

CHEM 311 (Term 132)

First Major Exam

2.0 HOURS

Sunday, March 2, 2014, 7-9 pm

Version 0

Sec. 1: Dr. Khaled, Sec. 2: Dr. Morsy, Sec. 3: Dr. Förner, Sec. 4: Dr. Maung

STUDENT NAME:

(7)

STUDENT ID NUMBER:

Correct Answers (5 points each):

TOTAL Points out of 100:

PHYSICAL CONSTANTS:

$$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$R = 0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1}$$

$$R = 0.08314 \text{ L bar K}^{-1} \text{ mol}^{-1}$$

$$N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$$

$$k_B = 1.381 \times 10^{-23} \text{ J K}^{-1}$$

$$h = 6.626 \times 10^{-34} \text{ J s}$$

$$1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$$

$$F = 96,485 \text{ C mol}^{-1}$$

$$1 \text{ atm} = 1.101325 \times 10^5 \text{ Pa}$$

$$g = 9.81 \text{ m s}^{-2}$$

$$c = 2.998 \times 10^8 \text{ m s}^{-1}$$

$B = 0.5092 \text{ mol}^{-1/2} \text{ dm}^{3/2}$ (in H_2O , 25°C)
constant in DHLL in the \log_{10} form, for molarity

$$0 \text{ K} = -273.15 \text{ }^\circ\text{C}$$

$$\ln(x)/\log_{10}(x) = 2.30259 \text{ for all } x$$

$$(RT)/F = 25.6926 \text{ mV at } 25^\circ\text{C for the ln form}$$

$$e = 1.6022 \times 10^{-19} \text{ C}$$

and $RT/F = 59.15940^{\text{59}}$ mV at 25°C for the \log_{10} form of the Nernst equation

$$\epsilon_0 = 8.854 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}$$

$$I = \frac{1}{2} C_{NaCl} (1 \cdot (+1)^2 + 1 \cdot (-1)^2)$$

$$\neq \frac{1}{2} C_{Na_3PO_4} (3 \cdot (+1)^2 + 1 \cdot (-3)^2)$$

$$\neq \frac{1}{2} C_{Al_2S_3} (2 \cdot (+3)^2 + 3 \cdot (-2)^2)$$

- 1 Determine the molarity of $Al_2S_3(aq)$ in a solution which contains 0.100 M $NaCl(aq)$, 0.100 M $Na_3PO_4(aq)$, and $Al_2S_3(aq)$, assuming all electrolytes as strong and as easily soluble ones, when the ionic strength of the solution is 1.400 M?

(A) 0.0467 M

$$1.4 M = 0.7 M + 15 C_{Al_2S_3}$$

B) 0.0833 M

$$C_{Al_2S_3} = \frac{0.7}{15} M = 0.0467 M$$

C) 0.00667 M

D) 0.0233 M

E) 0.100 M

- 2 Consider a weak acid with a molar conductivity of $3.76 \text{ S cm}^2 \text{ mol}^{-1}$ at 298K and 0.0100 M concentration. The molar conductivity is found to be $1.27 \text{ S cm}^2 \text{ mol}^{-1}$ when the concentration is 0.0500 M. Given the molar conductivity at infinite dilution to be $39.56 \text{ S cm}^2 \text{ mol}^{-1}$ determine the dissociation equilibrium constant, calculated in terms of molarities, of the acid.

(A) 3.17×10^{-5}

$$\frac{1}{\Lambda} = \frac{1}{\Lambda^\circ} + \frac{C \cdot \Lambda}{(\Lambda^\circ)^2 K_a}$$

B) 1.25×10^{-3}

$$x = C \cdot \Lambda \quad y = \frac{1}{\Lambda}$$

C) 1.28×10^{-2}

$$\Delta x = x_2 - x_1 = (1.27 \cdot 0.05 - 3.76 \cdot 0.01) \frac{M \text{ S cm}^2}{\text{mol}}$$

D) 3.15×10^4

$$= 0.0259 \frac{M \text{ S cm}^2}{\text{mol}}$$

E) 3.17×10^{-4}

$$\Delta y = y_2 - y_1 = \left(\frac{1}{1.27} - \frac{1}{3.76} \right) \frac{\text{mol}}{\text{S cm}^2}$$

$$= 0.52144 \frac{\text{mol}}{\text{S cm}^2}$$

$$a = \frac{\Delta y}{\Delta x} = \frac{0.52144}{0.0259} \left(\frac{\text{mol}}{\text{S cm}^2} \right) \cdot \frac{1}{M} = 20.132819 \left(\frac{\text{mol}}{\text{S cm}^2} \right)^2 \frac{1}{M}$$

$$\frac{K_a}{a} = a = \frac{1}{(a^\circ)^2 K_a} \rightarrow K_a = \frac{1}{a (a^\circ)^2}$$

$$K_a = \frac{1}{20.132819 \left(\frac{\text{mol}}{\text{S cm}^2} \right)^2 \frac{1}{M} \cdot \left(39.56 \frac{\text{S cm}^2}{\text{mol}} \right)^2} = 3.17 \cdot 10^{-5} M$$

