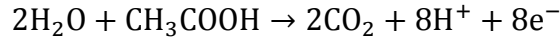
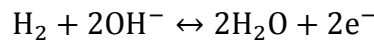
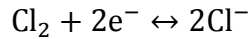


2.1 Write the associated electrochemical reactions and calculate the standard potential, U^θ from ΔG° for the following cells

- Chlor-alkali process to produce hydrogen and chlorine from a brine of NaCl (aqueous salt solution). Use the hydrogen reaction for an alkaline solution.
- Acetic acid/oxygen fuel cell with acidic electrolyte, where the acetic acid reacts to form liquid water and carbon dioxide. The reaction at the negative electrode is



a)



overall



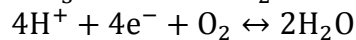
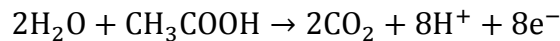
$$\Delta G_{Rx} = \Delta G_f^{\text{products}} - \Delta G_f^{\text{reactants}}$$

$$\Delta G_{Rx}^\circ = 2\Delta G_{f,\text{NaCl}}^\circ + 2\Delta G_{f,\text{H}_2\text{O}}^\circ - 2\Delta G_{f,\text{NaOH}}^\circ$$

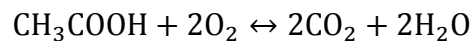
$$\Delta G_{Rx}^\circ = 2\{-393.1 - 237.19 - (-419.2)\} = -422.34 \text{ kJ mol}^{-1}$$

$$U^\theta = \frac{-\Delta G_{Rx}^\circ}{nF} = \frac{4223440}{(2)96485} = 2.188 \text{ V}$$

b) multiply second reaction by 2 to balance electrons and add together



overall

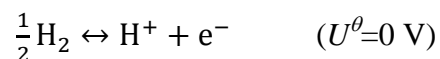
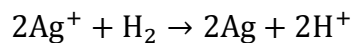


$$\Delta G_{Rx}^\circ = 2\Delta G_{f,\text{CO}_2}^\circ + 2\Delta G_{f,\text{H}_2\text{O}}^\circ - \Delta G_{f,\text{CH}_3\text{COOH}}^\circ$$

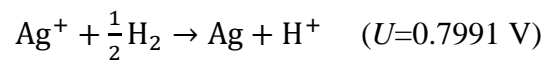
$$\Delta G_{Rx}^\circ = \{-(2)394.39 - (2)237.19 - (-389)\} = -874.18 \text{ kJ mol}^{-1}$$

$$U^\theta = \frac{-\Delta G_{Rx}^\circ}{nF} = \frac{874180}{(8)96485} = 1.113 \text{ V}$$

Does the redox reaction as written below proceed spontaneously at 25 °C and standard conditions?



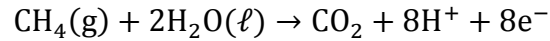
overall



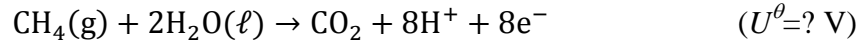
$$U^\theta = \frac{-\Delta G_{\text{Rx}}^\circ}{nF} = 0.7991 \text{ V}$$

Thus, ΔG is less than zero, and the reaction would proceed spontaneously as written at standard conditions.

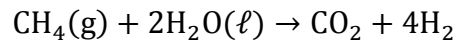
What is the standard half-cell potential for the oxidation of methane under acidic conditions?
The reaction for methane is as follows:



Which element is oxidized and how does its oxidation state change?



overall



Find the change in standard Gibbs energy of formation for the overall reaction

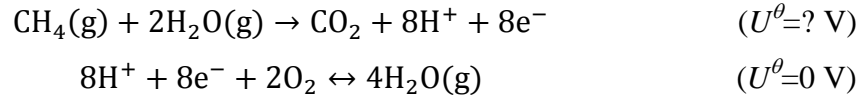
$$\Delta G_{Rx}^\circ = \Delta G_{f,\text{CO}_2}^\circ - 2\Delta G_{f,\text{H}_2\text{O}}^\circ - \Delta G_{f,\text{CH}_4}^\circ$$

$$\Delta G_{Rx}^\circ = \{-394.359 - 2(-237.19) - (-50.5)\} = -130.52 \text{ kJ mol}^{-1}$$

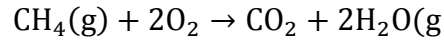
$$U^\theta = \frac{-\Delta G_{Rx}^\circ}{nF} = \frac{130520}{8F} = 0.1691 \text{ V}$$

The oxidation state of carbon changes.

What is the standard cell potential for a methane /oxygen fuel cell? The oxidation of methane produces CO_2 as shown in problem 2.3, but here assume the product water is a gas, rather than a liquid.



overall



Find the change in standard Gibbs energy of formation for the overall reaction

$$\Delta G_{Rx}^o = \Delta G_{f,\text{CO}_2}^o + 2\Delta G_{f,\text{H}_2\text{O}}^o - \Delta G_{f,\text{CH}_4}^o$$

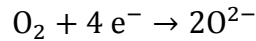
$$\Delta G_{Rx}^o = \{-394.359 + 2(-228.572) - (-50.5)\} = -801 \text{ kJ mol}^{-1}$$

$$U^\theta = \frac{-\Delta G_{Rx}^o}{nF} = \frac{801000}{8F} = 1.038 \text{ V}$$

Let's consider the oxidation of methane in a fuel cell that utilizes an oxygen conductor (O^{2-}) rather than a proton conductor as the electrolyte.

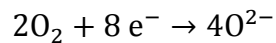
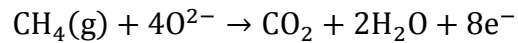
- At which electrode (oxygen or methane) is O^{2-} produced and at which is it consumed?
- In which direction does O^{2-} move through the electrolyte? Why?
- Propose two electrochemical half-cell reactions.
- Does U^θ change for this fuel cell relative to a fuel cell that utilizes a proton conductor? Why or why not?

a. O^{2-} is produced at the cathode; and O^{2-} is consumed at the anode

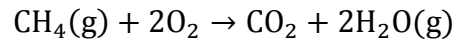


b. oxygen ions move from the cathode to the anode, since they are negatively charged this still represents a positive current from the anode to the cathode.

c.

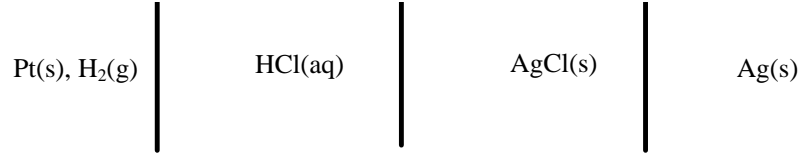


overall

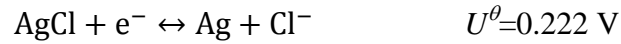


d. No, the standard potential depends on the overall reaction and the reference pressure, but since the overall reaction is the same regardless of the ion conductor.

Determine the equilibrium potential of the cell shown below.



The reaction at positive electrode (right) is



and for the negative (left)



overall



where the overall potential for the cell is the positive (right) – negative (left).

$$U = U^\theta_{\text{cell}} - \frac{RT}{nF} \ln \prod a_i^{s_i}, \quad (2-11)$$

$$U = U^\theta_{\text{cell}} - \frac{RT}{nF} \ln \frac{a_{\text{Ag}}^2 a_{\text{HCl}}^2}{a_{\text{H}_2} a_{\text{AgCl}}^2},$$

The activity of solids are assumed to be one, and $n=2$

$$U = U^\theta_{\text{cell}} + \frac{RT}{2F} \ln a_{\text{H}_2} - \frac{RT}{F} \ln a_{\text{HCl}},$$

Hydrogen is a gas, assume ideal

$$a_{\text{H}_2} = \frac{f_{\text{H}_2}}{f^\circ} = \frac{p_{\text{H}_2}}{p^\circ}$$

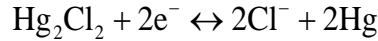
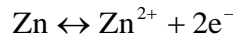
For the aqueous HCl

$$a_{\text{HCl}} = a_+^{v_+} a_-^{v_-} = m_+ \gamma_+ m_- \gamma_- = m^2 \gamma_\pm^2$$

substituting gives

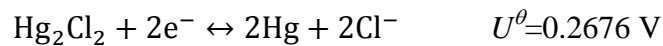
$$U = U^\theta_{\text{cell}} + \frac{RT}{2F} \ln \left(\frac{p_{\text{H}_2}}{p^\circ} \right) - \frac{2RT}{F} \ln (m \gamma_\pm)$$

Consider the electrochemical reactions shown below. Mercury(I) chloride, also known as *calomel*, is a solid used in reference electrodes. The two reactions are

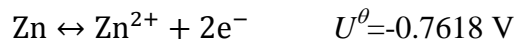


- What is the overall chemical reaction?
- Develop an expression for U , the equilibrium potential of the cell.
- Write down an expression for the standard potential of the cell in terms of the standard Gibbs energies of formation.
- Use standard half-cell potentials from the table to determine the standard Gibbs energy of formation for aqueous ZnCl_2 . Why is this value different than the value for solid ZnCl_2 ?
- What is the standard Gibbs energy of formation for Hg_2Cl_2 ?

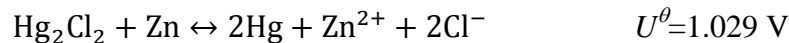
a) The reaction at positive electrode is



and for the negative



overall



b)

$$U = U^{\theta}_{\text{cell}} - \frac{RT}{nF} \ln \prod a_i^{s_i}, \quad (2-11)$$

$$U = U^{\theta}_{\text{cell}} - \frac{RT}{nF} \ln \frac{a_{\text{Hg}}^2 a_{\text{ZnCl}_2}}{a_{\text{Zn}} a_{\text{Hg}_2\text{Cl}_2}}$$

The activity of solid and liquid Hg are assumed to be one, and $n=2$

$$U = U^{\theta}_{\text{cell}} - \frac{RT}{2F} \ln a_{\text{ZnCl}_2},$$

$v_+ = 1, v_- = 2, v_{\pm} = 3$

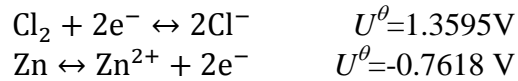
For the aqueous ZnCl_2

$$a_{\text{ZnCl}_2} = a_+^{v_+} a_-^{v_-} = m_+ \gamma_+ m_-^2 \gamma_-^2 = 4m^3 \gamma_{\pm}^3$$

substituting gives

$$U = U^{\theta}_{\text{cell}} - \frac{RT}{F} \ln 2 - \frac{3RT}{2F} \ln(m\gamma_{\pm})$$

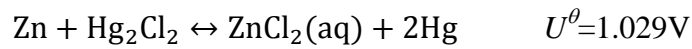
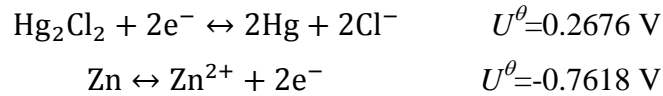
c,d) From the table of standard potentials



Given that the solids and liquids are in their standard state, we can right the change in Gibbs energy as

$$\Delta G_{Rx}^o = \Delta G_{f,ZnCl_2}^o = -nFU^\theta = -2(96485)(2.121\text{V}) = -409.3\text{ kJ}$$

e)



$$\Delta G_{Rx}^o = -nFU^\theta = -198,740\text{ J mol}^{-1}$$

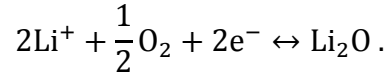
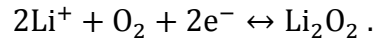
$$\Delta G_{Rx}^o = \Delta G_{f,ZnCl_2}^o - \Delta G_{f,Hg_2Cl_2}^o = -210.6\text{ kJ mol}^{-1}$$

The values are different because the standard states are different for a solid versus solution. There is some change in energy and entropy involved in the dissolution of the solid.

