CHEM 311 (132) **First Major Exam** 2 HOURS
Wednesday, Oct. 22, 2014

STUDENT NAME: ....

STUDENT ID NUMBER: ....

Test Code (000)

(20 Questions)

Worked out solutions of Code 000 at end of the file! WF

Solution codes at end of each Version!

Dr. Mazen Khaled	Section 1	16 students
Dr.Mohamed Morsy	Section 2	29 "
Dr. G. Oweimreen	Section 3	30 "
Dr. W Forner	Section 4	21 "

Useful Physical constants and Formula

PHYSICAL CONSTANTS:	**Useful Equations:**
$R = 8.314\ J\ mol^{-1}\ K^{-1}$	$\Lambda = \kappa/c$, $G = 1/R = \kappa(A/l)$
$R = 0.08314\ L\ bar\ K^{-1}\ mol^{-1}$	$\Lambda = \lambda_+ + \lambda_-$
$k_B = 1.381 \times 10^{-23}\ J\ K^{-1}$	$\alpha = \Lambda/\Lambda_0$
$1\ J = 1\ kg\ m^2\ s^{-2}$	$K = c\alpha^2/(1 - \alpha)$
$1\ atm = 1.101325 \times 10^5\ Pa$	$\Lambda_m = \Lambda^o_m - K\ (c/c_o)^{1/2}$ $1/\Lambda_m = 1/\Lambda^o_m + c\Lambda_m/[(\Lambda^o_m)^2\ K_a]$
$1\ atm = 1.01325 \times 10^5\ Pa$; $1\ bar = 10^5\ Pa$;	DHLL: $\log\gamma_\pm = -z_+ \mid z_- \mid B\sqrt{I}$ Davies Eq.: $\log\gamma_\pm = -B\,\lvert z_+z_-\rvert\,[(\sqrt{I})/\{1 + (\sqrt{I})\} - 0.30\,I]$ in water at 25 °C: B = ~~$0.5092\ M^{-1/2}$~~ $0.51\ m^{-1/2}$
$1\ Torr = 1\ mmHg = 133.322\ Pa$	$I = \frac{1}{2}\sum_i c_i z_i^2$
$g = 9.81\ m\ s^{-2}$	$\Delta\Phi = RT/zF\ \ln(c_1/c_2)$ $RT/F = 0.0257$ at 298 K
0 °C= 273.15 K	$E = E^o - (RT/z\,F)\ln(Q)$
$L = 6.022 \times 10^{23}\ mol^{-1}$ (Avogadro's number)	$\Delta G = -zFE$
$h = 6.626 \times 10^{-34}\ J\ s$	$\Delta S = z\,F\,(\partial E/\partial T)_p$
$F = 96500\ C\ mol^{-1}$	$\Delta G = \Delta H - T\Delta S$
$c = 2.998 \times 10^8\ m\ s^{-1}$ (speed of light)	$\gamma_\pm^{(\nu_+ + \nu_-)} = \gamma_+^{\nu_+}\gamma_-^{\nu_-}$
$\varepsilon_o = 8.854 \times 10^{-12} C^2 N^{-1} m^{-2}$ $\varepsilon = 78$ at 25°C	$pH = -\log[H^+]$ $K_w = [OH^-][H^+]$
$e = 1.602 \times 10^{-19}\ C$	$\Delta G^o_{solvation} = (1/\varepsilon_r - 1)z^2e^2N_A/(8\pi\varepsilon_o r)$
$E^o = (RT/z\,F)\ln(k^o)$	$\kappa = [2e^2N_A(1000\ L\ m^{-3})/(\varepsilon_o k_B T)]^{1/2}\,[\rho_{sol}\ I/\varepsilon_r]^{1/2}$
$aa' = t_-\ Q/FcA$ (travelled distance)	$\Delta G = RT\ \ln(c_1/c_2)$