Born model $\frac{z^2 e^2 N_A}{8 \pi \epsilon_0 r} \left(\frac{1}{\epsilon_v} - 1 \right) = \Delta G_{\text{solvation}}^{\circ}$

$$\frac{\Delta G_{\text{solv}}^{\circ}(\text{Sr}^{2+})}{\Delta G_{\text{solv}}^{\circ}(\text{Li}^{+})} = \frac{(z^2/r)_{\text{Sr}^{2+}}}{(z^2/r)_{\text{Li}^{+}}} = \frac{4/1.18}{1/0.59} = \frac{4 \cdot 0.59}{1.18} = 2 \quad 1.18 = 2 \cdot 0.59$$

$$\Delta G_{\text{solvation}}^{\circ}(\text{Sr}^{2+}) = 2 \Delta G_{\text{solvation}}^{\circ}(\text{Li}^{+})$$

3 Given the ionic radii of lithium and strontium in the gas phase as 0.59 pm and 1.18 pm respectively. Then, the following statement is true:

- A) Lithium ions dissolve better than strontium ions. *wrong, see C)*
- B) More heat is released when lithium ions are dissolved as compared to strontium ions. *wrong, see C)*
- C) The Gibbs energy of solvation for strontium ions is twice that for lithium ions.**
- D) There will be more deviations from the Debye-Hückel limiting model in the case of lithium ions as compared to strontium ions.
- E) The logarithm of the activity coefficient for lithium ions is *charge* expected to drop faster with concentration increase as compared to strontium ions (in the same electrolyte) in solution.

no, we have seen that deviations increase for increasing charge
no $\ln a_{\pm} \sim -|z_{+}z_{-}| \Rightarrow$ drop faster for Sr^{2+} than for Li^{+}

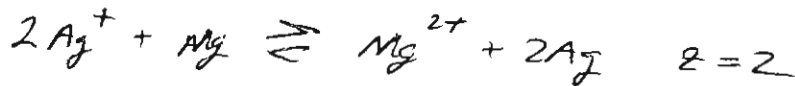
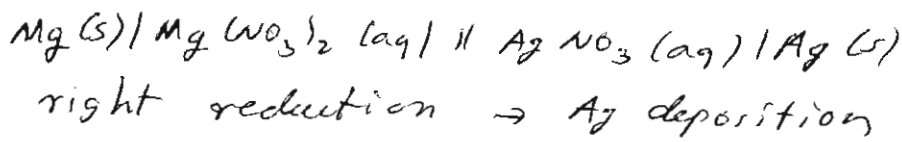
4 The solubility product of 0.00100 M PbCl_2 in pure water is 1.60×10^{-5} in terms of molarity. In order to decrease the amount of lead in the solution by the largest amount, we may add (assume that no precipitates are formed):

$$K_{\text{sp}} = \frac{c_{\text{Pb}^{2+}}}{c^{\circ}} \left(\frac{c_{\text{Cl}^{-}}}{c^{\circ}} \right)^2 \gamma_{\pm}^3$$

- A) 1.35 M NaCl**
- B) 0.00100 M Na_2SO_4
- C) 0.00100 M NaCl \rightarrow decrease of $c_{\text{Pb}^{2+}}$ when $c_{\text{Cl}^{-}}$ is increased
- D) 0.001 M Na_3PO_4
- E) 0.0034 M NaCl *the larger is the $c_{\text{Cl}^{-}}$ increase, the smaller becomes $c_{\text{Pb}^{2+}}$*

\rightarrow smallest $c_{\text{Pb}^{2+}}$ at largest c_{NaCl}

Na_2SO_4 and Na_3PO_4 only change γ_{\pm} a little, because of only 0.001 M in B) and D)



5 An electrochemical cell consists of a silver electrode in contact with 200. mL of 0.100 M AgNO₃ solution and a magnesium electrode in contact with 100. mL of 0.100 M Mg(NO₃)₂ solution (both aqueous solutions at 25°C). Determine the EMF of the cell at 298.15 K, before and after a current is passed leading to the deposition of 0.500 g of the silver (molar masses: Ag: 107.8682 g/mol, Mg: 24.30509 g/mol).

