = -0.0592 \log \left(\frac{[Ag^+]_{anode}}{0.001} \right)$$

$$[Ag^+] = 4.42 \times 10^{-9} \ M$$

10. **Good question.** Use the data from Question 9(b) to calculate the K_{sp} for AgCl(s). Hint: in your ICE table, the "initial" $[Ag^+]$ and $[Cl^-]$ should reflect a theoretical time point after KCl is added but before any precipitate forms.

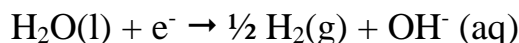| **AgCl(s)**	$\leftrightarrows$	**Ag⁺(aq)**	**+**	**Cl⁻(aq)**
-		0.000001		0.040
-		0		0.039999
-		+x		+x
-		x		0.039999 + x
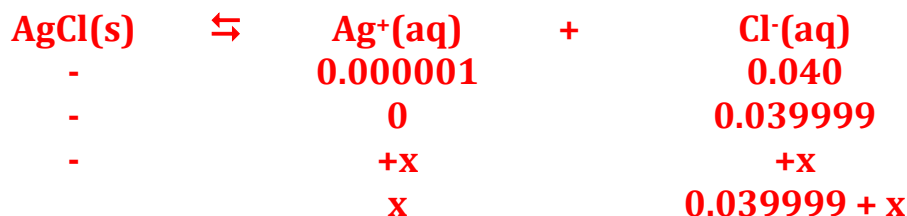
From Question 9b, we know x = 4.42 x 10⁻⁹

$$K_{sp} = 0.039999 \times (4.42 \times 10^{-9}) = 1.77 \times 10^{-10}$$

11. Automatic acid/base titrators work using electrochemical principles learned in CHEM 154. The concentration of H^+ ions in an unknown acid can be determined as follows:

A. A constant current cathode generates OH-:

$$H_2O(l) + e^- \rightarrow \tfrac{1}{2} H_2(g) + OH^- (aq)$$

B. OH- ions neutralize H+ ions in the acidic solution:

$$H^+(aq) + OH^- (aq) \rightarrow H_2O(l)$$
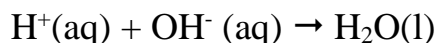
The pH of the solution is monitored over time using an acid/base indicator such as phenolphthalein. When the number of moles of H^+ ions is equal to the moles of OH^- ions generated, the pH increases rapidly and the reaction changes from colourless to pink.

To reach the endpoint, a student passed 30 mA of current for 70s through an aqueous solution (V = 50mL) containing an unknown concentration of HCl in a setup similar to the one shown. Calculate the concentration of HCl in the solution.

silver anode   carbon cathode

$$I = \frac{q}{t} \rightarrow 30 \times 10^{-3}A = 30 \times 10^{-3}\frac{C}{s} = \frac{q}{70s} \rightarrow q = 2.1C$$

$$2.1C \times \frac{1 \text{ mol } e^-}{96485 \text{ } C} = 2.176 \times 10^{-5} \text{ mol } e^-$$

$$= 2.176 \times 10^{-5} \text{ mol OH}^- = 2.176 \times 10^{-5} \text{ mol H}^+$$
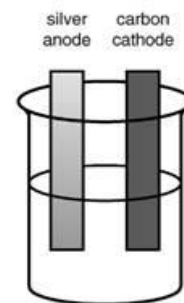
$$[H^+] = \frac{2.176 \times 10^{-5} \text{ mol H}^+}{50 \times 10^{-3}L} = 4.35 \times 10^{-4}M$$

12. **Good question.** Suppose our PEMFC is operated electrolytically, where a potential is applied in order to produce H_2 and O_2 gas so that you can drive your fuel cell car to and from school the next day. If the electrolytic cell draws a current of 0.775 A for 45.0 min, calculate the volume (in litres) of H_2 and O_2 produced if each gas is collected at 25 °C and p = 1.00 bar.