The lithium air cell offers the possibility of a very high energy battery. At the negative electrode,

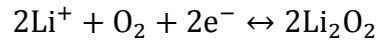


At the positive electrodes the following reactions are postulated



Estimate the standard potential for each of the two possible reactions at the positive electrode paired with a lithium anode.

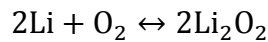
The reaction at positive electrode is



and for the negative



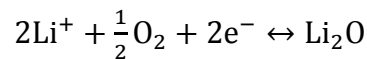
overall



$$\Delta G_{Rx}^o = \Delta G_{f,\text{Li}_2\text{O}_2}^o = -571.116 \text{ kJ} = -nFU^\theta$$

$$U^\theta = \frac{-\Delta G_{Rx}^o}{nF} = \frac{-571116}{2F} = \boxed{2.96 \text{ V}}$$

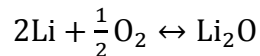
For the second reaction, at the positive electrode is



and for the negative



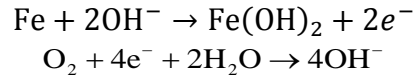
overall



$$\Delta G_{Rx}^o = \Delta G_{f,\text{Li}_2\text{O}}^o = -561.2 \text{ kJ} = -nFU^\theta$$

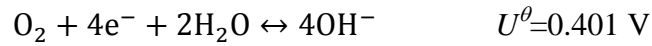
$$U^\theta = \frac{-\Delta G_{Rx}^o}{nF} = \frac{-561200}{2F} = \boxed{2.91 \text{ V}}$$

Develop an expression for the equilibrium potential for the cell below. The first reaction is the negative electrode of the Edison cell (battery).

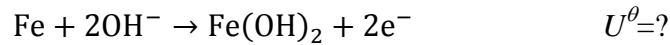


The Gibbs energy of formation for $\text{Fe}(\text{OH})_2$ is -486.6 kJ/mol .

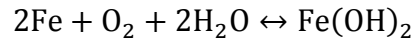
The reaction at positive electrode is



and for the negative



overall



$$U = U^\theta_{\text{cell}} - \frac{RT}{nF} \ln \prod a_i^{s_i}, \quad (2-11)$$

$$U = U^\theta_{\text{cell}} - \frac{RT}{nF} \ln \frac{a_{\text{Fe}(\text{OH})_2}^2}{a_{\text{Fe}}^2 a_{\text{O}_2} a_{\text{H}_2\text{O}}^2},$$

$$U = U^\theta_{\text{cell}} + \frac{RT}{2F} \ln a_{\text{H}_2\text{O}} + \frac{RT}{4F} \ln \left(\frac{p_{\text{O}_2}}{p^\circ} \right)$$

$$U^\theta = \frac{-\Delta G_{\text{Rx}}^\circ}{nF}$$

$$\Delta G_{\text{Rx}}^\circ = 2\Delta G_{f,\text{Fe}(\text{OH})_2}^\circ - 2\Delta G_{\text{H}_2\text{O}}^\circ = 2\{-486,600 - (-237,2 = 129)\} = -499.5 \text{ kJ mol}^{-1}$$

$$U^\theta = \frac{-\Delta G_{\text{Rx}}^\circ}{nF} = \frac{499500}{(4)96485} = 1.29 \text{ V}$$

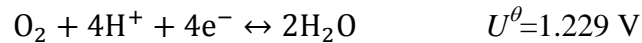
$$U = 1.29 + \frac{RT}{2F} \ln a_{\text{H}_2\text{O}} + \frac{RT}{4F} \ln \left(\frac{p_{\text{O}_2}}{p^\circ} \right)$$

Develop an expression for the equilibrium potential of a hydrogen-oxygen fuel cell operating under acidic conditions. The two electrochemical reactions are



Use the data in the Appendix C for standard Gibbs energy of formation. Compare with the value calculated from standard electrode potentials to identify whether the standard state for water in the table of Appendix A is liquid or gas.

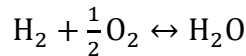
The reaction at positive electrode is



and for the negative



overall



$$U = U^\theta_{\text{cell}} - \frac{RT}{nF} \ln \prod a_i^{s_i}, \quad (2-11)$$

$$U = U^\theta_{\text{cell}} + \frac{RT}{nF} \ln \frac{a_{\text{O}_2}^{1/2} a_{\text{H}_2}}{a_{\text{H}_2\text{O}}}$$

$$U = U^\theta_{\text{cell}} + \frac{RT}{2F} \ln \frac{\left(\frac{p_{\text{H}_2}}{p^\theta}\right) \left(\frac{p_{\text{O}_2}}{p^\theta}\right)^{0.5}}{a_{\text{H}_2\text{O}}}$$

$$U^\theta = \frac{-\Delta G_{Rx}^\circ}{nF} = 1.229 \text{ V, where } n=2$$

Therefore, $\Delta G_{Rx}^\circ = -nFU^\theta = -2(96485)1.229 = -237 \text{ kJ mol}^{-1}$

From the Appendix C

liquid	$\Delta G_{f,\text{H}_2\text{O}}^\circ = -237 \text{ kJ mol}^{-1}$
--------	--

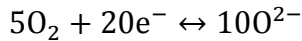
gas $\Delta G_{f,\text{H}_2\text{O}}^\circ = -229 \text{ kJ mol}^{-1}$

Thus, the 1.229 V corresponds to liquid water

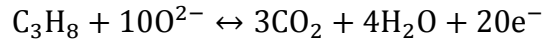
Write the associated electrochemical reactions, and calculate the standard potential, U^θ , from ΔG° for the following cells

- Propane fuel cell with solid oxygen conductor electrolyte
- Electrolysis of aluminum, where aluminum is produced from Al_2O_3 and carbon. Note that carbon is oxidized at the anode.

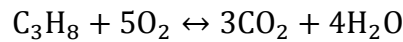
a) The reaction at positive electrode is



and for the negative



overall



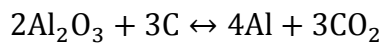
Since the oxygen ion does not appear in the overall reaction, the standard potential does not depend on its activity.

$$\Delta G_{Rx}^\circ = -nFU^\theta = 3\Delta G_{f,\text{CO}_2}^\circ + 4\Delta G_{f,\text{H}_2\text{O}}^\circ - \Delta G_{f,\text{C}_3\text{H}_8}^\circ$$

$$\Delta G_{Rx}^\circ = -nFU^\theta = 3(-394.3) + 4(-228.6) - (-24.3) = -2070 \text{ kJ mol}^{-1}$$

$$U^\theta = \frac{-2,070,000}{20F} = 1.074 \text{ V}$$

b) The overall reaction is

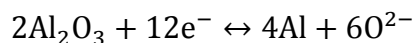
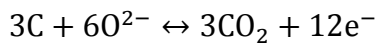


$$\Delta G_{Rx}^\circ = -nFU^\theta = 3\Delta G_{f,\text{CO}_2}^\circ - 2\Delta G_{f,\text{Al}_2\text{O}_3}^\circ$$

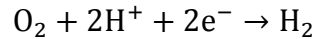
$$\Delta G_{Rx}^\circ = -nFU^\theta = 3(-394.3) - 2(-1582.3)$$

$$U^\theta = \frac{-1,981,500}{12F} = 1.711 \text{ V}$$

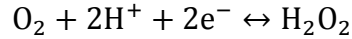
The actual reactions are complex, here is one set of reactions



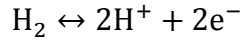
Calculate the equilibrium potential for peroxide formation in an acid fuel cell



The reaction at positive electrode is

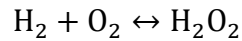


and for the negative



$$U^\theta = 0 \text{ V}$$

overall



Therefore for liquid peroxide

$$\Delta G_{Rx}^\circ = \Delta G_{f,H_2O_2}^\circ = -120.42 \text{ kJ mol}^{-1}$$

$$U_{\text{cell}}^\theta = \frac{-\Delta G_{Rx}^\circ}{nF} = \frac{120,420}{2F} = 0.624 \text{ V}$$

Alternatively, if peroxide is formed as an aqueous solution

$$\Delta G_{Rx}^\circ = \Delta G_{f,H_2O_2}^\circ = -134.1 \text{ kJ mol}^{-1}$$

$$U_{\text{cell}}^\theta = \frac{-\Delta G_{Rx}^\circ}{nF} = \frac{134,097}{2F} = 0.695 \text{ V}$$

From the Appendix C
liquid

$$\Delta G_{f,H_2O_2}^\circ = -120.4 \text{ kJ mol}^{-1}$$

aqueous solution

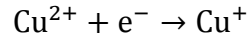
$$\Delta G_{f,H_2O_2}^\circ = -134.1 \text{ kJ mol}^{-1}$$

Value not in appendix

Use the half-cell reactions for the reduction of cupric ion (Cu^{2+}) to copper metal and cuprous ion (Cu^+) to copper metal to calculate the standard potential for the reduction of cupric ion to cuprous ion. Check your answer against the value given in Appendix A.



Subtract the second reaction from the first to get the desired reaction

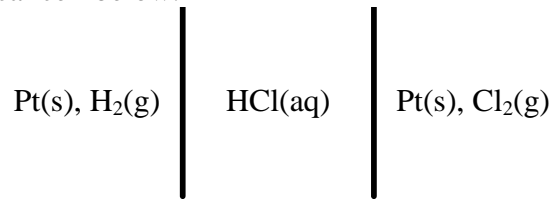


Because the electrons per copper atom are not the same for the two reactions, we need to use the ΔG method, we can't just subtract the two standard potentials.

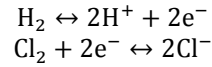
$$\begin{aligned} \Delta G_3^\theta &= \Delta G_1^\theta - \Delta G_2^\theta \\ -FU_3^\theta &= -2FU_1^\theta - (-FU_2^\theta) \\ U_3^\theta &= 2(0.337) - (0.521) = \boxed{0.153 \text{ V}} \end{aligned}$$

This is same value tabulated in Appendix A.

Consider the electrochemical cell below.



The two reactions are



Find an expression for U . If the pressure of hydrogen is 250 kPa and that of chlorine is 150 kPa, what is the numerical value of U at 25 °C in one molal HCl? Include the simplified activity corrections (you may neglect activity coefficients).