Hydrogen Electrode: $H^+ (aq) + e^- (g) \rightarrow \frac{1}{2}H_2$ $E^o = 0\ V$

Silver-Silver Chloride: $e^- + AgCl\ (s) \rightarrow Ag\ (s) + Cl^-\ (aq)$ $E^o = 0\ 22233\ V$

Calomel Electrode: $e^- + \frac{1}{2}Hg_2Cl_2(s) \rightarrow Cl^-\ (aq) + Hg\ (l)$ $E^o = 0.13337\ V$

1 Using activities, calculate the solubility of Ag_2SO_4 (silver sulfate) in 0.025 M aqueous KNO_3 solution at 25°C. You may ignore the contribution of Ag^+ and SO_4^{2-} to the ionic strength. [K_{sp} of Ag_2SO_4 = 1.5×10^{-5}]
A) 0.023 M
B) 0.052 M
C) 0.011 M
D) 0.0018 M
E) 0.0041 M

2. Which of the following inert electrolytes produces the largest increase in the degree of dissociation of acetic acid (using DHLL)?
A) 0.10 m $CuCl_2$
B) 0.001 m NaCl
C) 0.001 m KBr
D) 0.10 m CsCl
E) 0.01 m $CaCl_2$

3. Calculate the mean activity coefficient for a 0.002 M aqueous K_2SO_4 solution assuming complete dissociation and that DHLL is valid.
A) 0.834
B) 0.918
C) 0.711
D) 0.621
E) 0.781

0.150

4. What is the pH of a buffer solution that is ~~0.250~~ *m* in CH_3COOH and 0.150 *m* in CH_3COONa, using the Davies equation (ignore the contributions from acetic acid dissociation in the ionic strength) to calculate $\gamma_{\pm}$? [pK_a of acetic acid = 4.76]
A) 4.52
B) 4.63
C) 4.21
D) 4.81
E) 4.39

5. Calculate the mean ionic molality and the mean ionic activity of a 0.115 m K_3PO_4 solution for which the mean ionic activity coefficient is 0.125.
   A) 0.262 m and 0.0328
   B) 0.155 m and 0.0819
   C) 0.0531 m and 0.108
   D) 0.295 m and 0.0411
   E) 0.105 m and 0.0215

6. An electrochemical cell is made by connecting an aluminum strip in 0.40 M $Al_2(SO_4)_3$ solution to a copper strip in 1.00 M $CuSO_4$ solution at 25 °C. Given the standard potentials: $E^\circ_{Cu^{2+}/Cu} = 0.34$ V and $E^\circ_{Al^{3+}/Al} = -1.67$ V, determine the cell voltage, assuming that the copper strip is gaining mass and that the aluminum strip is losing mass.
   A) 2.01 V
   B) 2.20 V
   C) 1.02 V
   D) 1.11 V
   E) 0.00 V

7. Determine the cell voltage for the following electrochemical reaction at 25 °C:

$$Sn(s) + 2\,Ag^+(aq) \longrightarrow Sn^{2+}(aq) + 2\,Ag(s) \qquad E^\circ_{cell} = 0.94\ V$$

   given that aqueous 0.10 M $AgNO_3$ and aqueous 0.050 M $Sn(NO_3)_2$ solutions are used to set up the cell.
   A) 0.92 V
   B) 0.97 V
   C) 0.86 V
   D) –0.92 V
   E) –0.97 V

8. The correct Nernst equation for the reaction

$$Al(s) + OH^-(aq) + 3\,H_2O(l) \longrightarrow Al(OH)_4^-(aq) + 3/2\,H_2(g)$$

   is (do not use activities in the reaction ratio Q):
   A) $E = E^\circ - (RT/3F)\ln Q$ with $Q = (P(H_2))^{3/2}[Al(OH)_4^-]/[OH^-]$
   B) $E = E^\circ - (RT/3F)\ln Q$ with $Q = [H_2]^{3/2}\,[Al(OH)_4^-]/\{[Al(s)][OH^-]\}$
   C) $E = E^\circ - (RT/4F)\ln Q$ with $Q = [Al(OH)_4^-]P(OH^-)/[OH^-]$
   D) $E = E^\circ - (RT/3F)\ln Q$ with $Q = (P(H_2))^{3/2}\,[Al][(OH)^-]/[Al(s)]$
   E) $E = E^\circ - (RT/4F)\ln Q$ with $Q = (P(H_2))^{3/2}\,[Al(OH)_4^-]/[OH^-]$

