

**Problem 1.3 (10 points)** You can easily tell which reactions are reduction and which are oxidation by finding which side of the reaction the electrons appear on.

1.  $Cu \rightarrow Cu^{2+} + 2e^-$  Electrons are liberated, so this is an Oxidation reaction
2.  $2H^+ + 2e^- \rightarrow H_2$  Reduction
3.  $O^{2-} \rightarrow \frac{1}{2}O_2 + 2e^-$  Oxidation
4.  $CH_4 + 4O^{2-} \rightarrow CO_2 + 2H_2O + 8e^-$  Oxidation
5.  $O^{2-} + CO \rightarrow CO_2 + 2e^-$  Oxidation
6.  $\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2(OH)^-$  Reduction
7.  $H_2 + 2(OH)^- \rightarrow 2H_2O + 2e^-$  Oxidation

**Problem 1.4 (15 points)** You can write full-cell reactions and then split them into the half-cell reactions. You don't need to be an expert chemist to do this, just use the half-cell reactions given and make sure your equations balance with species number (ie. that  $O$  is conserved) and charge (ie. electrons are conserved).

1.  $CO + \frac{1}{2}O_2 \rightarrow CO_2$  is a full-cell reaction common in SOFCs; the half-cell reactions would be  $O^{2-} + CO \rightarrow CO_2 + 2e^-$ , which is an Oxidation, or anode, reaction, and  $\frac{1}{2}O_2 + 2e^- \rightarrow O^{2-}$  which is a reduction, or cathode reaction.
2.  $\frac{1}{2}O_2 + H_2 \rightarrow H_2O$  is a full cell reaction in SOFCs or PEMs, depending on the circulating ion ( $O^{2-}$  or  $H^+$ , respectively). The half-cell reactions would be:  $\frac{1}{2}O_2 + 2e^- + 2H^+ \rightarrow H_2O$  at the cathode of a PEM and  $H_2 \rightarrow 2H^+ + 2e^-$  at the anode of a PEM; or  $\frac{1}{2}O_2 + 2e^- \rightarrow O^{2-}$  at the cathode of an SOFC and  $O^{2-} + H_2 \rightarrow H_2O$  at the anode of an SOFC.
3. another full cell reaction in an SOFC could be  $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$  with the half cell reactions  $8e^- + 2O_2 \rightarrow 4O^{2-}$  as the reducing, or cathode reaction, and  $CH_4 + 4O^{2-} \rightarrow CO_2 + 2H_2O + 8e^-$  as the oxidizing, or anode reaction.
4. to use the circulating ion  $(OH)^-$ , you may construct the full cell reaction  $\frac{1}{2}O_2 + H_2 + H_2O \rightarrow 2H_2O$  from the half-cell reactions  $H_2 + 2(OH)^- \rightarrow 2H_2O + 2e^-$  as the oxidizing, or anode reaction, and  $\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2(OH)^-$  as the cathode (reducing) reaction.

**Problem 2.5 (6 points)** The Nernst equation

$$E = E_T - \frac{RT}{nF} \ln \frac{\prod a_{prod}^{\nu_i}}{\prod a_{react}^{\nu_i}} \quad (3)$$

shows that increasing the activity of the reactants decreases the argument of the ln, which raises the reversible cell voltage ( $E$ ) because the ln term is negative. This, in essence, is Le'Chatlier's principle.

**Problem 2.10 (15 points)** Two ways of attacking this problem yield the same result. First, you could imagine a box with water, air, and hydrogen, and the reaction  $H_2 + \frac{1}{2}O_2 \rightleftharpoons H_2O(l)$  is in equilibrium. To find how much hydrogen is consumed by oxygen, find the equilibrium quantity of hydrogen when oxygen is present. That is to say, find at what  $P_{H_2}$  does  $\Delta G_{rxn} = 0$ . From the van't Hoff isotherm

$$\Delta G = \Delta G^\circ + RT \ln \frac{\prod a_{prod}^{\nu_i}}{\prod a_{react}^{\nu_i}} \quad (20)$$

assuming air at the cathode ( $x_{O_2} = 0.21$ )

$$\Delta G = \Delta G^\circ + RT \ln \frac{a_{H_2O}^1}{a_{H_2}^1 a_{O_2}^{0.5}} = \Delta G^\circ + RT \ln \frac{1}{(P/P_o)^{1.5} x_{H_2} x_{O_2}^{0.5}} = \Delta G^\circ - RT \ln(1)^{1.5} (x_{H_2}) (0.21)^{0.5} \quad (21)$$

Solving for  $x_{H_2}$ ,

$$\frac{\Delta G^\circ}{RT} = \ln [(0.21)^{0.5} x_{H_2}] \quad (22)$$

$$x_{H_2} = \frac{1}{0.21^{0.5}} \exp \left[ \frac{\Delta G^\circ}{RT} \right] = (2.18) \exp \left[ \frac{(-237 \text{ kJ/mol})}{(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K})} \right] = 5.41 \cdot 10^{-42} \quad (23)$$

so  $\boxed{P_{H_2} = 5.41 \cdot 10^{-42} \text{ atm}}$

Note that the partial pressure is very low, because it is very energetically favorable for hydrogen to react with oxygen to form water.

The alternate way to solve the problem is to solve a concentration cell where a voltage develops (1.23 V because it is a hydrogen/air system) but  $E^\circ = 0$  because the concentration cell reaction is  $H_2 + O_2 \rightarrow H_2 + O_2$ . In this formulation, you solve the Nernst equation where the reactants have activity 1 because they are pure

$$1.23 = 0 - \frac{RT}{nF} \ln \frac{P_{H_2}/P_o (0.21)^{0.5}}{1} \quad (24)$$

This gives the same equation

$$x_{H_2} (0.21)^{0.5} = \exp \left[ -\frac{1.23 * nF}{RT} \right] \quad (25)$$