The equilibrium potential for the chlorine reaction is 1.3595 V, which is the standard cell potential. The overall reaction is



$$U = U_{\text{cell}}^{\theta} - \frac{RT}{nF} \ln \prod a_i^{s_i}, \quad (2-11)$$

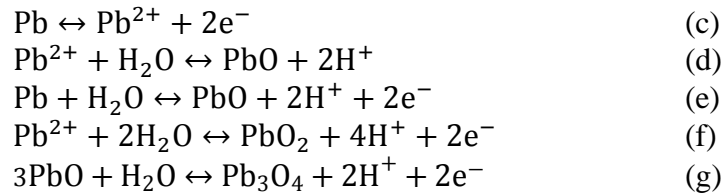
$$U = U_{\text{cell}}^{\theta} - \frac{RT}{nF} \ln \frac{a_{\text{HCl}}^2}{a_{\text{H}_2} a_{\text{Cl}_2}},$$

$$U = 1.3595 - \frac{RT}{F} \ln a_{\text{HCl}} + \frac{RT}{2F} \ln \left(\frac{p_{\text{Cl}_2}}{p^o} \right) \left(\frac{p_{\text{H}_2}}{p^o} \right),$$

for a 1 molal solution, the activity is one assuming that $\gamma_{\pm}=1$

$$U = 1.3595 + \frac{RT}{2F} \ln \left(\frac{150}{100} \right) \left(\frac{250}{100} \right) = \boxed{1.376 \text{ V}}$$

Create a Pourbaix diagram for Pb. Treat the following reactions



from text in Chapter 2

$$U_a = -\frac{RT}{2F} \ln \frac{1}{\left(\frac{c_{\text{H}^+}}{c^\circ}\right)^2} = \frac{RT}{F} \ln \left(\frac{c_{\text{H}^+}}{c^\circ}\right) = -\frac{RT}{F} 2.303 \text{ pH} = -0.0592 \text{ pH} \quad \text{(a)}$$

$$U_b = U_{b/\text{SHE}}^\theta - \frac{RT}{F} 2.303 \text{ pH} = 1.229 - 0.0592 \text{ pH}, \quad \text{(b)}$$

For the first reaction, (c)



$$U_c = U_{c/\text{SHE}}^\theta - \frac{RT}{nF} \ln \frac{c^\circ}{c_{\text{Pb}^{2+}}}$$

$$U_c = -0.126 + 2.303 \frac{RT}{2F} \log[\text{Pb}^{2+}]$$

Assume the concentration of lead ion is 10^{-6} M,

$$U_c = -0.126 + 2.303 \frac{RT}{2F} (-6) = -0.304 \text{ V}$$

The second reaction (d) is a chemical equilibrium

$$K_{sp} = \frac{(a_{\text{Pb}^{2+}})(a_{\text{H}_2\text{O}})}{(a_{\text{PbO}})(a_{\text{H}^+}^2)} = e^{\frac{nFU^\theta}{RT}}$$

$$a_{\text{H}_2\text{O}} = a_{\text{PbO}} = 1, n=2$$

Obtain Gibbs energy of formation from Appendix C

$$\Delta G_{f,\text{Pb}^{2+}}^\circ = -24.39 \text{ kJ mol}^{-1}$$

$$\Delta G_{f,\text{PbO}}^\circ = -187.9 \text{ kJ mol}^{-1}$$

$$\Delta G_{f,\text{H}_2\text{O}}^\circ = -237.129 \text{ kJ mol}^{-1}$$

$$\Delta G_{\text{Rx}}^\circ = (-187.9) - (-24.39) - (-237.129) = 73.619 \text{ kJ}$$

$$U^\theta = \frac{-\Delta G_{Rx}^\circ}{nF} = \frac{73,619}{(2)96485} = 0.382 \text{ V}$$

$$K_{sp} = \frac{(a_{\text{Pb}^{2+}})}{(a_{\text{H}^+}^2)} = e^{\frac{nFU^\theta}{RT}} = 8.22 \times 10^{12}$$

$$a_{\text{Pb}^{2+}} = 10^{-6}, \text{ and } pH = \log(a_{\text{H}^+})$$

$$a_{\text{H}^+}^2 = \frac{10^{-6}}{8.22 \times 10^{12}}$$

$$a_{\text{H}^+} = 3.49 \times 10^{-10}$$

$$pH = \log(a_{\text{H}^+}) = 9.46$$

Reaction (e)

$$U_e = U_{d/\text{SHE}}^\theta - \frac{RT}{nF} \ln \frac{(a_{\text{Pb}})(a_{\text{H}_2\text{O}})}{(a_{\text{H}^+}^2)(a_{\text{PbO}})}$$

$$a_{\text{PbO}} = a_{\text{Pb}} = a_{\text{H}_2\text{O}} = 1$$

$$U_e = U_{e/\text{SHE}}^\theta + \frac{2.303RT}{F} \log(a_{\text{H}^+}) = U_{e/\text{SHE}}^\theta - \frac{2.303RT}{F} pH$$

Use Gibbs energy of formation to obtain the standard potential

$$\Delta G_{Rx}^\circ = (-237.129) - (-187.9) = -nFU_e^\theta$$

$$U_e^\theta = 0.255 \text{ V}$$

$$U_e = 0.255 - 0.0592pH$$

Reaction (f)

Use Gibbs energy of formation to obtain the standard potential

$$\Delta G_{Rx}^\circ = (-24.39) + 2(-237.129) - (-217.3) = -nFU_f^\theta$$

$$n=2,$$

$$U_f^\theta = \frac{-\Delta G_{Rx}^\circ}{nF} = 1.458 \text{ V}$$

$$U_f = U_{f/\text{SHE}}^\theta - \frac{RT}{nF} \ln \frac{(a_{\text{Pb}^{2+}})(a_{\text{H}_2\text{O}}^2)}{(a_{\text{H}^+}^4)(a_{\text{PbO}_2})}$$

$$a_{\text{PbO}_2} = a_{\text{H}_2\text{O}} = 1, \text{ and } a_{\text{Pb}^{2+}} = 10^{-6}$$

$$U_f = U_{f/SHE}^{\theta} - \frac{RT}{2F} \ln(10^{-6}) + \frac{2RT}{F} \ln(a_{H^+})$$

$$U_f = 1.458 + 0.1775 + \frac{2RT}{F} \ln(a_{H^+})$$

$$U_f = 1.6355 - 0.1183\text{pH}$$

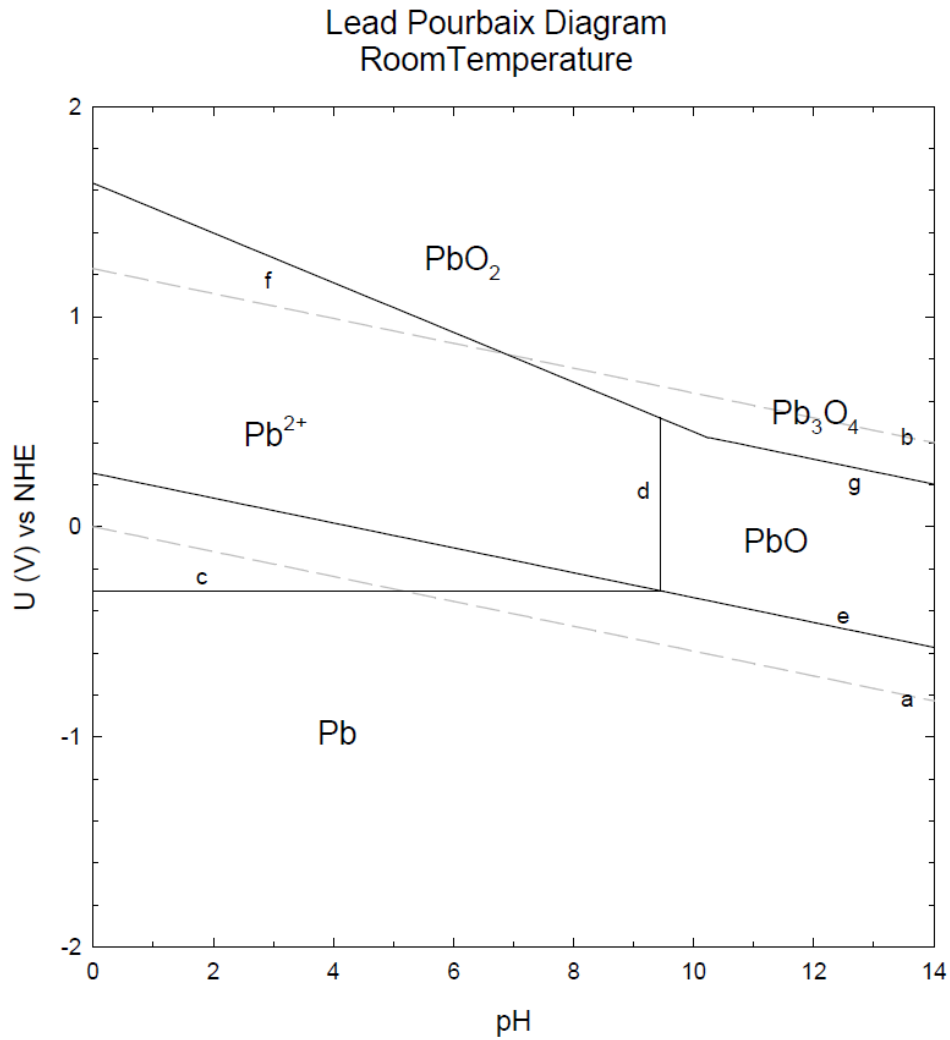
Reaction (g)

$$\Delta G_{Rx}^{\circ} = 3(-187.9) + (-237.129) - (-601.7) = -nFU_g^{\theta}$$

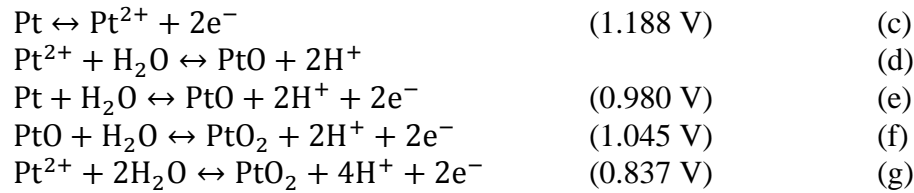
$$U_g^{\theta} = \frac{-\Delta G_{Rx}^{\circ}}{2F} = 1.032 \text{ V}$$

$$U_g = U_g^{\theta} + \frac{RT}{F2} \ln(a_{H^+})$$

$$U_g = 1.032 - 0.0592\text{pH}$$



Create a Pourbaix diagram for Pt. Focus on the low pH range ($-2 \leq \text{pH} \leq 1$), and consider the following reactions.



from text in Chapter 2

$$U_a = -\frac{RT}{2F} \ln \frac{1}{\left(\frac{c_{\text{H}^+}}{c^\circ}\right)^2} = \frac{RT}{F} \ln \left(\frac{c_{\text{H}^+}}{c^\circ}\right) = -\frac{RT}{F} 2.303 \text{ pH} = -0.0592 \text{ pH} \quad \text{(a)}$$

$$U_b = U_{b/\text{SHE}}^\theta - \frac{RT}{F} 2.303 \text{ pH} = 1.229 - 0.0592 \text{ pH}, \quad \text{(b)}$$

For the first reaction, (c)



$$U_c = U_c^\theta - \frac{RT}{nF} \ln \frac{c^\circ}{c_{\text{Pt}^{2+}}}$$

$$U_c = 1.188 + 2.303 \frac{RT}{2F} \log[\text{Pt}^{2+}]$$

Assume the concentration of platinum ion is 10^{-6} M ,

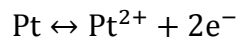
$$U_c = 1.011 \text{ V}$$

The second reaction (d) is a chemical equilibrium

$$K_{sp} = \frac{(a_{\text{Pt}^{2+}})(a_{\text{H}_2\text{O}})}{(a_{\text{PtO}})(a_{\text{H}^+}^2)} = \frac{(a_{\text{Pt}^{2+}})}{(a_{\text{H}^+}^2)} = e^{\frac{nFU^\theta}{RT}}$$

$$a_{\text{H}_2\text{O}} = a_{\text{PtO}} = 1, n=2$$

This equilibrium reaction (d) is the difference of



$$U^\theta = 0.980 - 1.188 = -0.208 \text{ V}$$

Using the equation above for K_{sp} and the definition of pH,

$$\text{pH} = \frac{1}{2} \left\{ \frac{nFU^\theta}{2.303RT} \right\} - \log[\text{Pt}^{2+}] = -0.516$$