Given Standard reduction potentials: E°_{Ag+/Ag} = +0.80V,

E°_{Mg2+/Mg} = -2.37V

$$E^{\circ} = (E^{\circ}_{right} - E^{\circ}_{left}) = (E^{\circ}_{Ag^+/Ag} - E^{\circ}_{Mg^{2+}/Mg})$$

(A) 3.14 V, ~~3.13 V~~

$$= (0.80 - (-2.37))V = 3.17V$$

B) ~~3.14 V, 3.14 V~~ 2.80 kV

C) ~~3.14 V, 3.15 V~~ 4.15 V

$$E = E^{\circ} - \frac{RT}{2F} \ln \frac{[Mg^{2+}]}{[Ag^+]^2}$$

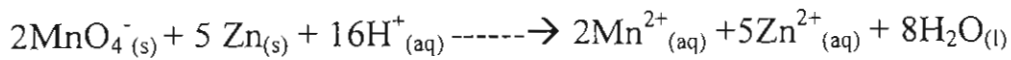
D) ~~3.14 V, 1.11 V~~ 3.14 kV

$$= 3.17V - \frac{25.6926 \text{ mV}}{2} \ln \frac{0.1}{(0.1)^2}$$

E) ~~3.14 V~~ 3.13 mV

$$= 3.17V - 12.8463 \text{ mV} \cdot \ln 10 = 3.14V$$

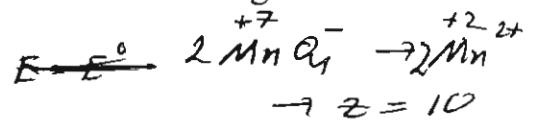
6 Consider the following cell reaction:



E° = 2.27 V - Nernst equ.: Zn(s) and H₂O(l) not in Q

Which of the following conditions would increase the voltage of the cell:

(A) Reducing the pH of the solution



B) Decreasing the MnO₄⁻ concentration
opposite, E decreases

C) Increasing the Mn²⁺(aq) concentration
opposite, E decreases

D) Adding more solid Zn(s)
no change

E) Decreasing the amount of Zn(s)
no change

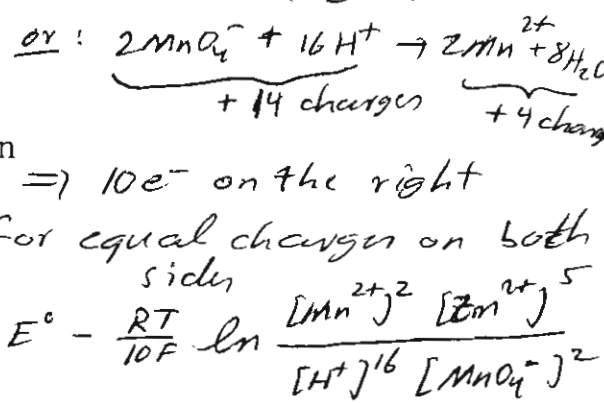
less subtracted from E°

when Q increases = ln Q increases or better activity

increase of ln Q ⇒ less subtracted from E°

⇒ E increases

pH = -log₁₀ [H⁺]
 → pH smaller
 → a_{H+} larger
 → Q decreases
 → E increases
 a_{H+} = 10^{-pH}



$$\begin{aligned}\Delta G_R^\circ &= -nFE^\circ \\ &= -1 \text{ mol} \cdot 96485 \frac{\text{As}}{\text{mol}} \cdot 3.65 \text{ V} \\ &= -3.52 \cdot 10^5 \frac{\text{J}}{\text{mol}}\end{aligned}$$

- 7 If the standard potential of a cell is $E^\circ = 3.65 \text{ V}$ at 298.15 K and $(dE^\circ/dT)_p = -6.20 \times 10^{-5} \text{ VK}^{-1}$, the thermodynamic parameter ΔH_R° in J/mol for a single electron transfer is:

$$\begin{aligned}\Delta S_R^\circ &= nF \left(\frac{\partial E^\circ}{\partial T} \right)_p \\ &= 1 \text{ mol} \cdot 96485 \frac{\text{As}}{\text{mol}} \left(-6.2 \cdot 10^{-5} \frac{\text{V}}{\text{K}} \right) \\ &= -5.98 \frac{\text{J}}{\text{K}} \\ \Delta H_R^\circ &= \Delta G_R^\circ + T \Delta S_R^\circ \\ &= (-3.52 \cdot 10^5 - 298.15 \cdot 5.98) \text{ J} \\ &= -3.54 \cdot 10^5 \text{ J}\end{aligned}$$

- 8 How can it be decided if an electrolyte is a weak electrolyte and how can the molar conductivity at infinite dilution be determined?