9. Assume that the following reaction has a zero voltage (by definition as new standard):

$$Fe^{2+}(aq) + 2\ e^- \longrightarrow Fe(s)$$

What will be the voltage of the following reaction versus this new standard.

$$I_2(s) + 2\ e^- \longrightarrow 2\ I^-(aq)$$

given: $E^o_{Fe^{2+}/Fe} = -0.447$ V and $E^o_{I2/I^-} = 0.536$ V versus standard hydrogen electrode?

A) 0.983 V
B) -0.536 V
C) 0.447 V
D) 0.259 V
E) 0.931 V

10. Which statement is **TRUE**?

A) The Gibbs energy change of an electrochemical reaction at equilibrium is equal to zero.
B) The Gibbs energy change of a spotaneous electrochemical reaction at equilibrium is negative.
C) The sign of the Gibbs energy change of an electrochemical reaction at equilibrium can be changed by changing the ionic strength.
D) The Gibbs energy change of an electrochemical reaction at equlibrium can be changed by an applied electric potential.
E) The sum of the stoichiometric coefficients multiplied by the charges of each reactant and product in an electrochemical reaction is always negative.

11. Which of the following statements is **NOT CORRECT**?

A) The attractive and repulsive interactions between ions depend only on their chemical identity.
B) Deviations from ideal behavior begin at lower concentrations for electrolyte solutions than for nonelectrolyte solutions.
C) In electrolyte solutions the main interaction is the long-range electrostatic Coulomb interaction between ions.
D) The attractive and repulsive interactions between ions depend on their charge and size.
E) Henry's law is obeyed up to concentrations of unit molality according to its hypothetical standard state.

12. In the relation $\mu_{Fe_2(SO_4)_3} = \mu_{\pm} + \nu RT \ln\left(\frac{m}{m}\right) + \nu RT \ln \gamma_{\pm}$ the value of V is:

A) 5
B) 2
C) 1
D) 4
E) 3

13. Enough of the salt $AB(s)$ is dissolved in a certain amount of water to bring it into equilibrium with the ions $A^{2+}(aq)$ and $B^{2-}(aq)$. If the equilibrium concentration of A^{2+} is $7.6\times10^{-5}\ mol\ kg^{-1}$, and the Debye Hückel Limiting Law (DHLL) is obeyed at this concentration, K_{sp} for the salt is:

A) 4.90×10^{-9}
B) 5.22×10^{-9}
C) 5.78×10^{-9}
D) 4.59×10^{-9}
E) 8.46×10^{-8}

14. With respect to the mean ionic activity coefficient variation, $\gamma_{\pm}$, with the square root of the ionic strength, $\sqrt{I}$, for an electrolyte which of the following statements is **CORRECT**?

A) At high ionic strength $\gamma_{\pm} > 1$, solubility decreases to keep the solubility product constant, resulting in the salting out effect.
B) The $\gamma_{\pm}$ increases as $\sqrt{I}$ increases, at all electrolyte concentrations
C) The $\gamma_{\pm}$ decreases as $\sqrt{I}$ increases, at all electrolyte concentrations.
D) The $\gamma_{\pm}$ decreases as $\sqrt{I}$ increases, and in turn solubility must decrease resulting in the salting out effect.
E) At high ionic strength $\gamma_{\pm} > 1$, solubility increases to keep the solubility product constant, resulting in the salting in effect.