Reaction (e)

$$U_e = U_e^\theta + \frac{RT}{F} \ln(a_{\text{H}^+})$$

$$U_e = 0.980 + 2.303 \frac{RT}{F} \log(a_{\text{H}^+})$$

$$U_e = 0.980 - 0.0592 \text{ pH}$$

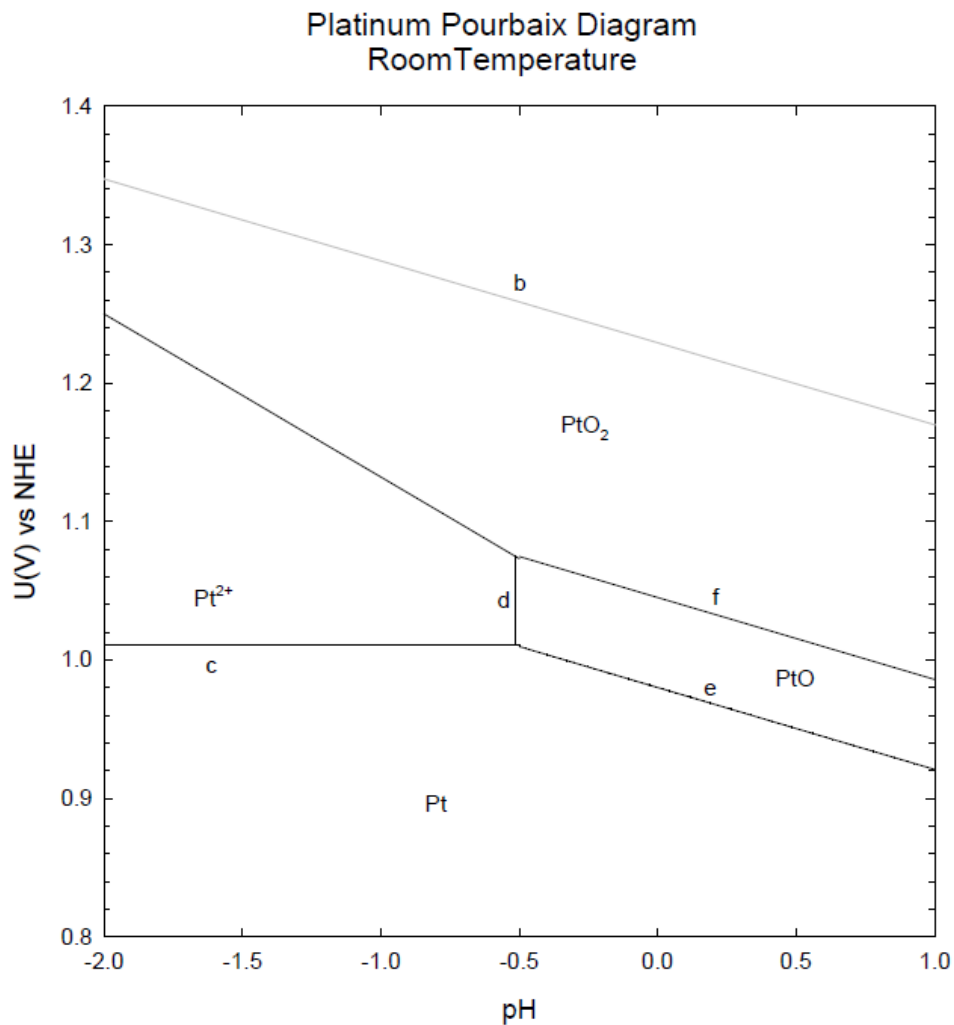
Reaction (f), same approach as for reaction (e)

$$U_f = 1.045 - 0.0592 \text{ pH}$$

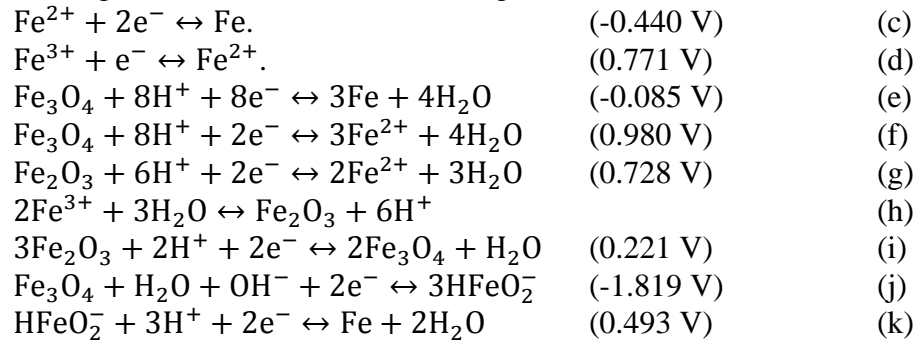
Reaction (g)

$$U_g = U_g^\theta - \frac{RT}{2F} \ln[10^{-6}] + 2.303 \frac{4RT}{2F} \log(a_{\text{H}^+})$$

$$U_g = 1.014 - 0.118 \text{ pH}$$



Create a Pourbaix diagram for Fe. Treat the following reactions



from text in Chapter 2

$$U_a = -\frac{RT}{2F} \ln \frac{1}{\left(\frac{c_{\text{H}^+}}{c^o}\right)^2} = \frac{RT}{F} \ln \left(\frac{c_{\text{H}^+}}{c^o}\right) = -\frac{RT}{F} 2.303 \text{ pH} = -0.0592 \text{ pH} \quad (\text{a})$$

$$U_b = U_{b/\text{SHE}}^{\theta} - \frac{RT}{F} 2.303 \text{ pH} = 1.229 - 0.0592 \text{ pH}, \quad (\text{b})$$

For the first reaction, (c)



$$U_c = U_c^{\theta} - \frac{RT}{nF} \ln \frac{c^o}{c_{\text{Fe}^{2+}}}$$

$$U_c = -0.440 + 2.303 \frac{RT}{2F} \log[\text{Fe}^{2+}]$$

Assume the concentration of iron ion is 10^{-6} M,

$$U_c = -0.6175 \text{ V}$$

For the second reaction, (d)



$$U_d = U_d^{\theta} - \frac{RT}{nF} \ln \frac{c_{\text{Fe}^{2+}}}{c_{\text{Fe}^{3+}}}$$

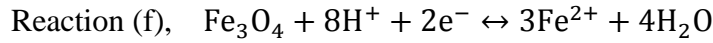
if the concentration of iron (II) and iron (III) are the same

$$U_d = U_d^{\theta} = 0.771 \text{ V}$$

Reaction (e) $\text{Fe}_3\text{O}_4 + 8\text{H}^+ + 8\text{e}^- \leftrightarrow 3\text{Fe} + 4\text{H}_2\text{O}$

$$U_e = U_e^{\theta} + \frac{RT}{F} \ln(a_{\text{H}^+})$$

$$U_e = -0.085 - 0.0592 \text{ pH}$$

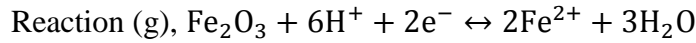


$$U_f = U_f^\theta - \frac{RT}{nF} \ln \frac{(a_{\text{Fe}^{2+}}^3)(a_{\text{H}_2\text{O}}^4)}{(a_{\text{H}^+}^8)}$$

$$U_f = U_f^\theta - 0.0296 \log(a_{\text{Fe}^{2+}}^3) + 0.0296 \log(a_{\text{H}^+}^8)$$

$$U_f = U_f^\theta - 0.0887 \log[\text{Fe}^{2+}] - 0.2366 \text{ pH}$$

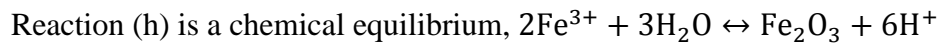
$$U_f = 1.5124 - 0.2366 \text{ pH}$$



$$U_g = U_g^\theta - \frac{RT}{2F} \ln \frac{(a_{\text{Fe}^{2+}}^2)(a_{\text{H}_2\text{O}}^3)}{(a_{\text{H}^+}^6)}$$

$$U_g = 0.728 - 0.592 \log[10^{-6}] - 0.1775 \text{ pH}$$

$$U_g = 1.083 - 0.1775 \text{ pH}$$

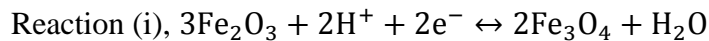


$$K_{sp} = \frac{(a_{\text{Fe}^{3+}}^2)(a_{\text{H}_2\text{O}}^3)}{(a_{\text{H}^+}^6)} \approx \frac{(a_{\text{Fe}^{3+}}^2)}{(a_{\text{H}^+}^6)} = e^{\frac{nFU^\theta}{RT}}$$

$a_{\text{H}_2\text{O}} = 1$, $n=2$ From, equilibrium data $U^\theta = -0.043 \text{ V}$ (reactions d and g)

$$2 \ln(a_{\text{Fe}^{2+}}) - 6 \ln(a_{\text{H}^+}) = \frac{2FU^\theta}{RT}$$

$$\text{pH} = \frac{FU^\theta}{(2.303)3RT} - \frac{1}{3} \log[10^{-6}] = 1.76$$



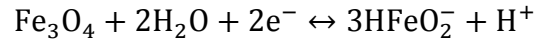
$$U_i = U_i^\theta - \frac{RT}{nF} \ln \frac{1}{(a_{\text{H}^+}^2)}$$

$$U_i = 0.221 - 0.0592 \text{ pH}$$

Reaction (j), $\text{Fe}_3\text{O}_4 + \text{H}_2\text{O} + \text{OH}^- + 2e^- \leftrightarrow 3\text{HFeO}_2^-$

add this reaction to $\text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{OH}^-$

which results in a form of the same equation in terms of the proton activity



$$U_j = U_j^\theta - \frac{RT}{nF} \ln \frac{(a_{\text{HFeO}_2^-})^3}{(a_{\text{H}^+})}$$