- (A) If a plot of the inverse molar conductivity vs. the electrical conductivity is linear, and the molar conductivity at infinite dilution is the inverse of the intercept of this straight line.
- B) If a plot of the inverse molar conductivity vs. the electrical conductivity is linear, and the molar conductivity at infinite dilution is the intercept of this straight line. *no intercept = $\frac{1}{\Lambda^\circ}$*
- C) If a plot of the inverse molar conductivity vs. the electrical conductivity is linear, and the molar conductivity at infinite dilution is the inverse of the slope of this straight line. *no slope = $\frac{1}{\Lambda^\circ R K_a}$*
- D) If a plot of the molar conductivity vs the square root of c/c_0 ($c_0 = 1 \text{ M}$, and c is the concentration of the electrolyte) is linear and the molar conductivity at infinite dilution is the slope of this straight line. *no Λ vs $\sqrt{c/c_0}$ linear \rightarrow strong not weak*
- E) If a plot of the molar conductivity vs the square root of c/c_0 ($c_0 = 1 \text{ M}$, and c is the concentration of the electrolyte) is linear and the molar conductivity at infinite dilution is the intercept of this straight line. *no Λ vs $\sqrt{c/c_0}$ linear \rightarrow strong not weak*

weak:

$$\frac{1}{\Lambda} = \frac{1}{\Lambda^\circ} + \frac{c \cdot \kappa}{(\Lambda^\circ)^2 K_a} = \frac{1}{\Lambda^\circ} + \frac{\kappa}{(\Lambda^\circ)^2 K_a}$$

$\rightarrow \frac{1}{\Lambda}$ vs κ straight line

$$\Lambda^\circ = \frac{1}{\text{intercept}}$$

9 How can a plot of $\Delta G^{\circ}_{\text{solvation}}$ vs z^2/r be made better linear for different ions to improve the model?

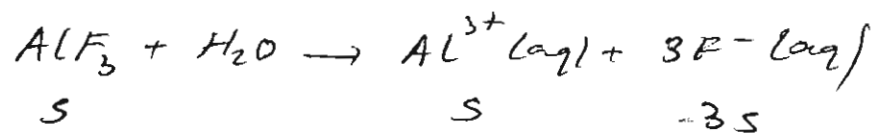
- A) Use of z^2/r_{eff} instead of z^2/r , where r_{eff} is the average distance between the center of the ion and the center of charge of a water molecule in the solution. *see book: discussion of Born model in chapter 10*
- B) Use of z^2/r_{eff} instead of z^2/r , where r_{eff} is the average distance between two water molecules in the solution.
- C) Use of z^2/r_{eff} instead of z^2/r , where r_{eff} is the average distance between two ions in the solutions.
- D) Use of z^2/r_{eff} instead of z^2/r , where r_{eff} is the maximum distance an ion can move during electrolysis.
- E) Use of z_{eff}^2/r instead of z^2/r , where z_{eff} is the average charge of cation and anion.

10 Use the Debye-Hückel Limiting Law (DHLL) and do three steps of an iteration to calculate an approximate value of the solubility of aluminum fluoride (AlF_3) ($K_{\text{sp}} = 3.51 \times 10^{-10}$) in water at 25°C . Assume aluminum fluoride to be a strong electrolyte and assume all concentration units to be M with $c_0 = 1$ M.

- A) 2.99×10^{-3} M
- B) 1.90×10^{-3} M
- C) 0.018 M
- D) 0.0114 M
- E) 1.99×10^{-2} M

see next page

10



$$K_{sp} = \frac{C_{\text{Al}^{3+}}}{c_0} \left(\frac{C_{\text{F}^-}}{c_0} \right)^3 \gamma_{\pm}^4$$

step 1 : $\gamma_{\pm} = 1$

$$K_{sp} = \frac{s}{c_0} \left(\frac{3s}{c_0} \right)^3 = 27 \frac{s^4}{c_0^4}$$

$$\begin{aligned}
 s &= \sqrt[4]{\frac{K_{sp}}{27}} \cdot M = \sqrt[4]{\frac{3.51 \cdot 10^{-10}}{27}} \text{ M} \\
 &= 1.899 \cdot 10^{-3} \text{ M} \quad (1)
 \end{aligned}$$

step 2 $I = \frac{1}{2} (s(3)^2 + 3s) = \frac{1}{2} (12s) = 6s = 0.0114 \text{ M}$

$$\begin{aligned}
 \ln \gamma_{\pm} &= -1.173 |z_+ z_-| \sqrt{I/M} = -1.173 \cdot 3 \cdot \sqrt{0.0114} \\
 &= -0.376
 \end{aligned}$$

$$\gamma_{\pm} = \exp(-0.376) = 0.687$$

$$s = \sqrt[4]{\frac{K_{sp}}{27}} \cdot \frac{1}{\gamma_{\pm}} = 1.899 \cdot 10^{-3} \frac{\text{M}}{0.687} = 2.764 \cdot 10^{-3} \text{ M} \quad (2)$$

step 3 $I = 6s = 6 \cdot 2.764 \cdot 10^{-3} \text{ M} = 0.0166 \text{ M}$

$$\ln \gamma_{\pm} = -1.173 \cdot 3 \cdot \sqrt{0.0166} = -0.453$$

$$\gamma_{\pm} = 0.636$$

$$s = \sqrt[4]{\frac{K_{sp}}{27}} \cdot \frac{1}{\gamma_{\pm}} = \frac{1.899 \cdot 10^{-3} \text{ M}}{0.636} = 2.986 \cdot 10^{-3} \text{ M}$$

