Solutions to Problem Set 11

1. Starting from $\Delta_{rxn}\boldsymbol{G} = - \nu\mathcal{F}\mathcal{E}$

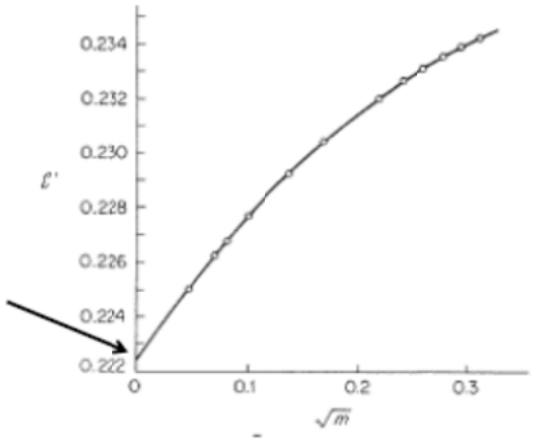
Equation	Basis for the equation	Eq. #
(a)	$d\mathbf{G} = Vdp - \mathbf{S}dT$ Fundamental equation of thermodynamics	1
	$(\partial \mathbf{G} / \partial T)_p = - \mathbf{S}$	2
	$(\partial \Delta_{rxn}\mathbf{G} / \partial T)_p = - \Delta_{rxn}\mathbf{S}$ when Eq 2 is applied to products and reactants of a chemical reaction	3
	$\Delta_{rxn}\boldsymbol{G} = - \nu\mathcal{F}\mathcal{E}$	4
$\nu\mathcal{F} (\partial \mathcal{E} / \partial T)_p = \Delta_{rxn}\mathbf{S}$	Substituting Eq 4 into Eq 3	5
(b)	$(\partial \Delta_{rxn}\mathbf{G}^{\ominus} / \partial T)_p = - \Delta_{rxn}\mathbf{S}^{\ominus}$ Eq 3 at 1 bar	6
	$\Delta_{rxn}\boldsymbol{G}^{\ominus} = - \nu\mathcal{F}\mathcal{E}^{\ominus}$ Eq 4 at 1 bar	7
$\nu\mathcal{F} (\partial \mathcal{E}^{\ominus}{}_T / \partial T)_p = \Delta_{rxn}\mathbf{S}^{\ominus}$	Substituting Eq 7 into Eq 6	8
(c)	$\mathbf{G} = \mathbf{H}\text{-}T\mathbf{S}$	9
	$\Delta_{rxn}\mathbf{H} = \Delta_{rxn}\mathbf{G}_T + T\Delta_{rxn}\mathbf{S}$ when Eq 9 is applied to products and reactants of a chemical reaction	10
$\Delta_{rxn}\mathbf{H} = - \nu\mathcal{F}\mathcal{E} + T\nu\mathcal{F} (\partial \mathcal{E} / \partial T)_p$	Substituting Eq 4 &5 into Eq 10	11
$\Delta_{rxn}\mathbf{H} = - \nu\mathcal{F} [\mathcal{E} - T(\partial(\mathcal{E} / \partial T)_p]$		12
(d)	$\Delta_{rxn}\mathbf{H}^{\ominus} = \Delta_{rxn}\mathbf{G}^{\ominus}{}_T + T\Delta_{rxn}\mathbf{S}^{\ominus}$ when Eq 9 is applied to products and reactants of a chemical reaction at 1 bar	13
$\Delta_{rxn}\mathbf{H}^{\ominus} = - \nu\mathcal{F}\mathcal{E}^{\ominus}{}_T + T\nu\mathcal{F} (\partial \mathcal{E}^{\ominus} / \partial T)_p$	Substituting Eq 7 &8 into Eq 13	
$= - \nu\mathcal{F} [\mathcal{E}^{\ominus}{}_T - T(\partial(\mathcal{E}^{\ominus})/\partial T)_p]$		14
(e)	$(\partial(\mathbf{G} /T)/\partial T)_p = - \mathbf{H}/T^2$ Gibbs-Helmholtz equation	15
	$(\partial(\Delta_{rxn}\mathbf{G}^{\ominus} /T)/\partial T)_p = - \Delta_{rxn}\mathbf{H}^{\ominus}/T^2$ when Eq 15 is applied to products and reactants of a chemical reaction	16
$- \nu\mathcal{F} (\partial(\mathcal{E}^{\ominus}/T)/\partial T)_p$	Substituting Eq 7 into Eq 16	
$= - T^{-2}\Delta_{rxn}\mathbf{H}^{\ominus}$		17
$\nu\mathcal{F} T^2(\partial(\mathcal{E}^{\ominus}/T)/\partial T)_p = \Delta_{rxn}\mathbf{H}^{\ominus}$	Rearranging	
$\nu\mathcal{F} T^2[T^{-1}(\partial(\mathcal{E}^{\ominus})/\partial T)_p - T^{-2}\mathcal{E}^{\ominus}] = \Delta_{rxn}\mathbf{H}^{\ominus}$	Doing the differentiation	
$- \nu\mathcal{F} [\mathcal{E}^{\ominus}{}_T - T(\partial(\mathcal{E}^{\ominus})/\partial T)_p] = \Delta_{rxn}\mathbf{H}^{\ominus}$	Same as Eq 14	
(f)	$d(\ln K_p)/dT = - \Delta_{rxn}\mathbf{H}^{\ominus}/T^2$	18
$d(\ln K_p)/dT = - \nu\mathcal{F} (\partial(\mathcal{E}^{\ominus}/T)/\partial T)_p$	Using Eq 17 into Eq 18	19
(g)	$\mu(T) = \mu^{\ominus}(T) + RT \ln \boldsymbol{a}$	20
	$\Delta_{rxn}\mathbf{G}_T = \Delta_{rxn}\mathbf{G}^{\ominus}{}_T + RT \ln \boldsymbol{Q}$ when Eq 20 is applied to products and reactants of a chemical reaction where $\boldsymbol{Q}$ is the expression containing activities of products and reactants raised to the powers which are the stoichiometric coefficients in the	21