$$U_i = -1.819 - 0.0887 \log[10^{-6}] - 0.0295 \text{ pH}$$

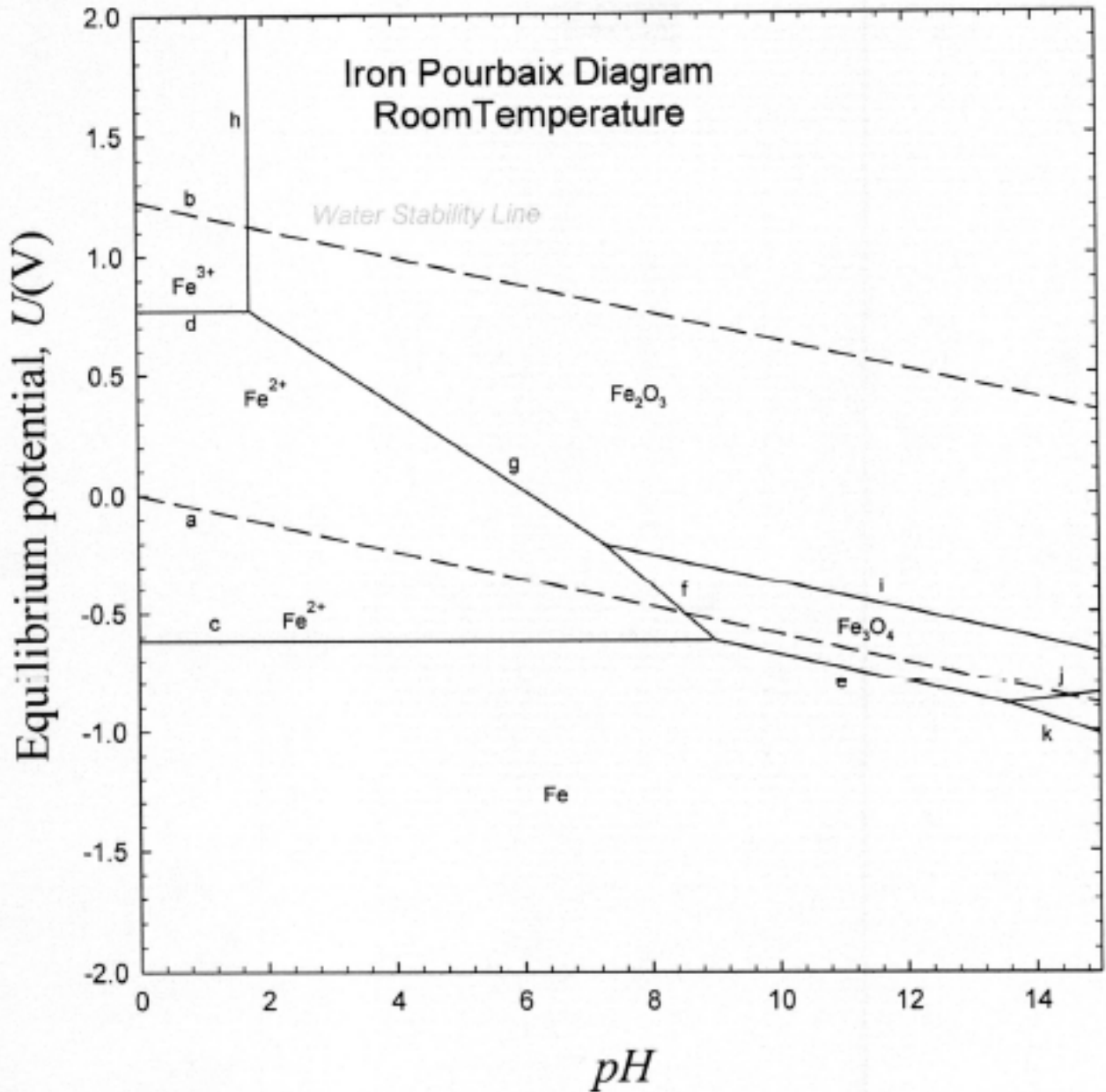
$$U_i = -1.2869 - 0.0295 \text{ pH}$$

Reaction (k), $\text{HFeO}_2^- + 3\text{H}^+ + 2e^- \leftrightarrow \text{Fe} + 2\text{H}_2\text{O}$

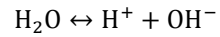
$$U_k = U_k^\theta - \frac{RT}{nF} \ln \frac{1}{(a_{\text{HFeO}_2^-})(a_{\text{H}^+})^3}$$

$$U_i = 0.493 + 0.0295 \log[10^{-6}] - 0.0886 \text{ pH}$$

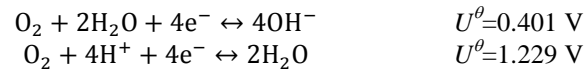
$$U_i = 0.316 - 0.0886 \text{ pH}$$



Use the information in Appendix A to determine the dissociation constant for water, K_w .



Use entries 4 and 9 from Appendix A

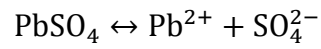


$$\frac{nFU^\theta}{RT} = \ln \frac{(a_{\text{H}^+})(a_{\text{OH}^-})}{a_{\text{H}_2\text{O}}}$$

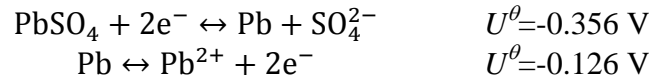
$$K_w = \frac{(a_{\text{H}^+})(a_{\text{OH}^-})}{a_{\text{H}_2\text{O}}} \approx (a_{\text{H}^+})(a_{\text{OH}^-}) = e^{\frac{nFU^\theta}{RT}} = e^{\frac{F(0.401-1.229)}{RT}} = \boxed{10^{-14}}$$

Determine the solubility product K_{sp} for PbSO_4 .

The desired equilibrium is



We can write this as the sum of two electrochemical equations



$$K = e^{\frac{nFU^\theta}{RT}} = e^{\frac{2F(-0.356+0.126)}{RT}} = 1.67 \times 10^{-8}$$

PROBLEM 2-21

$$U1 = 0.153 \text{ [V] oxidation of Cu}$$

$$U2 = 0.521 \text{ [V] oxidation of Cu}^+$$

$$K = \exp \left[F \cdot \left(\frac{U1 - U2}{R \cdot T} \right) \right]$$

$$R = 8.314 \text{ [J/mol-K]}$$

$$T = 298.15 \text{ [K]}$$

$$F = 96485 \text{ [Coulomb/mol]}$$

SOLUTION

Unit Settings: SI C kPa kJ mass deg

$$F = 96485 \text{ [Coulomb/mol]}$$

$$T = 298.2 \text{ [K]}$$

$$\frac{K = 6.014E-07}{U1 = 0.153 \text{ [V]}}$$

$$R = 8.314 \text{ [J/mol-K]}$$

$$U2 = 0.521 \text{ [V]}$$

No unit problems were detected.



$$U_1^\ominus = 0.153 \text{ V}$$



$$U_2^\ominus = 0.521 \text{ V}$$

Subtract to get



$$K = \exp \frac{F}{RT} (U_1^\ominus - U_2^\ominus) = \underline{\underline{6 \times 10^{-7}}}$$

at 298 K

Explain what a liquid junction is and why the potential of cells with liquid junctions cannot be determined from thermodynamics alone.

In many electrochemical cells, the two electrodes are exposed to solutions of different composition. Since an ionic path must exist between the two electrodes, diffusion of ions from across the region of non-uniform composition can occur even in the absence of current flow. A small potential difference is associated with this liquid junction. Thermodynamics analysis, however, assumes that the system is in equilibrium, which is not valid when transport across this liquid junction is present. To account for small correction in potential associated with this liquid junction, transport must be treated.

PROBLEM 2-22

$$c = 100 \text{ [mol/m}^3\text{]} \text{ concentration of lithium salt}$$

$$\rho = 1286 \text{ [kg/m}^3\text{]} \text{ density of electrolyte}$$

basis of 1 m3 of electrolyte

$$m = \frac{c}{\rho - c \cdot MW}$$

$$MW = 0.1519 \text{ [kg/mol]}$$

Calculate Debye length

$$R = 8.314 \text{ [J/mol-K]}$$

$$T = 303.15 \text{ [K]}$$

$$F = 96485 \text{ [coulomb/mol]}$$

$$dc = 64$$

$$\rho = 8.85419 \times 10^{-12} \text{ [coulomb/(V-m)]}$$

$$\varepsilon = dc \cdot \rho$$

$$\text{sum} = 2 \cdot c$$

$$\lambda = \sqrt{\varepsilon \cdot R \cdot \frac{T}{F \cdot F \cdot \text{sum}}}$$

convert molality to ionic strength, 1:1 electrolyte, no change

ACTIVITY COEFFICIENT

solvent constants

$$e = 1.6 \times 10^{-19} \text{ [coulomb]}$$

$$\rho_s = 1205 \text{ [kg/m}^3\text{]}$$

$$\alpha = \sqrt{\rho_s} \cdot \frac{F \cdot F \cdot e \cdot \sqrt{2}}{8 \cdot \pi \cdot [\varepsilon \cdot R \cdot T]^{1.5}}$$

$$I = m$$

$$Ba = 1 \text{ [(kg/mol)}^{0.5}\text{]}$$

$$\ln[\gamma] = \frac{-\alpha \cdot \sqrt{I}}{1 + Ba \cdot \sqrt{I}}$$

SOLUTION

Unit Settings: SI C kPa kJ mass deg

$$\alpha = 1.705 \text{ [(kg/mol)}^{0.5}\text{]}$$

$$Ba = 1 \text{ [(kg/mol)}^{0.5}\text{]}$$

$$c = 100 \text{ [mol/m}^3\text{]}$$

$$dc = 64$$

$$e = 1.600\text{E-}19 \text{ [coulomb]}$$

$$\varepsilon = 5.667\text{E-}10 \text{ [Coulomb/(V-m)]}$$

$$F = 96485 \text{ [coulomb/mol]}$$

$$\gamma = 0.6884$$

$$I = 0.07869 \text{ [mol/kg]}$$

$$\lambda = 8.758\text{E-}10 \text{ [m]}$$

$$m = 0.07869 \text{ [mol/kg]}$$

$$MW = 0.1519 \text{ [kg/mol]}$$

$$\rho = 8.854\text{E-}12 \text{ [coulomb/(V-m)]}$$

$$R = 8.314 \text{ [J/mol-K]}$$

$$\rho = 1286 \text{ [kg/m}^3\text{]}$$

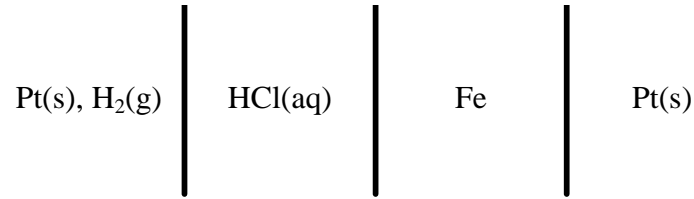
$$\rho^s = 1205 \text{ [kg/m}^3\text{]}$$

$$\text{sum} = 200 \text{ [mol/m}^3\text{]}$$

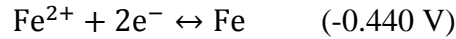
$$T = 303.2 \text{ [K]}$$

No unit problems were detected.

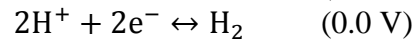
Consider the electrochemical cell below. Iron corrodes to form Fe^{2+} . Develop an expression for U , and determine the value of the standard potential.



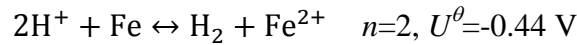
At the negative electrode



Positive



The overall reaction is



$$U = U_{\text{cell}}^\theta - \frac{RT}{nF} \ln \prod a_i^{s_i}, \quad (2-11)$$

$$U = U_{\text{cell}}^\theta - \frac{RT}{2F} \ln \frac{a_{\text{H}_2} a_{\text{Fe}^{2+}}}{a_{\text{H}^+}^2},$$

$$U = 0.440 - \frac{RT}{2F} \ln \left(\frac{p_{\text{H}_2}}{p^\circ} \right) - \frac{RT}{2F} \ln \frac{a_{\text{Fe}^{2+}}}{a_{\text{H}^+}^2},$$

This is not the desired form, we'd like to have this expression in terms of common, measurable activity coefficients: $m_{\text{FeCl}_2} \gamma_{\text{FeCl}_2}$.

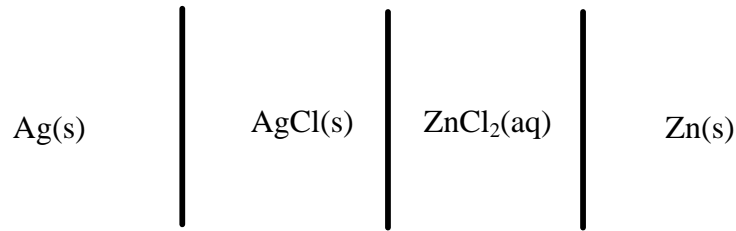
$$\text{HCl} \quad a_{\text{HCl}} = (a_{\text{H}^+})(a_{\text{Cl}^-})$$

$$a_{\text{FeCl}_2} = (a_{\text{Fe}^{2+}})(a_{\text{Cl}^-}^2)$$

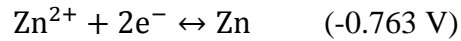
$$\frac{a_{\text{Fe}^{2+}}}{a_{\text{H}^+}^2} = \frac{a_{\text{FeCl}_2}}{a_{\text{HCl}}^2} = \frac{4(\gamma_{\mp}^{\text{FeCl}_2} m_{\text{FeCl}_2})^3}{1(\gamma_{\mp}^{\text{HCl}} m_{\text{HCl}})^4}$$

$$U = 0.440 - \frac{RT}{2F} \ln \left(\frac{p_{\text{H}_2}}{p^\circ} \right) - \frac{RT}{F} \ln(2) - \frac{3RT}{2F} (\ln \gamma_{\mp}^{\text{FeCl}_2} m_{\text{FeCl}_2}) + \frac{2RT}{F} (\gamma_{\mp}^{\text{HCl}} m_{\text{HCl}})$$

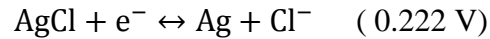
Find the expression for the equilibrium potential of the cell at 25 °C.