15. Which of the following statements is **NOT CORRECT**?

A) At all electrolyte concentrations, the mean ionic activity coefficient $\gamma_{\pm}$ is less than 1.

B) The mean ionic activity coefficient of an electrolyte $\gamma_{\pm}$ may be experimentally measured.

C) At very low electrolyte concentrations, the experimentally measured mean ionic activity coefficient, $\gamma_{\pm}$, is close to the $\gamma_{\pm}$ value calculated using the Debye-Huckel limiting law (DHLL).

D) The activities γ_{+} and γ_{-} for the positive and negative ions of an electrolyte cannot be measured experimentally.

E) At very high electrolyte concentrations, the mean ionic activity coefficient $\gamma_{\pm}$ may reach values greater than 1.

16. Consider the following cell at 25 °C.

$$Co(s)|Co^{2+}(aq, a = 0.832)||Cr^{3+}(aq, a = 0.342)|Cr(s)$$

Using the standard potentials $E^{o}_{Co^{2+}/Co} = -0.280$ V and $E^{o}_{Cr^{3+}/Cr} = -0.744$ V, what happens spontaneously in the cell?

A) Chromium dissolves.

B) Chromium is deposited.

C) Cobalt dissolves.

D) Electrons flow from Cobalt to Chromium

E) Cannot be determined

17. Consider the following cell at 25 °C:

$$Ag(s)|AgNO_3(aq)|AgI(s)|Ag(s)$$

Given the standard potentials: $E^{o}_{Ag^{+}/Ag} = 0.799V$ and $E^{o}_{AgI/Ag} = 0.061V$, calculate pK_{sp} of AgI.

A) 12.5

B) −12.5

C) 14.5

D) -14.5

E) 3.352×10^{-13}

18. For fluorine, F_2, the standard potential is $E^\circ_{F_2/F^-} = 2.87$ V. Given that

$$E^\circ_{Zn^{2+}/Zn} = -0.761 \text{ V}, E^\circ_{Ag^+/Ag} = 0.800, \text{ and } E^\circ_{Au^+/Au} = 1.68 \text{ V}$$

and assuming a fluorine electrode is made from fluorine bubbling over an inert metal surface, what will happen in a cell made of this fluorine electrode and one of the above mentioned metals in the standard state?

A) Fluorine oxidizes Zn, Ag, and Au.
B) Flourine oxidizes Zn and Ag, but not Au.
C) Fluorine oxidizes Zn, but not Ag and Au.
D) Fluorine oxidizes none of these metals.
E) Fluorine reduces all those metals.

19. In an electrochemical cell the oxidation of oxalic acid (HOOCCOOH) to carbon dioxide and water by permanganate ions, MnO_4^-, in acidic solution has an equilibrium for which ln$K$ = 778. What can be concluded from that fact?

A) Almost complete conversion from reactants into products happens
B) No reaction happens.
C) Almost only reactants can be found in the cell.
D) Permanganate cannot oxidize oxalic acid.
E) Carbon dioxide and water are reduced to oxalic acid.

20. Consider the cell

$$Pt(s)|Cl_2(g)|ClO_2^-(aq)||Cr_2O_7^{2-}(aq)|Cr(s).$$

In acidic medium, how many electrons are exchanged in this cell reaction (balanced with the smallest possible set of integer coefficients)?