$-\nu\mathcal{F}\mathcal{E} = -\nu\mathcal{F}\mathcal{E}^{\ominus}_T + RT \ln \frac{a_P^p a_R^r}{a_B^b a_C^c}$	chemical reaction as written, $\frac{a_P^p a_R^r}{a_B^b a_C^c}$ Substituting Eq 4 and Eq 7 into Eq 21 This is the Nernst Equation	22
(h) $\nu\mathcal{F}\mathcal{E}^{\ominus}_T = RT \ln K$	$\Delta_{rxn}G^{\ominus}_T = -RT \ln K$ when Eq 21 is applied to a system in equilibrium, for which $\Delta_{rxn}G_T = 0$, so that K has the activity values at chemical equilibrium Substituting Eq 7 into Eq 23	23 24

2. The cell reaction is

Right electrode : $AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$
Left electrode $H^+(aq) + e^- \rightarrow \frac{1}{2}H_2(g)$.
Right - left = $AgCl(s) + \frac{1}{2}H_2(g) \rightarrow Ag(s) + Cl^-(aq) + H^+(aq)$

Equation	Basis for the equation	Eq. #
$Q = \frac{a_{Ag}\, a_{Cl^-}\, a_{H^+}}{a_{AgCl}\, a_{H_2}^{1/2}}$	Using the chemical reaction as written above	1
$a_{Ag} = 1$	activity of pure solid is defined to be 1	2
$a_{AgCl} = 1$		3
$a_{H_2} = 1$	activity of H_2 gas = 1 at 1 atm (ideal gas)	4
$Q = a_{Cl^-}\, a_{H^+}$	Substituting Eq 2,3,4 into Eq 1	5
$-\nu\mathcal{F}\mathcal{E} = -\nu\mathcal{F}\mathcal{E}^{\ominus}_T + RT \ln a_{Cl^-}\, a_{H^+}$	Using equation derived in problem 1 (Eq 22)	6
Here $\nu = 1$		
$\mathcal{E} - \mathcal{E}^{\ominus}_{298} = -(RT/\mathcal{F}) \ln a_{Cl^-}\, a_{H^+}$		7
$a_{Cl^-} = m_{Cl^-} \bullet \gamma_{Cl^-}$	Definition of activity coefficient γ for solution of electrolyte using molality m as unit of concentration	8
$a_{H^+} = m_{H^+} \bullet \gamma_{H^+}$		9
$m_{Cl^-} = m \qquad m_{H^+} = m$		10
$Q = a_{Cl^-}\, a_{H^+} = m^2 \bullet (\gamma_\pm)^2$	combine the activity coefficients into one mean ionic activity coefficient	11
$\mathcal{E} - \mathcal{E}^{\ominus}_{298} = -(RT/\mathcal{F}) \ln a_{Cl^-}\, a_{H^+}$	Substituting Eq 11 into Eq 7	12
$\mathcal{E} - \mathcal{E}^{\ominus}_{298} = -(RT/\mathcal{F}) \ln\{m^2 \bullet (\gamma_\pm)^2\}$		
$\mathcal{E} - \mathcal{E}^{\ominus}_{298} = -(2RT/\mathcal{F}) \ln\{m \bullet \gamma_\pm\}$		
$\mathcal{E} - \mathcal{E}^{\ominus}_{298} = -(2RT/\mathcal{F}) 2.303 \log_{10}\{m \bullet \gamma_\pm\}$		13
where $2.303\,(2RT/\mathcal{F}) =$ $2.303 \bullet 2(8.31451)(298)/96485 =$ 0.1183 volt	volt•coulomb = Joule	