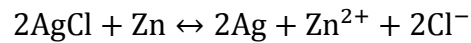
At the negative electrode



Positive



The overall reaction is



$$U_{\text{cell}}^{\theta} = U_{+}^{\theta} - U_{-}^{\theta} = 0.222 + 0.763 = 0.985 \text{ V}$$

$$U = U_{\text{cell}}^{\theta} - \frac{RT}{nF} \ln \prod a_i^{s_i}, \quad (2-11)$$

$$U = U_{\text{cell}}^{\theta} - \frac{RT}{2F} \ln a_{\text{ZnCl}_2} = U_{\text{cell}}^{\theta} - \frac{RT}{2F} \ln 4 \left(\gamma_{\mp}^{\text{ZnCl}_2} m_{\text{ZnCl}_2} \right)^3$$

$$U = 0.985 - \frac{RT}{F} \ln(2) - \frac{3}{2} \frac{RT}{F} \ln m \gamma_{\mp}$$

"!PROBLEM 2-25"

$$I1=0.1$$

$$i2=0.3$$

$$Ba1=0.9992$$

$$Ba2=1.588$$

$$\ln(\gamma_{\text{NaCl}})=(-1.1762*1*\sqrt{I1})/(1+Ba1*\sqrt{I1})$$

$$\ln(\gamma_{\text{CaCl2}})=(-1.1762*2*\sqrt{I2})/(1+Ba2*\sqrt{I2})$$

SOLUTION**Unit Settings: SI C kPa kJ mass deg**

$$Ba1 = 0.9992$$

$$\gamma_{\text{CaCl2}} = 0.502$$

$$I1 = 0.1$$

$$Ba2 = 1.588$$

$$\gamma_{\text{NaCl}} = 0.7538$$

$$i2 = 0.3$$

No unit problems were detected.

Parametric Table: Table 1

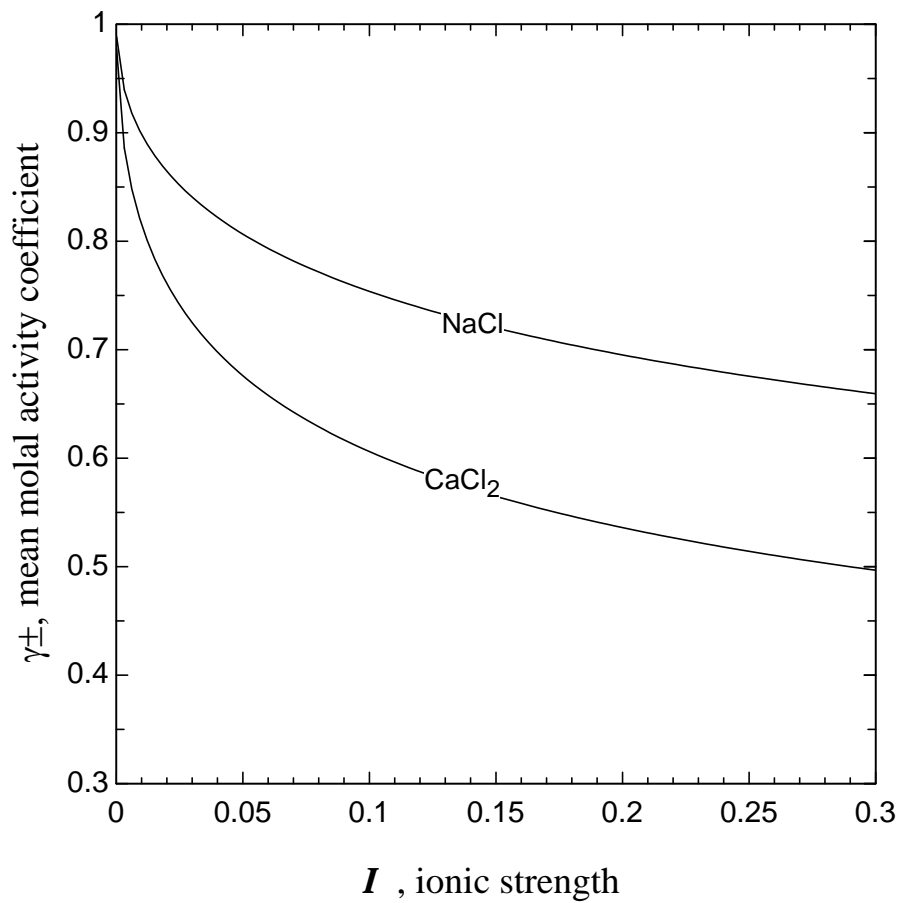
	I	γ_{NaCl}	γ_{CaCl2}
Run 1	0.0001	0.9884	0.977
Run 2	0.003129	0.9396	0.8828
Run 3	0.006159	0.918	0.8427
Run 4	0.009188	0.9022	0.814
Run 5	0.01222	0.8895	0.7912
Run 6	0.01525	0.8787	0.7722
Run 7	0.01828	0.8693	0.7557
Run 8	0.02131	0.8609	0.7411
Run 9	0.02433	0.8532	0.728
Run 10	0.02736	0.8462	0.7161
Run 11	0.03039	0.8398	0.7052
Run 12	0.03342	0.8338	0.6951
Run 13	0.03645	0.8281	0.6858
Run 14	0.03948	0.8228	0.6771
Run 15	0.04251	0.8178	0.6689
Run 16	0.04554	0.8131	0.6612
Run 17	0.04857	0.8086	0.6539
Run 18	0.0516	0.8043	0.6469
Run 19	0.05463	0.8002	0.6404
Run 20	0.05766	0.7963	0.6341
Run 21	0.06069	0.7925	0.6281
Run 22	0.06372	0.7889	0.6224
Run 23	0.06674	0.7854	0.6169
Run 24	0.06977	0.7821	0.6116
Run 25	0.0728	0.7788	0.6066
Run 26	0.07583	0.7757	0.6017
Run 27	0.07886	0.7726	0.597
Run 28	0.08189	0.7697	0.5924
Run 29	0.08492	0.7669	0.5881
Run 30	0.08795	0.7641	0.5838
Run 31	0.09098	0.7614	0.5797
Run 32	0.09401	0.7588	0.5757
Run 33	0.09704	0.7562	0.5719
Run 34	0.1001	0.7537	0.5681

Parametric Table: Table 1

	I	γ_{NaCl}	γ_{CaCl_2}
Run 35	0.1031	0.7513	0.5645
Run 36	0.1061	0.749	0.5609
Run 37	0.1092	0.7467	0.5575
Run 38	0.1122	0.7444	0.5541
Run 39	0.1152	0.7422	0.5509
Run 40	0.1182	0.7401	0.5477
Run 41	0.1213	0.738	0.5446
Run 42	0.1243	0.7359	0.5416
Run 43	0.1273	0.7339	0.5386
Run 44	0.1304	0.7319	0.5357
Run 45	0.1334	0.73	0.5329
Run 46	0.1364	0.7281	0.5301
Run 47	0.1394	0.7262	0.5274
Run 48	0.1425	0.7244	0.5248
Run 49	0.1455	0.7226	0.5222
Run 50	0.1485	0.7209	0.5197
Run 51	0.1516	0.7192	0.5172
Run 52	0.1546	0.7175	0.5148
Run 53	0.1576	0.7158	0.5124
Run 54	0.1607	0.7142	0.5101
Run 55	0.1637	0.7126	0.5078
Run 56	0.1667	0.711	0.5055
Run 57	0.1697	0.7094	0.5033
Run 58	0.1728	0.7079	0.5011
Run 59	0.1758	0.7064	0.499
Run 60	0.1788	0.7049	0.4969
Run 61	0.1819	0.7035	0.4949
Run 62	0.1849	0.702	0.4929
Run 63	0.1879	0.7006	0.4909
Run 64	0.1909	0.6992	0.4889
Run 65	0.194	0.6979	0.487
Run 66	0.197	0.6965	0.4851
Run 67	0.2	0.6952	0.4833
Run 68	0.2031	0.6939	0.4815
Run 69	0.2061	0.6926	0.4797
Run 70	0.2091	0.6913	0.4779
Run 71	0.2122	0.69	0.4762
Run 72	0.2152	0.6888	0.4744
Run 73	0.2182	0.6876	0.4728
Run 74	0.2212	0.6864	0.4711
Run 75	0.2243	0.6852	0.4694
Run 76	0.2273	0.684	0.4678
Run 77	0.2303	0.6828	0.4662
Run 78	0.2334	0.6817	0.4647
Run 79	0.2364	0.6805	0.4631
Run 80	0.2394	0.6794	0.4616
Run 81	0.2424	0.6783	0.4601
Run 82	0.2455	0.6772	0.4586
Run 83	0.2485	0.6761	0.4571
Run 84	0.2515	0.675	0.4557
Run 85	0.2546	0.674	0.4543
Run 86	0.2576	0.6729	0.4529

Parametric Table: Table 1

	I	γ_{NaCl}	γ_{CaCl_2}
Run 87	0.2606	0.6719	0.4515
Run 88	0.2636	0.6709	0.4501
Run 89	0.2667	0.6699	0.4487
Run 90	0.2697	0.6689	0.4474
Run 91	0.2727	0.6679	0.4461
Run 92	0.2758	0.6669	0.4448
Run 93	0.2788	0.6659	0.4435
Run 94	0.2818	0.665	0.4422
Run 95	0.2849	0.664	0.4409
Run 96	0.2879	0.6631	0.4397
Run 97	0.2909	0.6622	0.4385
Run 98	0.2939	0.6613	0.4373
Run 99	0.297	0.6603	0.4361
Run 100	0.3	0.6594	0.4349



PROBLEM 2-26

$$I = 0.3 \text{ [mol/kg] ionic strength of } 0.1 \text{ m MgCl}_2$$

$$R = 8.314 \text{ [J/mol-K]}$$

$$T = 298.15 \text{ [K]}$$

$$F = 96485 \text{ [coulomb/mol]}$$

$$dc = 80.4 \text{ dielectric constant for water at } 25 \text{ C}$$

$$p = 8.85419 \times 10^{-12} \text{ [coulomb/(V-m)]}$$

$$\varepsilon = dc \cdot p$$

ACTIVITY COEFFICIENT*solvent constants*

$$e = 1.602 \times 10^{-19} \text{ [coulomb]}$$

$$\rho_s = 997.1 \text{ [kg/m}^3\text{] density of water}$$

$$\alpha = \sqrt{\rho_s} \cdot \frac{F \cdot F \cdot e \cdot \sqrt{2}}{8 \cdot \pi \cdot [\varepsilon \cdot R \cdot T]^{1.5}}$$

$$B = F \cdot \frac{\sqrt{\rho_s}}{\sqrt{\varepsilon \cdot R \cdot \frac{T}{2}}}$$

$$a1 = 8.0 \times 10^{-10} \text{ [m]}$$

$$a2 = 3.0 \times 10^{-10} \text{ [m]}$$

$$a = 0.5 \cdot [a1 + a2]$$

$$\ln [\gamma] = \frac{-2 \cdot \alpha \cdot \sqrt{I}}{1 + B \cdot a \cdot \sqrt{I}}$$

SOLUTION**Unit Settings: SI C kPa kJ mass deg**

$$a = 5.500\text{E-}10 \text{ [m]}$$

$$a1 = 8.000\text{E-}10 \text{ [m]}$$

$$a2 = 3.000\text{E-}10 \text{ [m]}$$

$$\alpha = 1.13 \text{ [(kg/mol)}^{0.5}\text{]}$$

$$B = 3.244\text{E+}09 \text{ [(kg/mol)}^{0.5}\text{/m]}$$

$$dc = 80.4$$

$$e = 1.602\text{E-}19 \text{ [coulomb]}$$

$$\varepsilon = 7.119\text{E-}10 \text{ [Coulomb/(V-m)]}$$

$$F = 96485 \text{ [coulomb/mol]}$$

$$\gamma = 0.5345$$

$$I = 0.3 \text{ [mol/kg]}$$

$$\rho = 8.854\text{E-}12 \text{ [coulomb/(V-m)]}$$

$$R = 8.314 \text{ [J/mol-K]}$$

$$\rho_s = 997.1 \text{ [kg/m}^3\text{]}$$

$$T = 298.2 \text{ [K]}$$

No unit problems were detected.

