1. Two identical glass beakers are each filled with 1 liter of aqueous 1M NaCl. HCl is added to Beaker #1 so that the pH of the aqueous solution is 4. NaOH is added to Beaker #2 so that the pH of the aqueous solution is 10. Both solutions are saturated with 1 atm of nitrogen gas.

(a) 5pts. What are the electrochemical reactions that occur on the surface of a piece of iron inserted into Beaker #1?

② $Fe \rightarrow Fe^{++} + 2e^-$

③ $2H^+ + 2e^- \rightarrow H_2$

(b) 5 pts. What are the electrochemical reactions that occur on the surface of a piece of iron inserted into Beaker #2?

② $Fe \rightarrow Fe^{++} + 2e^-$

③ $2H_2O + 2e^- \rightarrow H_2 + 2(OH)^-$

(c) 10 pts. What is the steady-state partial pressure of $H_2(g)$ on the iron surface in Beaker #1 and Beaker #2?

$$\Delta\phi_e(H) = \Delta\phi_e^\circ(H) - \frac{.0592V}{2}\log\frac{P_{H_2}}{(H^+)^2}$$

Initially, $P_{H_2} = 0$

$\Rightarrow \Delta\phi_e(H) = \infty$

As H^+ is reduced, P_{H_2} increases so that $\Delta\phi_e(H)$ decreases. $\Delta\phi_e(H)$ continues to decrease and P_{H_2} continues to increase until $P_{H_2} = 1atm$.

In an open beaker P_{H_2} cannot exceed 1atm.

(d) The aqueous solutions in Beakers #1 and #2 are replaced by 1M NaCl with a pH of 7. In Beaker #1, the solution is saturated with air. In Beaker #2, the solution is saturated with N2(g).

(d)(i) 5 pts. What are the electrochemical reactions that occur on the surface of a piece of iron inserted into Beaker #1 and Beaker #2?

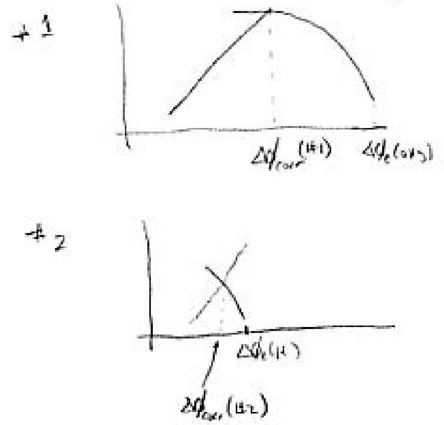
#1 : $Fe \rightarrow Fe^{++} + 2e^-$

$\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2(OH)^-$

#2 $Fe \rightarrow Fe^{++} + 2e^-$

$2H_2O + 2e^- \rightarrow H_2 + 2(OH)^-$

(d)(ii) 10 pts. A salt-bridge now connects the solutions in Beaker #1 and Beaker #2. A high input impedance voltmeter is used to measure the voltage between the two samples of iron located in Beaker #1 and Beaker #2. What is the maximum possible value of the measured voltage?



$V_{meas} = \Delta\phi_{corr}(\#1) - \Delta\phi_{corr}(\#2)$

V_{meas}^{MAX} corresponds to the case in which a protective scale forms on Fe so that the kinetics of oxidation is given by a horizontal line.

For $\beta(H_2) = \beta(O_2)$,

$V_{meas}^{max} = \Delta\phi_e(ox_2) - \Delta\phi_e(H_2)$

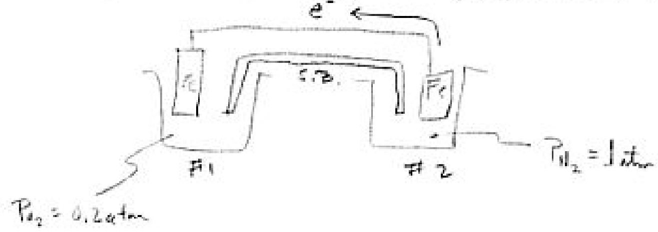
$\Delta\phi_e(H_2) = -0.828\,V - \frac{.0592}{1}\log\left[OH^- P_{H_2}^{1/2}\right]$; $\Delta\phi(ox_2) = 0.401 - \frac{.0592}{2}\log\frac{(OH^-)^2}{P_{O_2}^{1/2}} = 0.805$