$\mathcal{E} = \mathcal{E}^{\ominus}_{298} - 0.1183 \log_{10} m - 0.1183 \log_{10} \gamma_\pm$		
$\mathcal{E} + 0.1183 \log_{10} m = \mathcal{E}^{\ominus}_{298} - 0.1183 \log_{10} \gamma_\pm$		14

What to do about the term in $\log_{10} \gamma_\pm$? $\log_{10} \gamma_\pm = AI^{½}$ where the ionic strength, $I = ½\sum c_i z_i$ Here $z_+ = 1$ $z_- = 1$ and concentration is in terms of molality, $I = ½ \{m_+(1) + m_-(1)\} = m$ $\log_{10} \gamma_\pm = AI^{½} = Am^{½}$ Take the limit of $\gamma_\pm$ approaching 1, or $\log_{10} \gamma_\pm$ approaching zero, that is, $Am^{½}$ approaching zero $\mathcal{E} + 0.1183 \log_{10} m$ $= \mathcal{E}^{\ominus}_{298} - 0.1183A\, m^{½}$	We make use of the fact that $\gamma_\pm \rightarrow 1$ at ideal limit Debye-Huckel limiting behavior Substituting Eq 16 into Eq 13 Infinitely dilute solution approaches ideality, that is, $\gamma_\pm$ approaching 1 Eq 14 is of the form : $y = am^{½} + \mathcal{E}^{\ominus}_{298}$ where $\mathcal{E}^{\ominus}_{298}$ is the intercept	15 16 17 18 19 20
$\mathcal{E}' = \mathcal{E} + 0.1183 \log_{10} m$  lim $_{m^{½} \rightarrow 0}$ $\mathcal{E}' = \mathcal{E} + 0.1183 \log_{10} m$ $= \mathcal{E}^{\ominus}_{298}$ The plot intercept = 0.2225 volt, thus, $\mathcal{E}^{\ominus}_{298} = 0.2225$ volt **Answer**	Given the function describing the experimental data. This means that to get the value corresponding to $\gamma_\pm = 1$, as shown in Eq 19, we need to extrapolate the plot $\mathcal{E}'$ vs $m^{½}$ of the given function (Eq 21) to the limit $m^{½} = 0$ We can see now the reason why the function plotted was $\mathcal{E} + 0.1183 \log_{10} m$ rather than $\mathcal{E}$ itself and why the x axis is in terms of $m^{½}$ rather than m positive $\mathcal{E}^{\ominus}_{298}$ means reaction is spontaneous as written	21 22 22 24
$\mathcal{E}^{\ominus}_{298} = (RT/\nu\mathcal{F}) \ln \boldsymbol{K}$ $0.2225 = + (0.1183/2.303) \ln \boldsymbol{K}$ $\ln \boldsymbol{K} = 4.3315$ $\boldsymbol{K} = 76.06$	Using Eq 24 from prob 1 Using $\mathcal{E}^{\ominus}_{298} = 0.2225$ volt from Eq 24 in this problem	
reactions at the electrodes (cathode) $H^+(aq) + e^- \rightarrow ½H_2(g)$ (anode): $Ag(s) + Cl^-(aq) \rightarrow AgCl(s) + e^-$	**C**athode: where the redu**C**tion occurs **A**node: where oxid**A**tion occurs	