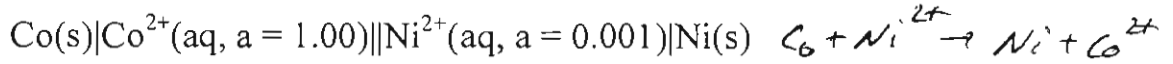
⇒ after 3 steps $s(\text{step 3}) = 2.99 \cdot 10^{-3} \text{ M}$

$$E^{\circ} = E^{\circ}_{\text{right}} - E^{\circ}_{\text{left}} = E^{\circ}_{\text{Ni}^{2+}/\text{Ni}} - E^{\circ}_{\text{Co}^{2+}/\text{Co}}$$

$$= (-0.257 - (-0.280)) \text{ V}$$

$$= 0.023 \text{ V}$$

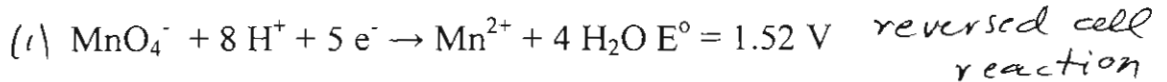
11 What will happen in the electrochemical cell at 25°C:



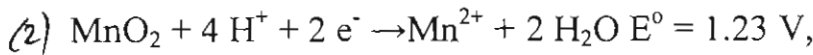
if $E^{\circ}_{\text{Co}^{2+}/\text{Co}} = -0.280 \text{ V}$ and $E^{\circ}_{\text{Ni}^{2+}/\text{Ni}} = -0.257 \text{ V}$.

- (A) Cobalt (Co) is deposited at the Co electrode.
 $E = E^{\circ} - \frac{RT}{2F} \ln \frac{a_{\text{Co}^{2+}}}{a_{\text{Ni}^{2+}}}$
 $= 0.023 \text{ V} - \frac{25 \cdot 6926 \text{ mV}}{2} \cdot \ln \frac{1.00}{0.001} \text{ mV}$
 $= 0.023 \text{ V} - 12.8463 \text{ mV} \cdot 6.9078$
 $= 0.023 \text{ V} - 0.0887 \text{ V}$
 $= -0.0657 \text{ V} < 0$
- B) The concentration of nickel (Ni) ions decreases.
no, increases
- C) The concentration of cobalt (Co) ions increases.
no, decreases
- D) Nickel (Ni) is deposited at the Ni electrode.
no, Ni dissolves
- E) Nickel (Ni) is deposited at the Co electrode.
no, Ni dissolves

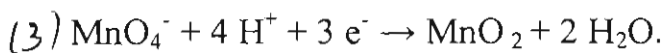
12 Given



and



calculate E° for the half-cell reaction



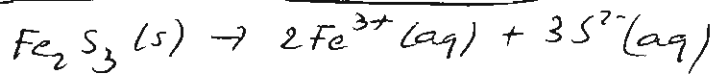
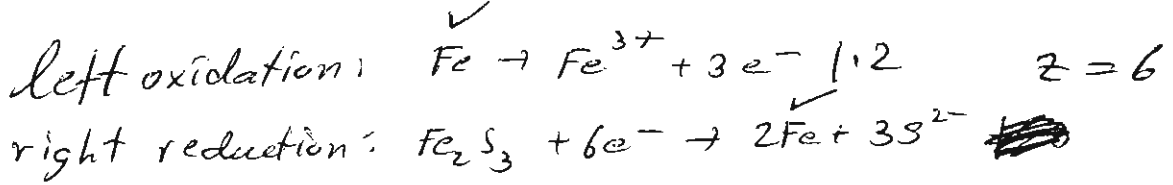
- (A) 1.71 V
 (1) - (2) = + (1) keep MnO_4^- on right side
 - (2) puts MnO_2 to the left
- B) -1.71 V
 (1) - (2): $\text{MnO}_4^- + 4\text{H}^+ + 3\text{e}^- + \text{Mn}^{2+} + 2\text{H}_2\text{O}$
 $\rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O} + \text{MnO}_2 + 4\text{H}^+ + 2\text{e}^-$
- C) 3.35 V
 $= \text{MnO}_4^- + 4\text{H}^+ + 3\text{e}^- \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$
 $= (3)$
- D) -3.35 V
- E) 5.13 V

$$\Delta G_3^{\circ} = \Delta G_1^{\circ} - \Delta G_2^{\circ}$$

$$-n_3 F E_3^{\circ} = -n_1 F E_1^{\circ} + n_2 F E_2^{\circ}$$

$$E_3^{\circ} = \frac{n_1}{n_3} E_1^{\circ} - \frac{n_2}{n_3} E_2^{\circ} = \left(\frac{5}{3} \cdot 1.52 - \frac{2}{3} \cdot 1.23 \right) \text{ V}$$