A) 12
B) 9
C) 6
D) 3
E) 15

Answer Key

1. A
2. A
3. A
4. A
5. A
6. A
7. A
8. A
9. A
10. A
11. A
12. A
13. A
14. A
15. A
16. A
17. A
18. A
19. A
20. A

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(20 Questions)

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Useful Physical constants and Formula

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$1\ J = 1\ kg\ m^2\ s^{-2}$	$K = c\alpha^2/(1-\alpha)$
$1\ atm = 1.101325 \times 10^5\ Pa$	$\Lambda_m = \Lambda^o_m - K\ (c/c_o)^{1/2}$ $1/\Lambda_m = 1/\Lambda^o_m + c\Lambda_m/[(\Lambda^o_m)^2\ K_a]$
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$1\ Torr = 1\ mmHg = 133.322\ Pa$	$I = \frac{1}{2}\sum_i c_i z_i^2$
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$c = 2.998 \times 10^8\ m\ s^{-1}$ (speed of light)	$\gamma_{\pm}^{(\nu_{+}+\nu_{-})} = \gamma_{+}^{\nu_{+}}\gamma_{-}^{\nu_{-}}$
$\varepsilon_o = 8.854 \times 10^{-12} C^2N^{-1}m^{-2}$ $\varepsilon = 78$ at 25°C	$pH = -\text{Log}\ [H^{+}]$ $K_w = [OH^{-}]\ [H^{+}]$
$e = 1.602 \times 10^{-19}\ C$	$\Delta G°_{solvation} = (1/\varepsilon_r - 1)z^2e^2N_A/(8\pi\varepsilon_o r)$
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Hydrogen Electrode: $H^{+}\ (aq) + e^{-}\ (g) \rightarrow \frac{1}{2}H_2$ $E° = 0\ V$

Silver-Silver Chloride: $e^{-} + AgCl\ (s) \rightarrow Ag\ (s) + Cl^{-}\ (aq)$ $E° = 0.22233\ V$

Calomel Electrode: $e^{-} + \frac{1}{2}Hg_2Cl_2(s) \rightarrow Cl^{-}\ (aq) + Hg\ (l)$ $E° = 0.13337\ V$

1. For fluorine, F_2, the standard potential is $E^\circ_{F_2/F^-} = 2.87$ V. Given that

$$E^\circ_{Zn^{2+}/Zn} = -0.761 \text{ V}, E^\circ_{Ag^+/Ag} = 0.800, \text{ and } E^\circ_{Au^+/Au} = 1.68 \text{ V}$$

and assuming a fluorine electrode is made from fluorine bubbling over an inert metal surface, what will happen in a cell made of this fluorine electrode and one of the above mentioned metals in the standard state?

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2. What is the pH of a buffer solution that is ~~0.250~~ *m* in CH_3COOH and 0.150 *m* in CH_3COONa, using the Davies equation (ignore the contributions from acetic acid dissociation in the ionic strength) to calculate $\gamma_\pm$? [pK_a of acetic acid = 4.76]

A) 4.21
B) 4.52
C) 4.81
D) 4.39
E) 4.63

3. Which of the following inert electrolytes produces the largest increase in the degree of dissociation of acetic acid (using DHLL)?

A) 0.001 m KBr
B) 0.10 m $CuCl_2$
C) 0.001 m NaCl
D) 0.10 m CsCl
E) 0.01 m $CaCl_2$

4. Assume that the following reaction has a zero voltage (by definition as new standard):

$$Fe^{2+}(aq) + 2\ e^- \longrightarrow Fe(s)$$

What will be the voltage of the following reaction versus this new standard:

$$I_2(s) + 2\ e^- \longrightarrow 2\ I^-(aq)$$

given: $E°_{Fe^{2+}/Fe} = -0.447$ V and $E°_{I_2/I^-} = 0.536$ V versus standard hydrogen electrode?

A) 0.447 V
B) 0.931 V
C) 0.983 V
D) 0.259 V
E) -0.536 V

5. Which of the following statements is **NOT CORRECT**?

A) At very high electrolyte concentrations, the mean ionic activity coefficient $\gamma_\pm$ may reach values greater than 1.
B) At all electrolyte concentrations, the mean ionic activity coefficient $\gamma_\pm$ is less than 1.
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6. In the relation $\mu_{Fe_2(SO_4)_3} = \mu_\pm + \nu RT \ln\left(\frac{m}{m}\right) + \nu RT \ln \gamma_\pm$ the value of V is:

A) 3
B) 5
C) 2
D) 1
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7. Enough of the salt $AB(s)$ is dissolved in a certain amount of water to bring it into equilibrium with the ions $A^{2+}(aq)$ and $B^{2-}(aq)$. If the equilibrium concentration of A^{2+} is 7.6×10^{-5} $mol\ kg^{-1}$, and the Debye Hückel Limiting Law (DHLL) is obeyed at this concentration, K_{sp} for the salt is:

   A) 5.78×10^{-9}

   B) 8.46×10^{-8}

   C) 4.90×10^{-9}

   D) 4.59×10^{-9}

   E) 5.22×10^{-9}

8. Which statement is **TRUE**?
   A) The sign of the Gibbs energy change of an electrochemical reaction at equilibrium can be changed by changing the ionic strength.
   B) The Gibbs energy change of a spotaneous electrochemical reaction at equilibrium is negative.
   C) The Gibbs energy change of an electrochemical reaction at equilibrium is equal to zero.
   D) The sum of the stoichiometric coefficients multiplied by the charges of each reactant and product in an electrochemical reaction is always negative.
   E) The Gibbs energy change of an electrochemical reaction at equlibrium can be changed by an applied electric potential.

9. Using activities, calculate the solubility of Ag_2SO_4 (silver sulfate) in 0.025 M aqueous KNO_3 solution at 25°C. You may ignore the contribution of Ag^+ and SO_4^{2-} to the ionic strength. [K_{sp} of $Ag_2SO_4 = 1.5 \times 10^{-5}$]
   A) 0.023 M
   B) 0.0041 M
   C) 0.0018 M
   D) 0.011 M
   E) 0.052 M

10. Calculate the mean activity coefficient for a 0.002 M aqueous K_2SO_4 solution assuming complete dissociation and that DHLL is valid.
    A) 0.918
    B) 0.781
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11. With respect to the mean ionic activity coefficient variation, $\gamma_{\pm}$, with the square root of the ionic strength, $\sqrt{I}$, for an electrolyte which of the following statements is **CORRECT**?
    A) At high ionic strength $\gamma_{\pm} > 1$, solubility increases to keep the solubility product constant, resulting in the salting in effect.
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15. Determine the cell voltage for the following electrochemical reaction at 25 °C:

$$Sn(s) + 2\ Ag^+(aq) \longrightarrow Sn^{2+}(aq) + 2\ Ag(s) \quad E°_{cell} = 0.94\ V$$

given that aqueous 0.10 M $AgNO_3$ and aqueous 0.050 M $Sn(NO_3)_2$ solutions are used to set up the cell.
    A) –0.97 V
    B) 0.92 V
    C) 0.97 V
    D) 0.86 V
    E) –0.92 V

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$$Ag(s)|AgNO_3(aq)|AgI(s)|Ag(s)$$

Given the standard potentials: $E^\circ_{Ag^+/Ag} = 0.799V$ and $E^\circ_{AgI/Ag} = 0.061V$, calculate pK_{sp} of AgI.

A) 12.5
B) 3.352×10^{-13}
C) -14.5
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17. Consider the cell

$$Pt(s)|Cl_2(g)|ClO_2^-(aq)||Cr_2O_7^{2-}(aq)|Cr(s).$$

In acidic medium, how many electrons are exchanged in this cell reaction (balanced with the smallest possible set of integer coefficients)?

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B) 6
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C) Electrons flow from Cobalt to Chromium
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E) Cannot be determined.