3. given cell reaction $Cd(s) + 2AgCl(s) \rightarrow CdCl_2$ (satd solution)$+ 2Ag(s)$

Equation	Basis for the equation	Eq. #
$\mathcal{E} = 0.6753$ volt $T = 298$ K $(\partial\mathcal{E}/\partial T)_p = -0.00065$ volt K^{-1} $\nu = 2$	Given for the cell as written above	1 2 3 4
$\Delta_{rxn}\mathbf{S} = \nu\mathcal{F}(\partial\mathcal{E}/\partial T)_p$ $= 2(96485)(-0.00065$ volt $K^{-1})$ $\Delta_{rxn}\mathbf{S} = -125.4$ J K^{-1} mol^{-1} **Answer**	Using Eq 5 derived in problem 1	5 6
$\Delta_{rxn}\mathbf{H} = -\nu\mathcal{F}[\mathcal{E} - T(\partial(\mathcal{E}/\partial T)_p]$ $= -2(96485)[0.6753 - 298\bullet - 0.00065]$ $\Delta_{rxn}\mathbf{H} = -167686$ J mol^{-1} **Answer**	Using Eq 12 derived in problem 1	7 8
$\Delta_{rxn}\mathbf{G} = \Delta_{rxn}\mathbf{H} - T\Delta_{rxn}\mathbf{S}$ $\Delta_{rxn}\mathbf{G} = -167686 - 298(-125.4)$ $\Delta_{rxn}\mathbf{G} = -130\,317$ J mol^{-1} **Answer** we should get the same result from $\Delta_{rxn}\mathbf{G} = -\nu\mathcal{F}\mathcal{E} = -2(96485)(0.6753)$ and indeed we do.	from **G** = **H** - T**S** at constant T applied to a reaction	9 10
$q_{REV} = T\Delta_{rxn}\mathbf{S}$ $q_{REV} = 298(-125.4$ J K^{-1} $mol^{-1})$ $= -37369$ J mol^{-1} **Answer**	Second law of thermodynamics Substituting Eq 6 into Eq 11	11 12
for the direct reaction, not in a cell, $Cd(s) + 2AgCl(s) \rightarrow CdCl_2$ (satd solution)$+ 2Ag(s)$ $q_p = \Delta_{rxn}\mathbf{H} = -167686$ J mol^{-1} **Answer**	$\mathbf{H} = \mathbf{H}(T,p)$ $d\mathbf{H} = C_p dT + (\partial\mathbf{H}/\partial p)_T dp$ $\Delta\mathbf{H} = q_p$ at constant p From Eq 8 Heat released by the direct reaction is not as great as in the reversible reaction.	13
total energy change = energy available to do work + energy not available to do work $\Delta\mathbf{H} = \Delta\mathbf{G} + T\Delta\mathbf{S}$ $-167686 = -130\,317 + -37369$ As indeed it should be	Using Eq 8 & 10 & 12	

4. right electrode $Cu^{2+}(aq) + e^- \rightarrow Cu^+(aq)$

left electrode $H^+(aq) + e^- \rightarrow \frac{1}{2}H_2(g)$.

chemical reaction $Cu^{2+}(aq) + \frac{1}{2}H_2(g, satd) \rightarrow Cu^+(aq) + H^+(aq)$ Eq 1

