

**Problem 1 – 1.5, 1.6, 2.1a, 2.3 from the B&F text:**

6 pts

1.5 Use equation (1) from page 15 of the text and the knowledge that the double-layer charging is 95% complete when  $t = 3\tau$ . The table below gives the correct answers:

$$\tau = R_s C_d \quad (1) \quad \text{4 pts for the equation}$$

$C_d$	$R_s$	$\tau$	$t_{95\%}$
2 $\mu\text{F}$	1 $\Omega$	2 $\mu\text{s}$	6 $\mu\text{s}$
2 $\mu\text{F}$	10 $\Omega$	20 $\mu\text{s}$	60 $\mu\text{s}$
2 $\mu\text{F}$	100 $\Omega$	200 $\mu\text{s}$	600 $\mu\text{s}$

2 pts for correct numbers and units

1.6 Use equation 1.2.15 from the text which describes the current during a potential sweep:

$$i = vC_d[1 - e^{-t/\tau}]$$

6 pts

The assumption that we can neglect transients means that we can assume  $t \gg \tau$ , which gives equation (2) which describes the steady-state current (p 17 of B&F):

$$i \approx vC_d \quad (2) \quad \text{4 pts for the equation}$$

Using the value of  $C_d = 2 \mu\text{F}$ , we get:

Sweep rate (V/s)	Current (A)
0.02	$4 \times 10^{-8}$
1	$2 \times 10^{-6}$
20	$4 \times 10^{-5}$

2 pts for correct numbers and units

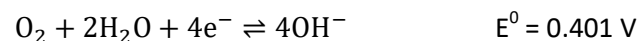
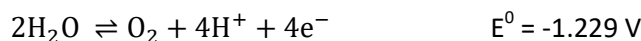
2.1 (a) There are at least two acceptable solutions to this problem. The first is:

14 pts



6 points for writing two balanced half-reactions that add up to the desired net reaction

Alternatively,



4 points for the correct cell potential

One cell that can accomplish this is:



2 pts for cell schematic  
2 pts for spontaneous or not and the rest of the questions

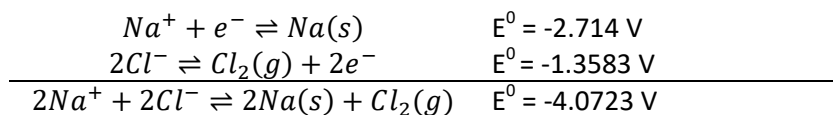
Another is:



To answer the questions at the bottom of the problem, we first see that the two half-reactions are given above. The overall cell potential is negative, which means that  $\Delta G$  will be positive. Therefore the reaction is non-spontaneous and this will need to be an electrolytic cell for the reaction to go from left to right. Thus, the cathode will be negative.

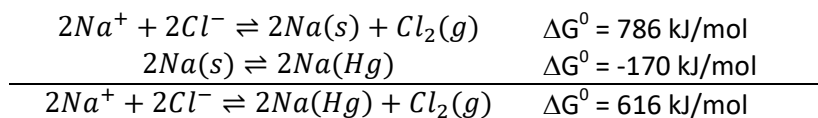
2.3 Again, there may be more than one valid answer to this problem. Here is one:

18 points



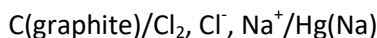
6 pts for writing two balanced half-reactions that add up to the desired net reaction

We can calculate  $\Delta G^0$  for the reaction above from  $\Delta G^0 = -nFE^0$ . Then, using the standard free energy of formation for Na(Hg) (multiplied by 2 since we need 2 moles according to the balanced equation above), we can write:



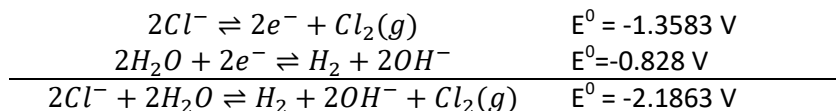
4 pts for getting the correct  $\Delta G$

This does not complete the reaction given, but no value for equilibration between  $\text{Cl}_2(\text{aq})$  and  $\text{Cl}_2(\text{g})$  was given in the text, so we'll just assume that the reaction is not exergonic enough to make this reaction spontaneous. Thus the reaction is *not spontaneous*. A possible design for this cell would be:

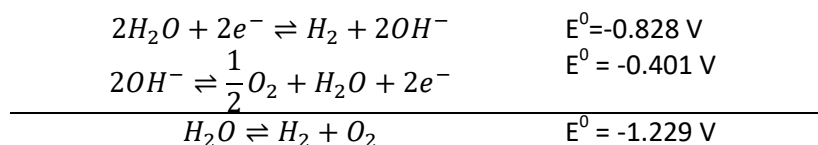


2 pts

Reaction(s) that should occur before this one, from a thermodynamic standpoint are the following:



4 pts for finding at least one reaction



Although these reactions are clearly more thermodynamically favorable, we know from the lectures that hydrogen evolution from a mercury electrode is kinetically terrible – there is a large overpotential required for the formation of hydrogen from water at a Hg electrode, which allows the (spontaneous) reaction for the Na(Hg) to take place with good current efficiency over the water reduction reaction. Note we are not given any numbers here to know what B&F mean by “good” current efficiency.

The B&F text says this process could be used to make either Cl<sub>2</sub> gas or Na metal commercially (assuming you can separate the Na from the amalgam), and is in fact used in the commercial production of Cl<sub>2</sub>. As a by-product in the commercial process, we get solutions of NaOH – water is used to regenerate the Hg and NaOH results. This NaOH solution is apparently concentrated enough to also be commercially useful.

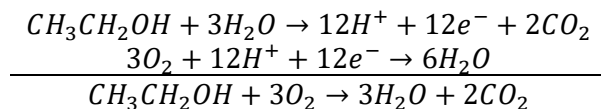
But, the wording of the question is whether the cell would have a “commercial value”, which really is more of an economic question than an electrochemistry question. We really don’t know what the efficiency is, or the value of the products, or cost of the power you have to put into the cell etc., so this part of the question was really not answerable with the information given.

2 pts for trying to answer these questions

## Problem 2

26 pts

(a) If all of the free energy of the reaction is converted to electrical energy, then the cell could achieve an open-circuit voltage equal to the cell potential. In order to calculate the cell potential correctly, we must first determine the number of moles of electrons transferred in the net reaction. The following balanced reactions give us the number of electrons for the overall reaction:



10 pts for correct VOC  
(if it's not correct, partial credit is split 6-4 between showing a balanced equation and using the correct equation for VOC)

Thus the reaction requires 12 moles of electrons for each mole of ethanol. We can now calculate the maximum open-circuit voltage. [Note: It’s probably best to ignore the bit about “standard conditions” since the value of ΔG is not given under standard conditions and no indication is given of what conditions are being employed here.]

$$V_{OC} = E = \frac{-\Delta G}{nF} = 1.14 \text{ V}$$

(b) We can use the Butler-Volmer equation:

$$i = i_0 [e^{-\alpha n f \eta} - e^{(1-\alpha) n f \eta}]$$

6 pts, (4 for correct equation plus 2 for an exchange current with correct number and unit)

Since we are at high overpotentials, one of the two exponential terms will be very close to zero. In this case, we have  $\eta = E_{eq} = 0.5 - 1.14 = -0.64 \text{ V}$ ,  $T = 383 \text{ K}$ , and we assume  $\alpha = 0.5$ . Solving for  $i_0$  and using  $n = 12$  above, we obtain (for a  $1 \text{ cm}^2$  electrode):

$$i_0 = \frac{i}{e^{-\alpha n f \eta}} = 5.5 \times 10^{-52} \text{ A}$$

This is a ridiculously small exchange current. That’s because we used the value of  $n$  for the full reaction (12, from above), and that isn’t the right value of  $n$  to use in the Tafel equation, which uses the  $n$  from

the rate-limiting electron-transfer step. But since we weren't told what the rate-limiting step is, we don't know the correct value of  $n$ . However, we were told in the text and lectures that  $n$  is typically more like 1 or 2, which will give us much more reasonable values for the exchange-current density:

$n$	$i_0$ (A cm <sup>-2</sup> )
1	$1.2 \times 10^{-5}$ A
2	$7.5 \times 10^{-10}$ A
12	$5.5 \times 10^{-52}$ A

4 points for the overpotential

(c) Since the total overpotential was -0.64 V, the overpotential associated with the ethanol electrode is therefore -0.24 V under the assumptions of this problem. Although it is tempting to ratio the overpotential to the current to obtain  $R_{CT}$ , we are not in the regime of low overpotential in this case. Thus, we will calculate what  $R_{CT}$  would be in the case of low overpotential using the value of  $i_0$ , which is independent of overpotential. In Bard we find equation (3.4.13) which gives the value of the charge-transfer resistance for a one-electron reaction. Since we do not know how many electrons are involved in the rate-determining step, we can write:

$$R_{CT} = \frac{RT}{nFi_0}$$

6 points (4 for the equation, 2 for correct number and units for  $R_{CT}$ )