$$= 1.71 \text{ V (333...)}$$



13 Use the cell at 25°C: $E = E^\circ - \frac{RT}{6F} \ln a_{\text{Fe}^{3+}}^2 \cdot a_{\text{S}^{2-}}^3$

$$\text{Fe}(s) | \text{Fe}^{3+}(aq, a_{\text{Fe}^{3+}}) || \text{S}^{2-}(aq, a_{\text{S}^{2-}}) | \text{Fe}_2\text{S}_3(s) | \text{Fe}(s) = E^\circ - \frac{25.6926 \text{ mV}}{6} \ln K_{sp}$$

to determine the solubility product of Fe_2S_3 , when $E^\circ_{\text{Fe}^{3+}/\text{Fe}} = 0.041 \text{ V}$

and $E^\circ_{\text{Fe}_2\text{S}_3/\text{Fe}} = -0.321 \text{ V}$. $E^\circ = E^\circ_{\text{right}} - E^\circ_{\text{left}} = E^\circ_{\text{Fe}_2\text{S}_3/\text{Fe}} - E^\circ_{\text{Fe}^{3+}/\text{Fe}}$

$$= (-0.321 - 0.041) \text{ V} = -0.362 \text{ V}$$

$$E = -0.362 \text{ V} - 4.2821 \frac{\text{mV}}{\ln K_{sp}}$$

Equilibrium ($Q = K_{sp}$): $E = 0$

$$0 = -0.362 \text{ V} - 4.2821 \cdot \text{mV} \cdot \ln K_{sp}$$

$$\ln K_{sp} = \frac{-0.362 \text{ V}}{4.2821 \cdot 10^{-3} \text{ V}} = -84.54$$

$$K_{sp} = \exp(-84.54) = 1.926 \cdot 10^{-37} = 1.93 \cdot 10^{-37}$$

14 The molar conductivity at 20°C of a 0.0100 M aqueous solution of ammonia (NH_4OH) is $9.6 \text{ S cm}^2 \text{ mol}^{-1}$. For NH_4Cl , $\Lambda_m^\circ = 129.8 \text{ S cm}^2 \text{ mol}^{-1}$ and the ionic equivalent conductance values for OH^- and Cl^- are 174 and $65.6 \text{ S cm}^2 \text{ mol}^{-1}$, respectively. Calculate the degree of ionization (α) for NH_3 in the 0.0100 M solution.

(A) $\alpha = 0.0403$ $\Lambda_m^\circ(\text{NH}_4\text{OH}) = \Lambda_m^\circ(\text{NH}_4\text{Cl}) - \lambda^\circ(\text{Cl}^-) + \lambda^\circ(\text{OH}^-)$

B) $\alpha = 0.0184$ $= (129.8 - 65.6 + 174) \frac{\text{S cm}^2}{\text{mol}}$

C) $\alpha = 0.781$ $= 238.2 \frac{\text{S cm}^2}{\text{mol}}$

D) $\alpha = 0.503$

E) $\alpha = 0.0784$

$$\alpha = \frac{\Lambda_m}{\Lambda_m^\circ} = \frac{9.6 \frac{\text{S cm}^2}{\text{mol}}}{238.2 \frac{\text{S cm}^2}{\text{mol}}} = 0.0403 (0)$$

$E = E^\circ - \frac{59.1574 \text{ mV}}{6} \log_{10} K_{sp}$
 $0 = -0.362 \text{ V} - \frac{59.1574 \text{ mV}}{6} \log_{10} K_{sp}$
 $\log_{10} K_{sp} = \frac{-0.362 \text{ V}}{9.8596 \cdot 10^{-3} \text{ V}} = -36.7143$
 $K_{sp} = 10^{-36.7143} = 1.93(0) \cdot 10^{-37}$

$$I(\text{NaCl}) = \frac{0.10 \text{ M}}{2} (1 \cdot (1)^2 + 1 \cdot (-1)^2)$$

$$= \frac{1}{2} 0.10 \text{ M} \cdot 2 = 0.10 \text{ M}$$

15 Which of the following solutions have the same ionic strength (I) as 0.10 M NaCl(aq)?

- (A) 0.0167 M Na_3PO_4 (aq) $I = \frac{1}{2} 0.0167 \text{ M} (3 \cdot (+1)^2 + 1 \cdot (-3)^2) = 0.10(02) \text{ M}$
- B) 0.280 M CuSO_4 (aq) $I = \frac{1}{2} \cdot 0.280 \text{ M} (1 \cdot (2)^2 + 1 \cdot (-2)^2) = 1.12 \text{ M}$
- C) 0.055 M CuSO_4 (aq) $I = \frac{1}{2} 0.055 \text{ M} \cdot 8 = 0.22 \text{ M}$
- D) 0.102 M $\text{Al}_2(\text{SO}_4)_3$ (aq) $I = \frac{1}{2} \cdot 0.102 \text{ M} (2 \cdot (+3)^2 + 3 \cdot (-2)^2) = 1.53 \text{ M}$
- E) 1.23 M BaSO_4 (aq) $I = \frac{1}{2} 1.23 \text{ M} (1 \cdot (+2)^2 + 1 \cdot (-2)^2) = 4.92 \text{ M}$