Equation	Basis for the equation	Eq. #
$\mathcal{E}^{\ominus} = -0.153$ volt for $Cu^+\|Cu^{2+}$ half cell therefore	Given	2

$\mathcal{E}^{\ominus}$ = - 0.153 for $Cu^{2+} + e^- \rightarrow Cu^+$ $\nu = 1$ T = 298 K p = 1 atm pH = 3, so $[H^+(aq)] = 10^{-3}$ mol L^{-1} $[Cu^{2+}(aq)] = 0.01$ m Assume activity coefficients to be ideal, can use m instead of activity		3 4 5 6 7
Cu^{2+} (aq) + ½H_2(g, satd) $\rightarrow$ Cu^+(aq) + H^+(aq) $\mathcal{E}^{\ominus} = \mathcal{E}^{\ominus}[Cu^{2+}(aq) + e^- \rightarrow Cu^+(aq)]$ $- \mathcal{E}^{\ominus}[H^+(aq) + e^- \rightarrow ½H_2(g)]$ $\mathcal{E}^{\ominus}$ = - 0.153 - 0.0 volt	As seen in Eq 1 Using Eq 2 & standard $\mathcal{E}^{\ominus}[H^+(aq)+e^- \rightarrow ½H_2(g)] = 0$	 8
$\nu\mathcal{F}\mathcal{E}^{\ominus}_{298} = RT \ln \boldsymbol{K}$ $1(96485)(-0.153) = (8.31451)(298)\ln \boldsymbol{K}$ $\ln \boldsymbol{K}$ = -5.96 $\boldsymbol{K}$ = exp(-5.96) = 2.58×10^{-3}	Derived in problem 1 (Eq 24) substituting values from Eq 3 & 8	9 10
For the reaction Cu^{2+} (aq) + ½H_2(g, satd) $\rightarrow$ Cu^+(aq) + H^+(aq) $\boldsymbol{K} = \frac{\boldsymbol{a}_{Cu+}\,\boldsymbol{a}_{H+}^{½}}{\boldsymbol{a}_{Cu++}\boldsymbol{a}_{H2}}$ $\boldsymbol{K} = \frac{\boldsymbol{m}_{Cu+}\,\boldsymbol{m}_{H+}^{½}}{\boldsymbol{m}_{Cu++}\boldsymbol{a}_{H2}}$ $2.58\times10^{-3} = \frac{\boldsymbol{m}_{Cu+}\,10^{-3}}{\boldsymbol{m}_{Cu++}\,(1)^{½}}$ $\frac{\boldsymbol{m}_{Cu+}}{\boldsymbol{m}_{Cu++}} = 2.58$ $\boldsymbol{m}_{Cu+}/(0.01 - \boldsymbol{m}_{Cu+}) = 2.58$ $\boldsymbol{m}_{Cu+} = 0.0072$	Assume activity coefficients to be ideal, then can use m instead of activity. Use K value from Eq 10, and Eq 7 gives 10^{-3} mol L^{-1} = 10^{-3} mol/kg water; $m_{H+} = 10^{-3}$ For an ideal gas $\boldsymbol{a}_{H2} = f_{H2} = p_{H2}$ = 1 atm solve for $\boldsymbol{m}_{Cu+}$	 10
Cu^+ (aq) + e^- $\rightarrow$ Cu (s) H^+(aq) + e^- $\rightarrow$ ½H_2(g) . Cu^+ (aq) + ½H_2(g) $\rightarrow$ Cu(s) + H^+(aq) $\nu\mathcal{F}\mathcal{E}^{\ominus}_{298} = RT \ln \boldsymbol{K}$ $1(96485)(0.52) = (8.31451)(298)\ln \boldsymbol{K}$ $\ln \boldsymbol{K}$ = -20.25 $\boldsymbol{K} = 1.6\times10^{-9}$ $\boldsymbol{K} = \frac{\boldsymbol{a}_{Cu}\,\boldsymbol{a}_{H+}^{½}}{\boldsymbol{a}_{Cu+}\boldsymbol{a}_{H2}}$ $1.6\times10^{-9} = \frac{(1)\,10^{-3}}{\boldsymbol{m}_{Cu+}\,(1)^{½}}$ $\boldsymbol{m}_{Cu+} = 0.6\times10^{6}$ **Answer**	 Derived in problem 1 (Eq 24) Look up $\mathcal{E}^{\ominus}$ = - 0.52 volt for the half cell Cu^+|Cu for Cu(s) $\boldsymbol{a}$ = 1, as for any pure solid This is practically unrealizable.	11 12 13