$$n_{electrons} = \frac{It}{F} = \frac{0.775 \text{ A} \times 45.0 \text{ min} \times \left(\frac{60 \text{ s}}{1 \text{ min}}\right)}{96485 \text{ C mol}^{-1}} = 2.168 \times 10^{-2} \text{ mol}$$

Convert to number of moles of H_2 and O_2 using stoichiometric relationship from half-reactions: (4 moles of electrons = 2 moles of H_2 and 1 mole of O_2)

$$n_{H_2} = (2.168 \times 10^{-2} \text{ mol e}^-)\left(\frac{2 \text{ mol } H_2}{4 \text{ mol e}^-}\right) = 1.084 \times 10^{-2} \text{ mol } H_2$$

$$n_{O_2} = (2.168 \times 10^{-2} \text{ mol e}^-)\left(\frac{1 \text{ mol } H_2}{4 \text{ mol e}^-}\right) = 0.5421 \times 10^{-2} \text{ mol } O_2$$

$$V_{H_2} = \frac{n_{H_2}RT}{P} = \frac{1.084 \times 10^{-2} \text{ mol} \times 0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}}{1.00 \text{ atm}}$$
$$= 0.265 \text{ L}$$

$$V_O = \frac{n_{O_2}RT}{P} = \frac{0.5421 \times 10^{-2} \text{ mol} \times 0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}}{1.00 \text{ atm}}$$
$$= 0.133 \text{ L}$$

13. **Good question.** Hydrogen gas can be a clean fuel when reacted with oxygen. Consider two possible ways of utilizing this reaction as an electrical energy source:

   A. Hydrogen and oxygen gases are combusted and used to drive a generator in a similar way as coal is currently used to produce electricity (operating temperature ~1000°C);

   B. Hydrogen and oxygen gases are combined as in the PEMFC, generating electricity in a fuel cell operating at 85 °C.

   a) Use the data provided to calculate $\Delta H°$ and $\Delta S°$ for the reaction of oxygen and hydrogen to produce water. Assume these values are temperature independent.

	$\Delta H°_f$ (kJ/mol)	$S_m°$ (J/mol K)
$H_2(g)$	0	130.6
$O_2(g)$	0	205.0
$H_2O(g)$	-258.8	69.91

Reaction is

$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l)$

$$\Delta H^0 = 2\ mol \times \Delta H_f^0(H_2O) - \left[2\ mol \times \Delta H_f^0(H_2) + 1\ mol \times \Delta H_f^0(O_2)\right]$$
$$= 2 \times (-285.8\ kJ) = -571.6\ kJ$$

$$\Delta S^0 = 2\ mol \times S_m^0(H_2O) - [2\ mol \times S_m^0(H_2) + 1\ mol \times S_m^0(O_2)] = 2 \times$$
$$69.91\ J\ K^{-1} - [2 \times 130.6\ J\ K^{-1} + 205.0\ J\ K^{-1}] = -326.38\ J\ K^{-1}$$

b) Based on the values calculated in part (a), what trend would you expect for the magnitude of ΔG^0 as the temperature increases?

$\Delta H°$ is negative and $\Delta S°$ is also negative. Knowing that

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

means the reaction will become less spontaneous at higher temperatures. In other words, the value for $\Delta G°$ will become more positive. The reaction is favoured at lower temperatures.

c) What is the significance of the change in the magnitude of ΔG with temperature with respect to the utility of hydrogen as a fuel?

Gibb's energy represents the ability to do useful work in a chemical reaction. If we are to use hydrogen as a fuel source, it makes sense to maximize the amount of work we can extract from the fuel. In this case, that means we should try and use temperatures as low as possible when using hydrogen as a fuel source.

d) Based on the analysis here, would it be more efficient to use the combustion method or the fuel-cell method to generate electrical energy from hydrogen?

Assuming the fuel-cell method is performed at a temperature significantly lower than the combustion method, it would be more efficient to generate electrical energy from hydrogen. This would have a greater (more negative) Gibb's energy that could be harnessed to perform work.