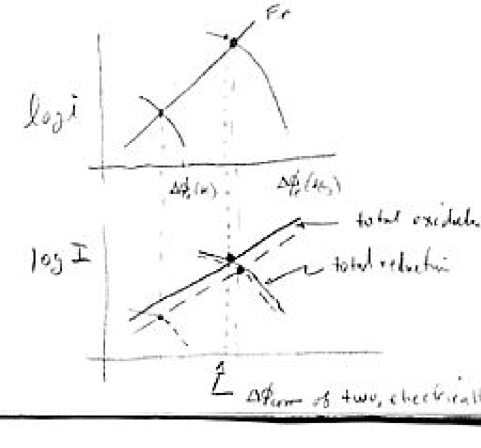
$\Delta\phi_e(H_2) = -0.414\,V$

$V_{meas} = 0.805 + 0.414 = 1.219\,V$

(d) (iii) 10 pts. In addition to the salt bridge, the two pieces of iron in Beakers #1 and #2 are joined together by a copper wire. In which direction will electrons flow in the copper wire? Explain your answer.

From the above sketches, (also, see sketch below)





$\Delta\phi_{corr}$ of two, electrically shorted electrodes of iron.

⇒ There is excess reduction on Fe in Beaker #1 and excess oxidation on Fe in Beaker #2.

2. In this course, the expression for the rate of an electrochemical reaction was derived using the Collision Model of chemical / electrochemical reactions.

(a) 18 pts. In the context of the Collision Model, explain the meaning of each of the following terms: d, (8πkT/m), $\Delta G^{\ddagger}$

d = diameter of "collision volume"

$\frac{8\pi kT}{m} = v^2$ = collision velocity

$\Delta G^{\neq}$ = activation energy

(b) 6 pts. Explain the meaning of the factor β.

Classically, β is that fraction of the reaction coordinate (between reactants and products) at which the total work of activation is a maximum.

(c) 6 pts. When applying the expression for the rate of an electrochemical reaction to the reduction of hydrogen cations, explain why the reduction reaction should be written as
$H^+ + e^- \rightarrow (1/2)\ H_2$
rather than as
$2H^+ + 2e^- \rightarrow H_2$

Rate of a reaction ∝ rate of the slowest step

The activation energy of a two-electron transfer step is very high.

Consequently, the reaction : $2H^+ + 2e^- \rightarrow H_2$

must consist of (at least) two steps : (1) $H^+ + e^- \rightarrow H$

(2) $H^+ + e^- \rightarrow H$

(3) $H + H \rightarrow H_2$

3. (a) 15 pts. Briefly explain why a potential difference develops across the interface between any two phases.

Two key factors are:

⑥ (1) At the interface between any two phases, the set of forces acting on the particles that make up the two phases is anisotropic. The anisotropic set of forces gives rise to a nonhomogeneous arrangement of particles in both phases at the interface.

⑥ (2) Since the particles are electrically charged (or have dipoles), there inhomogeneous arrangement results in a net amount of electrical charge. The magnitude of the electrical charge is the same on both side of the interface, but opposite in sign.

③ (3) A potential drop exists between the oppositely charged phases.

(b) 10 pts. Briefly explain why it is possible to change the value of the interface potential difference between a metal and aqueous 1M NaCl, but it is not possible to change the value of the interface potential difference between two metals.

Electrons are the mobile charge carrier in a metal.

② Ions are the mobile charge carriers in an aqueous solution.

Electrons have approximately zero solubility in the aqueous solution and the ions have approximately zero solubility in the metal.

④ Consequently, the interface between the Metal and the aqueous solution is impermeable to electrons and ions. As a result, excess electrons and ions can be piled up on either side. The potential drop across the interface is directly proportional to the charge density on either side of the interface.

④ In contrast, the metal/metal interface is completely permeable to electrons. As a consequence, an applied voltage will cause current (electron) flow, rather than a charging-up of the interface.