Note that we do not have the area of the electrode being used, which is needed to calculate resistance (since  $i_0$  is a current density here). As an approximation, we will assume 1 cm<sup>2</sup> electrodes so that a resistance value can be calculated from the data given. In general, the resistance will be inversely proportional to the area of the electrode. Again we give different values of the resistance for common choices of  $n$  (recall that the choice of  $n$  also influences the value of  $i_0$ ):

$n$	$R_{CT}$ ( $\Omega$ )
1	$2.7 \times 10^3 \Omega$
2	$2.2 \times 10^7 \Omega$
12	$5.0 \times 10^{48} \Omega$

### Problem 3

24 pts

First we calculate the theoretical maximum energy:

$$10 \text{ g EtOH} \times \frac{1 \text{ mol EtOH}}{46.0694 \text{ g EtOH}} \times \frac{1324 \text{ kJ}}{\text{mol EtOH}} = 287 \text{ kJ}$$

Next we calculate the total energy from the fuel-cell reaction at 0.5 V = 0.5 J/C:

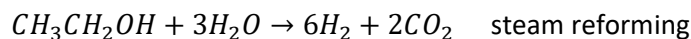
$$10 \text{ g EtOH} \times \frac{1 \text{ mol EtOH}}{46.0694 \text{ g EtOH}} \times \frac{12 \text{ mol } e^-}{\text{mol EtOH}} \times \frac{96485 \text{ C}}{\text{mol } e^-} \times \frac{0.5 \text{ J}}{\text{C}} = 126 \text{ kJ}$$

Thus, the energy-conversion efficiency of the direct ethanol fuel cell is:

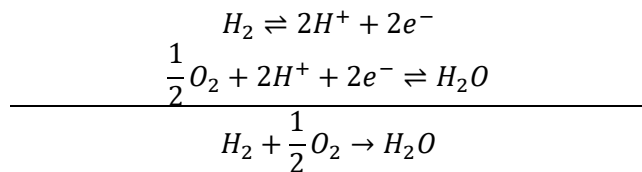
$$efficiency = \frac{126 \text{ kJ}}{287 \text{ kJ}} = 43.7\%$$

12 points - divided 4 pts each among the 3 steps: calculate total energy, electrical energy, and efficiency

Since the way efficiency is lost in the steam-reforming process is unclear from the problem, we can either assume that 80% of the energy available in the ethanol is lost in this step (i.e. energy must be put into the system to make it go) or that the reaction does not give 100% yield, or some combination of the two. The end result will be the same since the steam-reforming step and the fuel cell are in series. Thus, we can calculate the total energy output of the process assuming 100% efficiency for steam reforming and multiply the final value by 0.8 to obtain the correct energy output. The following reactions are relevant in this case:



And for the H<sub>2</sub> fuel cell:



12 pts - divided 3 pts each among getting the H<sub>2</sub> fuel cell equation, calculating total energy, electrical energy, and efficiency

Thus, we can calculate the energy output of the system assuming 100% efficiency in the steam-reforming step:

$$10 \text{ g EtOH} \times \frac{1 \text{ mol EtOH}}{46.0694 \text{ g EtOH}} \times \frac{6 \text{ mol } H_2}{1 \text{ mol EtOH}} \times \frac{2 \text{ mol } e^-}{\text{mol } H_2} \times \frac{96485 \text{ C}}{\text{mol } e^-} \times \frac{0.5 \text{ J}}{\text{C}} = 126 \text{ kJ}$$

We can see that this is the same number obtained for the direct ethanol fuel cell, which makes sense for a cell giving the same voltage, because the free energy is a state function, and therefore is the same no matter what intermediate steps you take along the reaction path. However, since the steam-reforming step is only 80% efficient, we multiply by 0.8 and find that the overall energy output of the system is only 100.5 kJ. Thus the efficiency of this process is 35% and the direct ethanol cell is actually more efficient in this case. The fact that the H<sub>2</sub> cell gives a higher current density makes it seem more efficiency at first glance, but it is running at the same voltage, so the energy of each electron harvested is exactly the same. Therefore, the inefficiency of the steam-reforming process reduces the overall energy efficiency.