Parametric Table: experimental data

	I	x	γ	gamm_{lim}	γ_{exp}
	[mol/kg]	[(mol/kg) ^{0.5}]			
Run 1	0.001	0.03162	0.9661	0.9649	0.965
Run 2	0.005	0.07071	0.9287	0.9232	0.927
Run 3	0.01	0.1	0.9035	0.8931	0.902
Run 4	0.05	0.2236	0.8174	0.7766	0.821
Run 5	0.1	0.3162	0.7687	0.6994	0.778
Run 6	1	1	0.5889	0.3229	0.657

PROBLEM 2-27

$$I = 0.1 \text{ [mol/kg]}$$

ionic strength of NaCl, equivalent to molality

$$R = 8.314 \text{ [J/mol-K]}$$

$$T = 298.15 \text{ [K]}$$

$$F = 96485 \text{ [coulomb/mol]}$$

$$\epsilon_{dc} = 80.4 \text{ *dielectric constant for water at 25 C*}$$

$$\rho = 8.85419 \times 10^{-12} \text{ [coulomb/(V-m)]}$$

$$\epsilon = \epsilon_{dc} \cdot \rho$$

ACTIVITY COEFFICIENT

solvent constants

$$e = 1.602 \times 10^{-19} \text{ [coulomb]}$$

$$\rho_s = 997.1 \text{ [kg/m}^3\text{] *density of water*}$$

$$\alpha = \sqrt{\rho_s} \cdot \frac{F \cdot F \cdot e \cdot \sqrt{2}}{8 \cdot \pi \cdot [\epsilon \cdot R \cdot T]^{1.5}}$$

$$B = F \cdot \frac{\sqrt{\rho_s}}{\sqrt{\epsilon \cdot R \cdot \frac{T}{2}}}$$

$$a_1 = 4.0 \times 10^{-10} \text{ [m]}$$

$$a_2 = 3.0 \times 10^{-10} \text{ [m]}$$

$$a = 0.5 \cdot [a_1 + a_2]$$

$$\ln [\gamma] = \frac{-\alpha \cdot \sqrt{I}}{1 + B \cdot a \cdot \sqrt{I}}$$

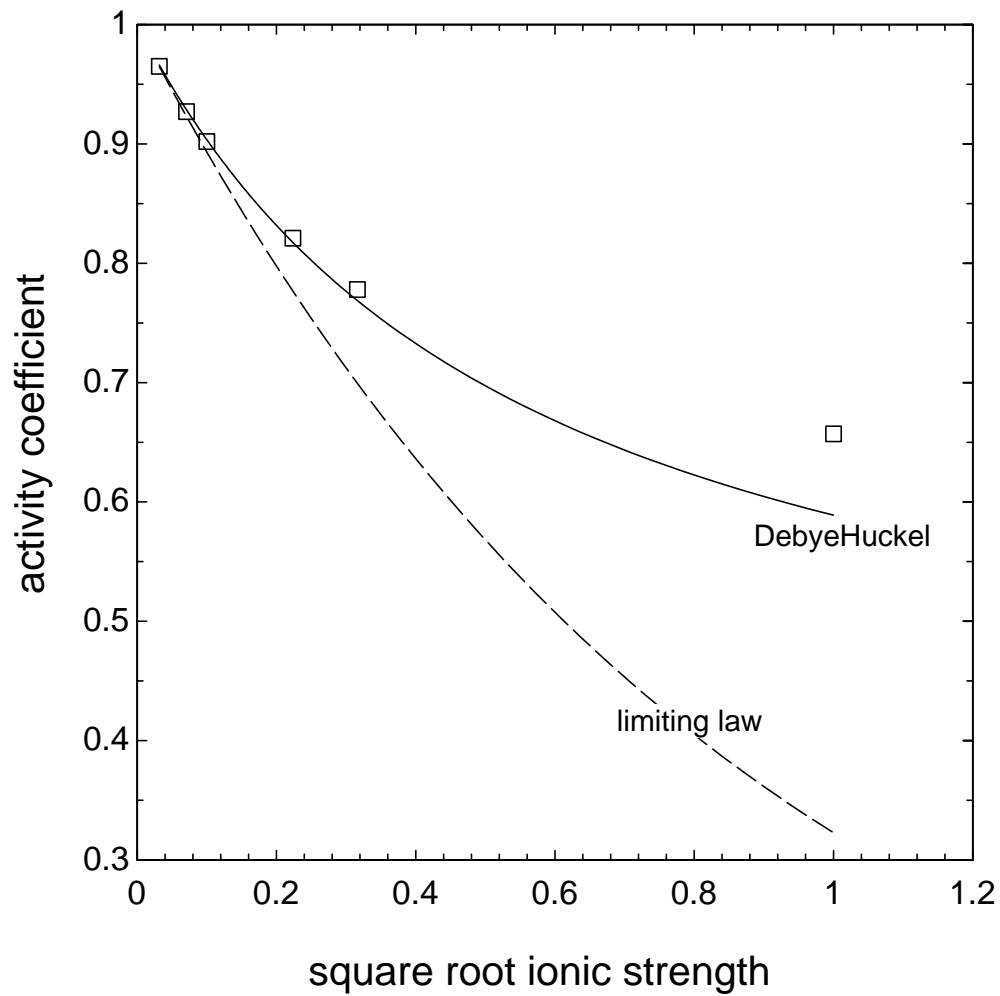
$$\text{gamm}_{lim} = \exp [-\alpha \cdot \sqrt{I}]$$

$$x = \sqrt{I}$$

$$\text{gamma}_{exp} = 1$$

Parametric Table: experimental data

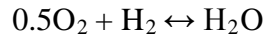
	I [mol/kg]	x [(mol/kg) ^{0.5}]	γ	gamm_{lim}	γ_{exp}
Run 1	0.001	0.03162	0.9661	0.9649	0.965
Run 2	0.005	0.07071	0.9287	0.9232	0.927
Run 3	0.01	0.1	0.9035	0.8931	0.902
Run 4	0.05	0.2236	0.8174	0.7766	0.821
Run 5	0.1	0.3162	0.7687	0.6994	0.778
Run 6	1	1	0.5889	0.3229	0.657



Before concerns about mercury became widespread, the calomel electrode was commonly used. Crystals of KCl are added to produce a saturated solution. What advantage does a saturated solution provide? The saturated calomel electrode has an equilibrium potential of 0.242 V, which is lower than the standard potential of 0.2676. Can this 25 mV difference be determined from thermodynamics? Why or why not? The solubility of KCl in water at 25 °C is 360 g KCl/100 g water.

Because the dissolved KCl can diffuse slowly out of the reference electrode, adding crystals keeps the solution saturated. This helps to maintain stable performance longer. The 25 mV offset cannot be determined from thermodynamics alone. The cell has a liquid junction. Transport is required to analyze the potential difference. Chloride and potassium ions will diffuse from high to low concentration. Unless you just happen to be measuring the potential in a solution of exactly the same concentration, ions will be moving and the concentration profile will affect the measured potential.

A solid oxide fuel cell operates at 1000 °C. The overall reaction is

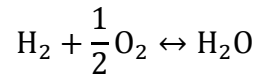


- Calculate the standard potential at 25 °C assuming that reactants and products are gases.
- Calculate the standard potential at 1000 °C using equation 2-18.
- Using the correlation for heat capacity as a function of temperature shown below, calculate the standard potential at 1000 °C. Comment on the assumption used in part (b) that ΔS° is constant.

$$C_p = A + BT + CT^{-2}$$

	A [J/mol-K]	$10^3 B$ [J/mol-K ²]	$10^{-5} C$ [J-K/mol]
H ₂ O	30.54	10.29	0
O ₂	29.96	4.184	-16.7
H ₂	27.28	3.26	0.50

(a) The overall reaction is



Using the data from Appendix C

$$\Delta G_{Rx} = \Delta G_{f,\text{H}_2\text{O}}^\circ = -228,572 \text{ J}$$

$$U^\theta = \frac{-\Delta G_{Rx}}{nF} = \frac{228,572}{(2)96485} = \boxed{1.184 \text{ V}}$$

(b) Appendix C has data for 25 °C

$$S_{\text{H}_2} = 130.5 \frac{\text{J}}{\text{mol K}}$$

$$S_{\text{H}_2} = 205.3 \frac{\text{J}}{\text{mol K}}$$

$$S_{\text{H}_2\text{O}} = 188.7 \frac{\text{J}}{\text{mol K}}$$

$$\Delta S_{Rx} = 188.7 - 130.5 - \frac{205.3}{2} = -44.45 \frac{\text{J}}{\text{mol} - \text{K}}$$

$$U(1000) = 1.184 + (1000 - 25) \left(\frac{-44.45}{(2)96485} \right) = \boxed{0.959 \text{ V}}$$

(c)

$$\frac{\partial \Delta H}{\partial T} = \Delta C_p$$

$$\Delta H(T) - \Delta H(T_o) = \int \Delta C_p dT$$

$$\Delta A = 30.54 - \frac{1}{2}(29.96) - 27.28 = -11.72$$

$$1000\Delta B = 10.29 - \frac{1}{2}(4.184) - 3.26 = 4.938$$

$$10^{-5}\Delta C = 0 - \frac{1}{2}(-16.7) - 0.5 =$$

$$\Delta H(T) = \Delta H(T_o) + \int_{T_o}^T \left(\Delta A + \Delta B T + \frac{\Delta C}{T^2} \right) dT$$

$$\Delta H(T) = \Delta H(T_o) + \Delta A(T - T_o) + \frac{\Delta B(T^2 - T_o^2)}{2} - \Delta C \left(\frac{1}{T} - \frac{1}{T_o} \right)$$

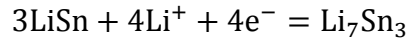
$$\left(\frac{\partial(U/T)}{\partial T} \right)_p = \frac{\Delta H(T)}{nFT^2}$$

$$n \left(\frac{U}{T} - \frac{U^\theta}{T_o} \right) = \int_{T_o}^T \frac{\Delta H(T)}{T^2} + \frac{\Delta A(T - T_o)}{T^2} + \frac{\Delta B(T^2 - T_o^2)}{2T^2} - \Delta C \left(\frac{1}{T^3} - \frac{1}{T^2 T_o} \right) dT$$

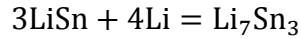
$$U = \left(\frac{T}{T_o} \right) U^\theta + \frac{T}{2F} \left[\Delta H^\circ \left(\frac{1}{T} - \frac{1}{T_o} \right) + \Delta A \left(\ln \frac{T}{T_o} + \frac{T}{T_o} - 1 \right) + \frac{(T - T_o)^2}{2T} \left(\Delta B + \frac{\Delta C}{TT_o^2} \right) \right]$$

at 1000 °C, $U=0.9219$ V. This is compared to the value calculated assuming that ΔS is constant, $U=0.959$ V. There is almost a 40 mV difference.