16 Calculate the pH of the HCl solution in the following cell at 25°C;

$\text{Pt}(s), \text{H}_2(1 \text{ atm}) | \text{HCl}(\text{aq}) | \text{AgCl}(s) | \text{Ag}(s)$; of which E_{cell} is 0.517 V.

(the $\text{AgCl} | \text{Ag}$ electrode has $E^\circ = 0.2224 \text{ V}$, and $\gamma_{\pm} = 1$)

- (A) 2.49 left oxidation: $\frac{1}{2} \text{H}_2 \rightarrow \text{H}^+ + e^-$
- B) 3.50 right reduction: $\text{AgCl} + e^- \rightarrow \text{Ag} + \text{Cl}^-$
- C) 4.32 overall: $\frac{1}{2} \text{H}_2(g) + \text{AgCl}(s) \rightarrow \text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq}) + \text{Ag}(s)$
- D) 5.21 $\text{AgCl}(s)$ and $\text{Ag}(s)$ not in Q
- E) 1.23 $\text{H}_2(g, 1 \text{ atm})$ also not in Q because

$$P_{\text{H}_2} = 1 \text{ atm} = \text{const.}$$

$$E = E^\circ - \frac{RT}{F} \ln a_{\text{H}^+} a_{\text{Cl}^-} \quad a_{\text{H}^+} = a_{\text{Cl}^-}$$

$$= E^\circ - 2 \frac{RT}{F} \ln a_{\text{H}^+} \quad E^\circ = 0.2224 \text{ V} \text{ since}$$

$$0.517 \text{ V} = 0.2224 \text{ V} - 51.3852 \text{ mV} \ln a_{\text{H}^+} \quad E^\circ(\text{H}_2 \text{ electrode}) = 0$$

$$0.517 \text{ V} = 0.2224 \text{ V} - 51.3852 \text{ mV} \cdot 2.30259 \log_{10} a_{\text{H}^+} \quad \text{pH} = -\log_{10} a_{\text{H}^+}$$

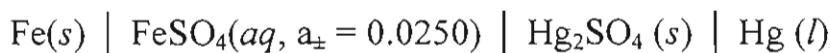
$$0.2946 \text{ V} = 118.3191 \text{ mV} \text{ pH}$$

$$\text{pH} = \frac{0.2946 \text{ V}}{118.3192 \cdot 10^{-3} \text{ V}} = 2.49 \text{ (0)}$$

17 Express a_{\pm} in terms of a_+ and a_- for $K_4Fe(CN)_6$

- A. $(a_{K^+}^4 \cdot a_{Fe(CN)_6^{4-}})^{\frac{1}{5}}$ $a_{\pm}^{\nu_+ + \nu_-} = a_+^{\nu_+} \cdot a_-^{\nu_-}$
- B. $(a_{K^+}^4 \cdot a_{Fe^{2+}} \cdot a_{(CN)_6^{4-}})^{\frac{1}{6}}$ $\nu_+ = 4$ for K^+ ions
 $\nu_- = 1$ for $Fe(CN)_6^{4-}$ ions
- C. $(a_{K_2Fe^{2+}} \cdot a_{(CN)_6^{4-}})^{\frac{1}{2}}$ $\nu_+ + \nu_- = 4 + 1 = 5$
- D. $(a_{K^+}^4 \cdot a_{Fe^{2+}} \cdot a_{(CN)_6^{4-}})^{\frac{1}{11}}$ $\rightarrow a_{\pm} = (a_{K^+}^4 \cdot a_{Fe(CN)_6^{4-}})^{\frac{1}{5}}$
- E. $(a_{K_2Fe^{2+}} \cdot a_{Fe(CN)_6^{4-}})^{\frac{1}{2}}$

18 Consider the cell:



ΔG_R in $kJ \text{ mol}^{-1}$ at $25.0^\circ C$ is $\rightarrow Hg_2^{2+}$ ions

$$[E_{Fe^{2+}/Fe(s)}^\circ = -0.447 \text{ V}, E_{Hg_2^{2+}/Hg(l)}^\circ = 0.7973 \text{ V}]$$