5. Disproportionation of Hg_2^{2+} (aq) ion: $Hg_2^{2+}(aq) \rightarrow Hg^{2+}(aq) + Hg^0(liq)$ net reaction

$$\tfrac{1}{2}Hg_2^{2+}(aq) + e^- \rightarrow Hg^0 \qquad \mathcal{E}^{\ominus}_{298} = 0.79$$
$$Hg^{2+}(aq) + e^- \rightarrow \tfrac{1}{2}Hg_2^{2+}(aq) \qquad \mathcal{E}^{\ominus}_{298} = 0.91$$

Equation	Basis for the equation	Eq. #
$\mathcal{E}^{\ominus}_{298} = 0.79 - 0.91 = -0.12$ volt	Look up standard half cell potentials	
$\nu\mathcal{F}\mathcal{E}^{\ominus}_{298} = RT \ln \boldsymbol{K}$ $1(96485)(-0.12) = (8.31451)(298)\ln \boldsymbol{K}$ $\ln \boldsymbol{K} = -4.673$ $\boldsymbol{K} = 0.00934$ $Hg_2^{2+}(aq) \rightarrow Hg^{2+}(aq) + Hg^0$ $\boldsymbol{K} = \frac{a_{Hg}\, a_{Hg2+}}{a_{Hg2++}}$ $0.0093 = \frac{(1)\, m_{Hg2+}}{(\approx 0.01)}$ $m_{Hg2+} = 0.00093$ degree of disproportionation is 0.00093/(0.01) = 0.093 or 9.3%	Derived in problem 1 (Eq 24) a_{Hg} = 1 for Hg^0(liq) as for any pure liquid	

6. K_{sp} for Ag_2SO_4(s) at 298 K

Equation	Basis for the equation	Eq. #
cell: $Ag\|Ag_2SO_4 \,\|\|\, H_2SO_4(m)\|H_2\|Pt$ $\mathcal{E}^{\ominus}_{298} = +0.80$ volt	Given	
$Ag_2SO_4 + 2e^- \rightarrow Ag^0$ $\mathcal{E}^{\ominus}_{298} = +0.80$ volt		1
$H^+(aq) + e^- \rightarrow \tfrac{1}{2}H_2(g)$ $\mathcal{E}^{\ominus}_{298} = 0.0$ volt		
$Ag^+ + e^- \rightarrow Ag^0$ $\mathcal{E}^{\ominus}_{298} = -0.627$ volt	Look up standard half-cell potential	2
$Ag_2SO_4 = 2Ag^+ + SO_4^{2-}$	Taking Eq (1) minus 2• Eq(2)	3
$\mathcal{E}^{\ominus}_{298} = 0.80 - (-0.627) = -0.173$ volt		4
$\nu\mathcal{F}\mathcal{E}^{\ominus}_{298} = RT \ln \boldsymbol{K}$ $2(96485)(-0.173) = (8.31451)(298)\ln \boldsymbol{K}$ $\ln \boldsymbol{K} = -13.47$ $\boldsymbol{K_{sp}} = 1.4\times10^{-6}$ **Answer**	Derived in problem 1 (Eq 24) Apply to solubility Eq 3, using value from Eq 4	

