Name Answer Key

$$E = E^0 + \frac{0.059\,V}{n} log\frac{[Ox]}{[Red]} = E^o + \frac{2.303RT}{nF} log\frac{[Ox]}{[Red]} \qquad \Delta G_{rxn} = -RTlnK_{eq} = -nFE_{cell}$$

R = 8.314 J/mol-K T= 298 K F = 96,500 coulombs/mol V = J/C

$$aA + bB = cC + dD \qquad E_{cell} = \left(E^0_{cathode} - E^0_{anode}\right) + \frac{0.059\,V}{n} log\frac{[A]^a[B]^b}{[C]^c[D]^d}$$

Exam III (100 pts)
CEM 434
Fall 2016

1. (10 pts). List the three different modes of mass transfer and provide a brief description of each.

1. Diffusion → movement of species from a high to a low conc. zone. Concentration gradient.
2. Convection → physical movement of analyte – stirring the solution.
3. Migration → movement of a charged analyte in an electric field.

2. (20 pts). For the following cell, determine E_{cell}, ΔG_{rxn} and K_{eq}.

$Cd(s)/Cd(NO_3)_2$ (0.015 M)//$AgNO_3$ (0.250 M)/Ag(s)

$Cd^{+2}_{(aq)} + 2e^- \rightleftharpoons Cd_{(s)}$ $E^o = -0.400\,V$

$Ag^+_{(aq)} + e^- \rightleftharpoons Ag_{(s)}$ $E^o = 0.800\,V$

$E_{Cd} = -0.400 + \frac{0.0592}{2} log(0.015) = -0.434\,V$ (less positive – anode)

$E_{Ag} = 0.800 + \frac{0.0592}{1} log(0.250) = 0.765\,V$ (more positive – cathode)

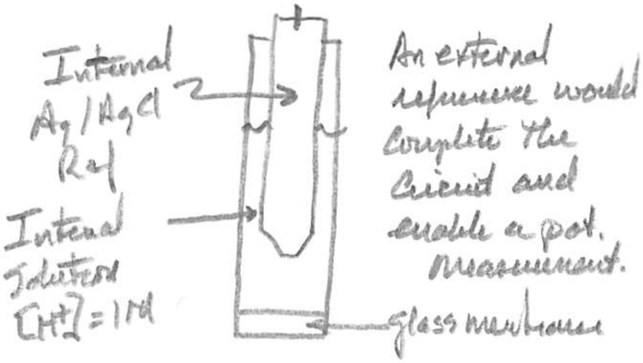
$E_{cell} = E_{Ag} - E_{Cd} = 0.765 - (-0.434) = \underline{1.20\,V}$ $C \cdot V = J$

$\Delta G = -nFE_{cell} = -(2)(96{,}500\ coul/mol)(1.20\,V) = -2.32 \times 10^5\ J/mol$ spontaneous!

$\Delta G = -RT\ln K_{eq}$ $\ln K_{eq} = \frac{\Delta G}{-RT} = \frac{-2.32\times10^5\ J/mol}{-(8.314\ J/mol\text{-}K)(298\ K)} = \underline{9.34\times10^1}$

$K_{eq} = 4.65\times10^{40}$

3. (15 pts). (i) Show the design and describe the function of a glass pH electrode, (ii) indicate what is measured and how this measured value is related to $[H^+]$, and (iii) list two errors that can occur in measurements with this ion selective electrode.



This ion selective electrode responds selectively to the H^+ activity on external side of membrane. Think of the glass membrane as a resistance to ion movement. At any time, the charge within the membrane must be net neutral. Therefore, if one side of the membrane is exposed to a high conc of H^+, protons will enter the membrane due to interactions with negatively charged silicate sites. To maintain neutrality, cations are expelled from the other side of membrane. This gives rise to charge separation across membrane and a potential!

$$E_{meas} = L + \frac{0.059}{1}\log[H^+]$$

$$E_{meas} = L + \frac{0.059}{1}\log\frac{a_{ext}}{a_{int}}$$

- Responds to Na^+ at high pH
- drying out of membrane

4. (15 pts). When a fluoride ion selective electrode was immersed in standard solutions (at constant ionic strength of 0.1 M with $NaNO_3$), the following data were obtained:

$\log[F^-]$	$[F^-]$ (M) (X)	E (mV) (Y)	
−5	1.00×10^{-5}	100.0	58.5
−4	1.00×10^{-4}	41.5	58.5
−3	1.00×10^{-3}	-17.0	

$pF = -\log[F^-]$

$[F^-]$ (M)	E (mV)
1.00×10^{-5}	100.1
1.00×10^{-5}	99.8
1.00×10^{-5}	98.3
1.00×10^{-5}	100.5
1.00×10^{-5}	100.6

Mean ± s = 9.99×10^1 ± ~~0.76~~ 0.93

Assess the reproducibility of the measurement by reporting the data as mean ± S.E.M. and mean ± CI (95%). Also find the $[F^-]$ in an unknown that gave a potential of 0.0 mV.