- A. 258.4 right reduction: $Hg_2SO_4 + 2e^- \rightarrow 2Hg + SO_4^{2-}$
- B. +258.4 left oxidation: $Fe \rightarrow Fe^{2+} + 2e^-$
- C. -221.8 overall, $z = 2$: $Hg_2SO_4(s) + Fe(s) \rightarrow 2Hg(l) + FeSO_4(aq)$
- D. +221.8 $E^\circ = E_{right}^\circ - E_{left}^\circ = E_{Hg_2^{2+}/Hg}^\circ - E_{Fe^{2+}/Fe}^\circ$
- E. -249.3 $= (0.7973 - (-0.447)) \text{ V}$
 $= 1.2443 \text{ V}$

$$E = E^\circ - \frac{RT}{zF} \ln a_{Fe^{2+}} a_{SO_4^{2-}} = E^\circ - \frac{RT}{zF} \ln a_{\pm}^2 = E^\circ - \frac{RT}{F} \ln a_{\pm}$$

$$= 1.2443 \text{ V} - 25.6926 \text{ mV} \ln 0.025 = 1.2443 \text{ V} - 25.6926 \text{ mV} \cdot (-3.68886)$$

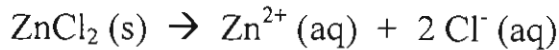
$$= 1.2443 \text{ V} + 0.09478 \text{ V} = 1.3391 \text{ V}$$

$$\Delta G_R = -zFE = -2 \cdot 96485 \frac{As}{mol} \cdot 1.3391 \text{ V}$$

$$z = 2$$

$$= -258406 \frac{J}{mol} = -258.4 \frac{kJ}{mol}$$

19 Calculate ΔG_R° in kJ mol^{-1} at 25.0°C for the reaction:



$[(\Delta H_f^\circ (\text{kJ mol}^{-1}) \& \Delta S^\circ (\text{J mol}^{-1} \text{K}^{-1}))$ of $\text{Zn}^{2+}(\text{aq})$, $\text{Cl}^{-}(\text{aq})$, and $\text{ZnCl}_2(\text{s})$ are $(-152.3 \& -109.8)$, $(-167.1 \& 56.6)$, and $(-415.1 \&$

$111.5)$, respectively] $\Delta H_R^\circ = \Delta H_f^\circ(\text{Zn}^{2+}) + 2\Delta H_f^\circ(\text{Cl}^{-}) - \Delta H_f^\circ(\text{ZnCl}_2)$

(A) -39.2 $\Delta H_R^\circ = (-152.3 - 2 \cdot 167.1 + 415.1) \frac{\text{kJ}}{\text{mol}} = -71.4 \frac{\text{kJ}}{\text{mol}}$

B. $+39.2$ $\Delta S_R^\circ = \Delta S_f^\circ(\text{Zn}^{2+}) + 2\Delta S_f^\circ(\text{Cl}^{-}) - \Delta S_f^\circ(\text{ZnCl}_2)$

C. -409.5 $= (-109.8 + 2 \cdot 56.6 - 111.5) \frac{\text{J}}{\text{K mol}} = -108.1 \frac{\text{J}}{\text{K mol}}$

D. $+409.5$ $\Delta G_R^\circ = \Delta H_R^\circ - T \Delta S_R^\circ$

E. -147.1 $= (-71.4 + 298.15 \cdot 108.1 \cdot 10^{-3}) \frac{\text{kJ}}{\text{mol}}$

$$= -39.17 \frac{\text{kJ}}{\text{mol}} = -39.2 \frac{\text{kJ}}{\text{mol}}$$

20 The Debye-Hückel screening length ($1/\kappa$) for a 1-1 electrolyte is 0.964 nm at a concentration of 0.1 m in water at 25°C ($\epsilon_r = 78$).

Estimate the screening length in nm of the same electrolyte in a solvent of $\epsilon_r = 38$, assuming that the density of both solvents is 1.0 kg m^{-3} (the equation for the inverse of the Debye-Hückel screening length (κ) is given at the end of the formula pages).

(A) 0.673 E. 0.213 $\kappa(\text{W}) = \frac{1}{0.964} \text{ nm}^{-1}$

B. 0.341 $= 1.03734 \text{ nm}^{-1}$

C. 0.456 $\kappa = \alpha \sqrt{1/\epsilon_r}$, $\alpha = \sqrt{\frac{2e^2 N_A 10^3 \frac{\text{L}}{\text{m}^3} I}{\epsilon_0 k_B T \epsilon_{\text{solvent}}}}$

D. 0.511

α is same for solvent S and for water κ

$$\frac{\kappa(\text{S})}{\kappa(\text{W})} = \frac{\epsilon_r(\text{W})}{\epsilon_r(\text{S})} = \sqrt{\frac{78}{38}} = 1.43270$$

$$\kappa(\text{S}) = 1.43270, \kappa(\text{W}) = 1.43270 \cdot 1.03734 \text{ nm}^{-1}$$

$$= 1.48620 \text{ nm}^{-1}$$

$$\frac{1}{\kappa(\text{S})} = 0.672(9) \text{ nm} = 0.673 \text{ nm}$$