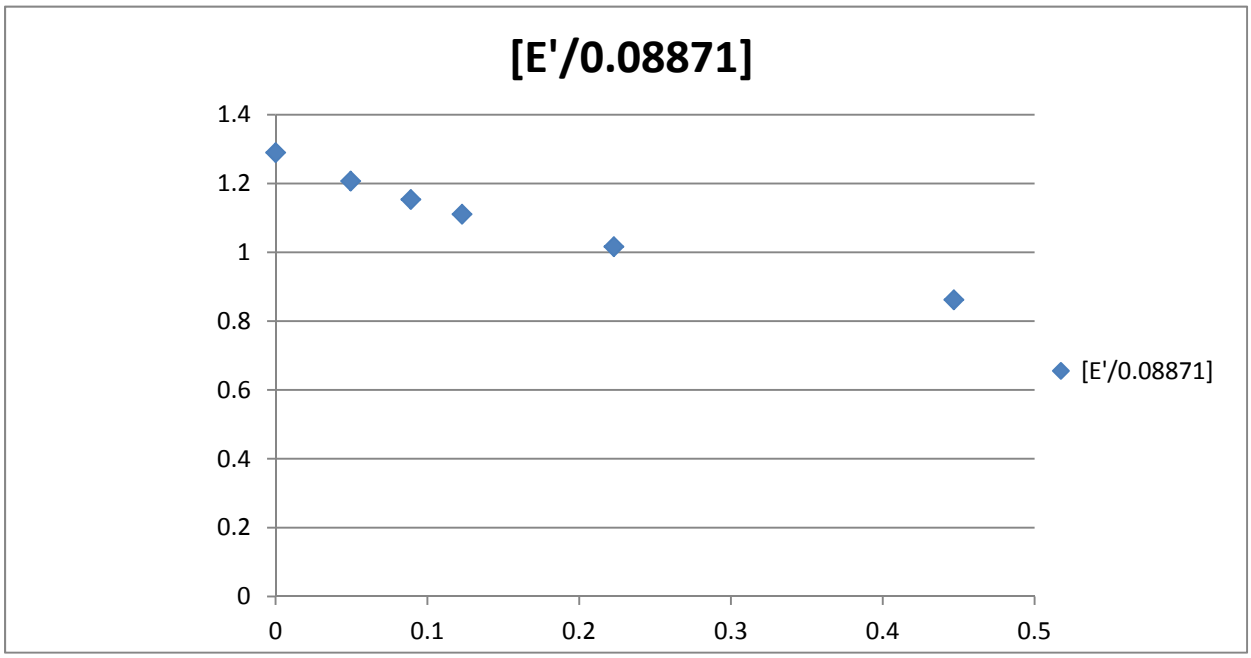
7. $Pt|H_2(1atm)|m\ Ba(OH)_2|Ba(amalgam)|0.1200\ m\ Ba(OH)_2|\ H_2(1atm)|Pt$

Equation	Basis for the equation	Eq. #
half cell reactions:	A concentration cell acts to dilute the more concentrated solution and concentrate the more dilute solution, creating a voltage as the cell	