Alloys of LiSn are possible electrodes for batteries. There are many phases possible, but we want to focus on the reaction



The standard potential of this reaction at 25 °C is 0.530 V (vs. reference Li electrode). If the enthalpy of the reaction



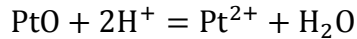
is -226kJ/mol Li_7Sn_3 , estimate the standard potential at 400 °C.

Assuming ΔH is constant

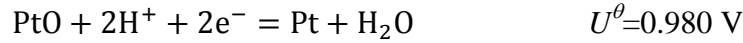
$$U = U_o \frac{T}{T_o} + \frac{\Delta H}{nF} \left(\frac{T}{T_o} - 1 \right)$$

$$U = 0.530 \frac{673}{298} + \frac{-226,000}{4F} \left(\frac{673}{298} - 1 \right) = 0.460 \text{ V}$$

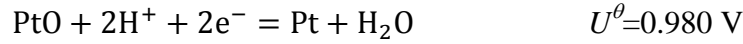
Find the equilibrium constant, K_{eq} , for Pt dissolution reaction at 25 °C.



The following thermodynamic data are provided, $\Delta G_f^{\text{Pt}^{2+}} = 229.248 \frac{\text{kJ}}{\text{mol}}$, and



Find the Gibbs energy of formation for PtO



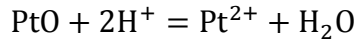
sum to get



$$\Delta G_{Rx} = \Delta G_{f,\text{H}_2\text{O}}^\circ - \Delta G_{f,\text{PtO}}^\circ = -nFU^\theta = 2F(0.980)$$

$$\Delta G_{\text{PtO}}^\circ = -48,014 \text{ J mol}^{-1}$$

dissolution reaction of interest is

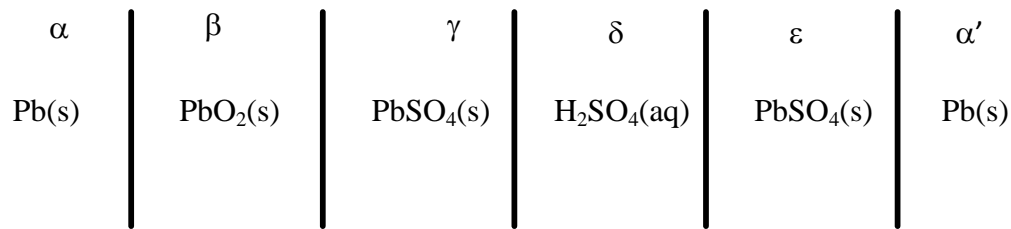


$$\Delta G_{Rx} = \Delta G_{f,\text{Pt}^{2+}}^\circ + \Delta G_{f,\text{H}_2\text{O}}^\circ - \Delta G_{f,\text{PtO}}^\circ = 40,133 \text{ J mol}^{-1}$$

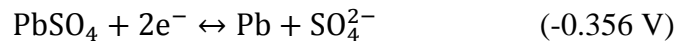
$$K_{sp} = e^{-\Delta G_{Rx}/RT} = 9.2 \times 10^{-8} = \frac{a_{\text{Pt}^{2+}}}{a_{\text{H}^+}^2}$$

- a. Write the overall reaction and determine the standard potential for the lead-acid battery.
- b. Develop an expression for the equilibrium potential, U , for the lead acid battery as a function of electrolyte composition. The final expression should include the molality and activity coefficient.
- c. The potentials of the two electrodes relative to a Hg-Hg₂SO₄ reference electrode at 25 °C has been measured. What is the likely reaction at the reference electrode? If the standard Gibbs energy of formation of Hg₂SO₄ is -625.8 kJ/mol and the standard Gibbs energy of formation of SO₄²⁻ is -744.62 kJ/mol, determine the standard potential of the positive (lead oxide electrode) relative to the reference electrode. How does this value compare to the measured value of 0.96 V? Explain the possible cause of any difference.
- d. Given that the potential difference between the positive electrode and the reference electrode is 1.14 V, estimate the activity coefficient for sulfuric acid (γ_{\pm}) at 6 m. For this evaluation, you may assume that the activity of water is one.
- e. Does the potential of the lead electrode (Pb) relative to the reference electrode depend on the molality of the sulfuric acid? Explain your answer.

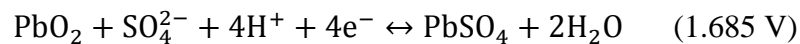
a. The cell can be written as



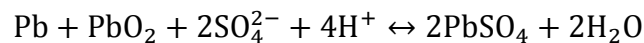
At the negative electrode



and the positive electrode



The overall reaction is



$$U_{\text{cell}}^{\theta} = U_{+}^{\theta} - U_{-}^{\theta} = 1.685 - (-0.356) = 2.041 \text{ V}$$

b)

$$U = U_{\text{cell}}^{\theta} - \frac{RT}{nF} \ln \prod a_i^{s_i} \quad (2-11)$$

$$U = U_{\text{cell}}^{\theta} - \frac{RT}{2F} \ln \frac{a_{\text{H}_2\text{O}}^2 a_{\text{PbSO}_4}^2}{a_{\text{H}_2\text{SO}_4}^2 a_{\text{Pb}} a_{\text{PbO}_2}}$$

the activity of solids is one

$$U = U_{\text{cell}}^{\theta} - \frac{RT}{2F} \ln \frac{a_{\text{H}_2\text{O}}^2}{a_{\text{H}_2\text{SO}_4}^2}$$

$$U = U_{\text{cell}}^{\theta} - \frac{RT}{F} \ln a_{\text{H}_2\text{O}} + \frac{RT}{F} \ln a_+^{v_+} a_-^{v_-}$$

$$a_+ = m_+ \gamma_+$$

$$a_- = m_- \gamma_-$$

$$m_+ = \nu_+ m$$

$$m_- = \nu_- m$$

$$a_+^{v_+} a_-^{v_-} = \nu_+^{v_+} m^{\nu_+} \nu_-^{v_-} m^{\nu_-} \gamma_+^{v_+} \gamma_-^{v_-}$$

$$\gamma_{\pm}^{\nu} \equiv \gamma_+^{\nu_+} \gamma_-^{\nu_-}$$

$$\nu \equiv \nu_+ + \nu_-$$

$$a_+^{v_+} a_-^{v_-} = m^{\nu} \nu_+^{\nu_+} \nu_-^{\nu_-} \gamma_{\pm}^{\nu}$$

for H_2SO_4 , $\nu_+ = 2$ $\nu_- = 1$ $\nu = 3$

$$a_+^2 a_-^1 = m^3 (2)^2 (1)^1 \gamma_{\pm}^3$$

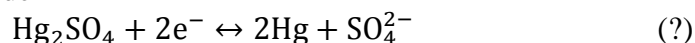
$$U = U_{\text{cell}}^{\theta} - \frac{RT}{F} \ln a_{\text{H}_2\text{O}} + \frac{RT}{F} \ln 4m^3 \gamma_{\pm}^3$$

$$U = U_{\text{cell}}^{\theta} - \frac{RT}{F} \ln a_{\text{H}_2\text{O}} + \frac{RT}{F} \ln 4 + \frac{3RT}{F} \ln m \gamma_{\pm}$$

c) and the positive electrode



reference or negative electrode



Use thermodynamic data from Appendix C to find the standard potential for the reference electrode

$$\Delta G_{\text{Rx}} = \Delta G_{f, \text{SO}_4^{2-}}^{\circ} - \Delta G_{f, \text{HgSO}_4}^{\circ}$$

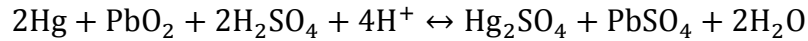
$$\Delta G_{\text{Rx}} = -744.62 - (-625.8) = -118.8 \text{ kJ mol}^{-1}$$

$$U_-^{\theta} = \frac{-\Delta G_{\text{Rx}}}{nF} = \frac{118,800}{(2)96485} = 0.6157 \text{ V}$$

$$U_{\text{cell}}^{\theta} = U_+^{\theta} - U_-^{\theta} = 1.685 - 0.6157 = 1.069 \text{ V}$$

The measured value at 1 m H_2SO_4 , 0.96 V, difference is about 100 mV. Likely because the activity coefficient of the sulfuric acid and that of water are not one.

d) The overall reaction is



$$U = U^\theta_{\text{cell}} - \frac{RT}{2F} \ln \frac{a_{\text{H}_2\text{O}}^2 a_{\text{Hg}_2\text{SO}_4} a_{\text{PbSO}_4}}{a_{\text{H}_2\text{SO}_4}^2 a_{\text{Hg}} a_{\text{PbO}_2}}$$

$$U = U^\theta_{\text{cell}} - \frac{RT}{F} \ln a_{\text{H}_2\text{O}} + \frac{RT}{2F} \ln a_{\text{H}_2\text{SO}_4}^2$$

$$U = U^\theta - \frac{RT}{F} \ln a_{\text{H}_2\text{O}} + \frac{RT}{F} \ln 4 + \frac{R3T}{F} \ln m\gamma_{\pm}$$

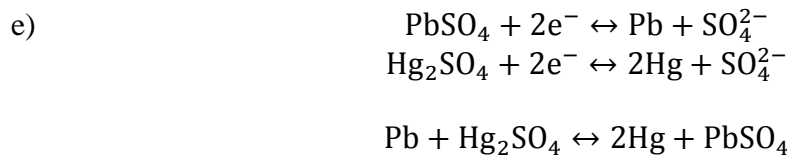
At 6 m, $U_{\text{PbO}_2} = 1.07 \text{ V}$ and $U_{\text{Hg}/\text{Hg}_2\text{SO}_4} = -0.07 \text{ V}$

$$U = 1.07 - (-0.07) = 1.14 \text{ V}$$

assume the activity coefficient of water is one

$$1.14 \text{ V} = 1.069 + 0.036 + 0.0771 \ln m\gamma_{\pm}$$

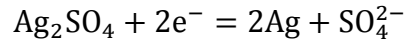
$$\gamma_{\pm} = 0.262$$



Although the sulfate ion appears in the reactions, it does not appear in the overall reaction. Therefore, U does not depend on the molality of the acid.

Rework Illustration 2-7 (reference electrode example) with a Ag_2SO_4 reference electrode rather than a Hg_2SO_4 reference electrode. The standard potential for this reference electrode reaction (below) is 0.654V.

$$U_{ref}^{\theta} = 0.654$$



Unchanged from Illustration 2.7 $U_{\text{O}_2/\text{SHE}} = 1.252$ $U_{\text{Cu}/\text{SHE}} = 0.3192$

$$U_{\text{Ag}_2\text{SO}_4/\text{SHE}} = U_{ref}^{\theta} - \frac{RT}{nF} \ln\left(\frac{c_{\text{SO}_4^{2-}}}{1M}\right)$$

assuming that the sulfate concentration is 1.8 M

$$U_{\text{Ag}_2\text{SO}_4/\text{SHE}} = 0.654 - \frac{RT}{2F} \ln(1.8) = 0.6588 \text{ V}$$

$$U_{\text{O}_2/ref} = U_{\text{O}_2/\text{SHE}} - U_{ref/\text{SHE}} = 1.252 - 0.6588 = 0.5931 \text{ V}$$

$$U_{\text{Cu}/ref} = U_{\text{Cu}/\text{SHE}} - U_{ref} = 0.3192 - 0.6588 = -0.3396 \text{ V}$$

$$U_{\text{O}_2/\text{Cu}} = U_{\text{O}_2/ref} - U_{\frac{\text{Cu}}{ref}} = 0.5931 + 0.3396 = 0.933 \text{ V}$$

As expected the value of the cell didn't change, each electrode was at a slightly different potential relative to the different reference electrode.