$$\text{mean} \pm \text{SEM} = \frac{s}{\sqrt{n}} = \frac{\sout{0.76}\ 0.93}{\sqrt{5}} = \sout{0.34}\ 0.42 \qquad 99.9 \pm \sout{0.3}\ 0.4$$

$$\text{mean} \pm CI(95\%) = t\frac{s}{\sqrt{n}} = \frac{(2.776)(\sout{0.76}\ 0.93)}{\sqrt{5}} = \sout{0.94}\ 1.15 \qquad 99.9 \pm \sout{0.9}\ 1.2$$

$$E = m\log[F^-] + b$$

(Y = E, X = $\log[F^-]$)

$m = -58.5\ mV/\log[F^-]$

$b = -192.5\ mV$

$R^2 = -1.000$ (Excellent Fit!)

$$0.00 = (-58.5\ mV/\log[F^-])\,X + -192.5\ mV$$

$$\frac{0.00 + 192.5\ mV}{-58.5\ mV/\log[F^-]} = -3.29 = \log[F^-]$$

$[F^-] = \text{antilog}(-3.29) = 5.1 \times 10^{-4}\ M$

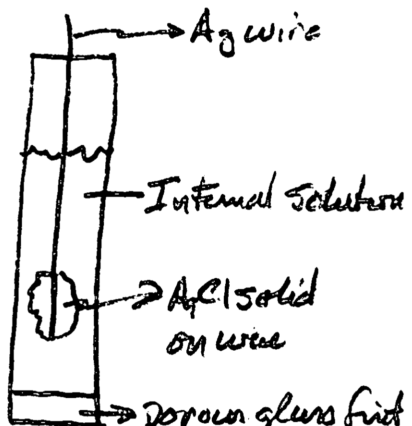
5. (10 pts) What are the acronyms SEM, XPS and XRD? Briefly describe these instruments and indicate what information they provide about a sample.

SEM = Scanning electron microscopy (morphology of sample)

XPS = X-ray photoelectron spectroscopy (surface chemistry, sensitive elemental analysis in near-surface region)

XRD = X-ray diffraction (bulk atomic structure of a solid, crystallinity of a material).

6. (15 pts) (i) Show the design of an Ag/AgCl reference electrode, (ii) indicate the redox reaction that is involved, (iii) show the Nernst equation that describes the potential of the electrode and (iv) indicate what the reference electrode's potential would be under standard conditions and if the [Cl⁻] was increased to 4 M.



$AgCl_{(s)} + e^- \rightleftharpoons Ag_{(s)} + Cl^-$

$E^\circ = 0.222 V$ vs. NHE under standard conditions

$$E = E^\circ + \frac{0.0592}{1} \log \frac{[AgCl]}{[Ag][Cl^-]}$$

AgCl and Ag are pure solids

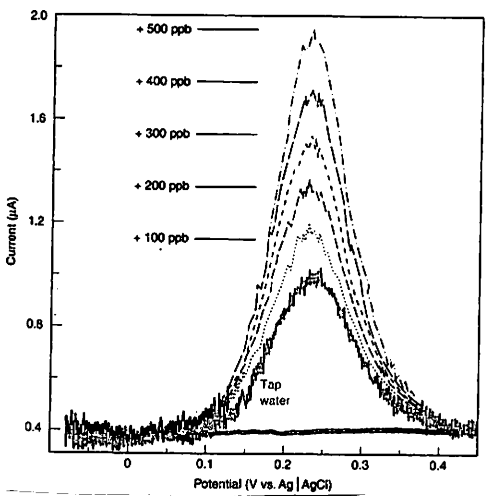
a = 1 or conc = 1M

So $E = E^\circ + \frac{0.0592}{1} \log \frac{1}{[Cl^-]}$

$$E = 0.222 V + \frac{0.059}{1} \log \frac{1}{(4)}$$

$E = \underline{0.186 V}$ (4M KCl)

7. (15 pts). Anodic stripping voltammetry is a voltammetric method of analysis commonly used for trace metal ion analysis. (i) explain what is done in ASV and what controls the sensitivity of the measurement. (ii) The figure below shows a series of ~~standard additions~~ of Cu^{+2} to acidified tap water measured by ASV at a solid electrode. The unknown and all standard additions were made up to the same final volume. What are the reaction reactions that occur during the concentration stage of the measurement and the stripping stage of the analysis? (iii) What is the $[Cu^{+2}]$ in the tap water



1. Preconcentration step at ca. −1.0V where all metal ions are reduced on the electrode to produce metal phase

2. Stripping step – potential is scanned from deposition potential toward more positive values to selectively oxidize each metal phase.

1. Deposition step: $Cu^{+2}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$

2. Stripping step: $Cu_{(s)} \rightarrow Cu^{+2}_{(aq)} + 2e^-$

y Current (μA)	x Conc (ppb)
1.1 − 0.4 = 0.7	100
1.3 − 0.4 = 0.9	200
1.5 − 0.4 = 1.1	300
1.7 − 0.4 = 1.3	400
1.9 − 0.4 = 1.5	500
1.0 − 0.4 = 0.6	unknown

plot current vs. conc

$m = 2.0 \times 10^{-3}$ μA/ppb

$b = 0.50$

$R^2 = 1.000$ excellent fit

current = m (unknown conc) + b

$0.6 = 2.0 \times 10^{-3}$ μA/ppb $(x) + 0.50$

$x = 5.0 \times 10^{1}$ ppb