$Ba(OH)_2$ 0.1200 m + 2e- = Ba^0 + $2OH^-$ $Ba(OH)_2$ m + 2e- = Ba^0 + $2OH^-$ net cell reaction (right -left): $Ba(OH)_2$ 0.1200 m = $Ba(OH)_2$ m $\mathcal{E}^{\ominus}_{298} = 0$ For m < 0.1200 m in $Ba(OH)_2$, the left compartment will form more $Ba(OH)_2$, while the right compartment will form more Ba^0 until equilibrium is reached, at which point $\mathcal{E}$ goes to zero.	reaches an equilibrium. This is achieved by transferring the electrons from the cell with the lower concentration to the cell with the higher concentration. Since both half cells are the same, the difference between the half-cell standard potentials is zero,	1 2 3
$\mathcal{E}$ - 0 = - (RT/2$\mathcal{F}$) ln $\frac{a_{Ba++}\, a_{OH-}^2}{a_{Ba++}\, a_{OH-}^2}$ $a_{Ba++} = m\,\gamma_{\pm}$ $a_{OH-} = 2m\,\gamma_{\pm}$ Let m_1 = 0.01200 m_2 = variable Q numerator has $a_{Ba++} = m_1(\gamma_{\pm})_{m1}$ $a_{OH-} = 2m_1(\gamma_{\pm})_{m1}$ denominator has $a_{Ba++} = m_2(\gamma_{\pm})_{m2}$ $a_{OH-} = 2m_2(\gamma_{\pm})_{m2}$ $\mathcal{E}$ = - (RT/2$\mathcal{F}$) ln $\frac{[(\gamma_{\pm})_{m1}]^3\, 4\, m_1^3}{[(\gamma_{\pm})_{m2}]^3\, 4\, m_2^3}$ (RT/2$\mathcal{F}$)2.303(3) = (8.31451)(298)(2.303)(3)/(2•96485) = 0.08871 $\mathcal{E}$ = - 0.08871• [$\log_{10} m_1(\gamma_{\pm})_{m1}$ - $\log_{10} m_2(\gamma_{\pm})_{m2}$] $\mathcal{E}$ - 0.08871 $\log_{10} m_2$ = 0.08871 $\log_{10}(\gamma_{\pm})_{m2}$ + 0.08871C where C = $-\log_{10} m_1 (\gamma_{\pm})_{m1}$, which is a constant since m_1 = 0.1200 Calculate $\mathcal{E}' = \mathcal{E}$ - 0.08871 $\log_{10} m_2$ $\mathcal{E}'$/ 0.08771 = $\log_{10}(\gamma_{\pm})_{m2}$ + C Plot $\mathcal{E}'$/0.08771 vs $m^{1/2}$. The intercept is C	Nernst equation Using a mean ion activity coefficient for both anion and cation Remember that $\gamma_{\pm}$ depends on concentration m Substituting Eq 7,8,9,10 into Eq 4 When m_2=m_1, then $\mathcal{E}$ = 0 How to find C? We make use of the fact that $\gamma_{\pm} \rightarrow 1$ at ideal limit Given table of data: $\mathcal{E}$ vs m_2 In the limit that $m^{1/2}$ goes to zero, $\log_{10}(\gamma_{\pm})$ is zero As in problem 2, make use of Debye Huckel limit Substitute C in Eq 14 to calculate $(\gamma_{\pm})_m$ at every m	4 5 6 7 8 9 10 11 12 13 14
Plot $(\gamma_{\pm})_m$ vs m and read off value for m = 0.1000 molal to get 0.47 **Answer**	See two plots & table below for numerical calculations.	

$\mathcal{E}$	-0.1245	-0.0840	-0.0630	-0.0254	0.0144	Given
$m = m_2$	0.00245	0.00793	0.01509	0.04970	0.1996	Given
$m^{½}$	0.04950	0.08905	0.1228	0.2229	0.4468	
$\log_{10} m$	-2.6108	-2.1007	-1.8213	-1.303	-0.6998	
$0.08871 \bullet \log_{10} m$	-0.23160	-0.18635	-0.16157	-0.11559	-0.06208	
$\mathcal{E}' = \mathcal{E} - 0.08871 \log_{10} m$	0.1071	0.10235	0.09857	0.09019	0.07648	$=0.08871 \log_{10}(\gamma_{\pm})_m + 0.08871C$
Plot $\mathcal{E}'/0.08871 = (\log_{10}(\gamma_{\pm})_{m2} + C)$ vs $m^{½}$. When $(\gamma_{\pm})$ approaches 1. Find the intercept C						
$[\mathcal{E}'/0.08871]$	1.2073	1.1538	1.1111	1.0166	0.8621	$= \log_{10}(\gamma_{\pm})_m + C$
$\log_{10}(\gamma_{\pm})_m$	-0.0827	-0.1362	-0.1789	-0.2734	-0.4279	Using value of C= 1.29
$(\gamma_{\pm})_m$	0.827	0.731	0.662	0.533	0.373	take the antilog
compare with $(\gamma_{\pm})_m$ published	0.820	0.726	0.657	0.531	0.370	Harned & Mason
From 2nd plot read off the value $(\gamma_{\pm}) = 0.47$ at m=0.1000						

Plot $\mathcal{E}'/0.08871 = (\log_{10}(\gamma_{\pm})_{m2} - C)$ vs $m^{½}$. Find intercept = 1.29



Plot ($\gamma_{\pm}$) vs m Read off 0.47 as the value of ($\gamma_{\pm}$) at m = 0.1000