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$$Al(s) + OH^-(aq) + 3\ H_2O(l) \longrightarrow Al(OH)_4^-(aq) + 3/2\ H_2(g)$$

is (do not use activities in the reaction ratio Q):

A) $E = E^\circ - (RT/3F) \ln Q$ with $Q = (P(H_2))^{3/2} [Al][(OH)^-]/[Al(s)]$
B) $E = E^\circ - (RT/4F) \ln Q$ with $Q = (P(H_2))^{3/2} [Al(OH)_4^-]/[OH^-]$
C) $E = E^\circ - (RT/4F) \ln Q$ with $Q = [Al(OH)_4^-]P(OH^-)/[OH^-]$
D) $E = E^\circ - (RT/3F) \ln Q$ with $Q = (P(H_2))^{3/2}[Al(OH)_4^-]/[OH^-]$
E) $E = E^\circ - (RT/3F) \ln Q$ with $Q = [H_2]^{3/2} [Al(OH)_4^-]/\{[Al(s)][OH^-]\}$

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    D) 0.262 m and 0.0328
    E) 0.0531 m and 0.108

Answer Key

1. A
2. B
3. B
4. C
5. B
6. B
7. C
8. C
9. A
10. C
11. C
12. C
13. B
14. E
15. B
16. A
17. D
18. B
19. D
20. D

CHEM 311 (132) **First Major Exam** **2 HOURS**

Wednesday, Oct. 22, 2014

STUDENT NAME: ....

STUDENT ID NUMBER: ....

Test Code (002)

(20 Questions)

Dr. Mazen Khaled	Section 1
Dr.Mohamed Morsy	Section 2
Dr. G. Oweimreen	Section 3
Dr. W Forner	Section 4

Useful Physical constants and Formula

PHYSICAL CONSTANTS:	**Useful Equations:**
$R = 8.314\ \mathrm{J\ mol^{-1}\ K^{-1}}$	$\Lambda = \kappa/c$, $G = 1/R = \kappa(A/l)$
$R = 0.08314\ \mathrm{L\ bar\ K^{-1}\ mol^{-1}}$	$\Lambda = \lambda_+ + \lambda_-$
$k_B = 1.381 \times 10^{-23}\ \mathrm{J\ K^{-1}}$	$\alpha = \Lambda/\Lambda_o$
$1\ \mathrm{J} = 1\ \mathrm{kg\ m^2\ s^{-2}}$	$K = c\alpha^2/(1-\alpha)$
$1\ \mathrm{atm} = 1.101325 \times 10^5\ \mathrm{Pa}$	$\Lambda_m = \Lambda^o{}_m - K\,(c/c_o)^{1/2}$ $1/\Lambda_m = 1/\Lambda^o{}_m + c\Lambda_m/[(\Lambda^o{}_m)^2 K_a]$
$1\ \mathrm{atm} = 1.01325 \times 10^5\ \mathrm{Pa}$; $1\ \mathrm{bar} = 10^5\ \mathrm{Pa}$;	DHLL: $\log \gamma_\pm = -z_+ \mid z_- \mid B\sqrt{I}$ Davies Eq.: $\log \gamma_\pm = -B\lvert z_+z_-\rvert\,[(\sqrt{I})/\{1+(\sqrt{I})\} - 0.30\,I]$ in water at 25 °C: $B = 0.51\ \mathrm{M}^{-1/2}$
$1\ \mathrm{Torr} = 1\ \mathrm{mmHg} = 133.322\ \mathrm{Pa}$	$I = \frac{1}{2}\sum_i c_i z_i^2$
$g = 9.81\ \mathrm{m\ s^{-2}}$	$\Delta\Phi = RT/zF \ln(c_1/c_2)$ $RT/F = 0.0257$ at 298 K
$0\ ^\circ\mathrm{C} = 273.15\ \mathrm{K}$	$E = E^\circ - (RT/zF)\ln(Q)$
$L = 6.022 \times 10^{23}\ \mathrm{mol^{-1}}$ (Avogadro's number)	$\Delta G = -zFE$
$h = 6.626 \times 10^{-34}\ \mathrm{J\ s}$	$\Delta S = zF(\partial E/\partial T)_p$
$F = 96500\ \mathrm{C\ mol^{-1}}$	$\Delta G = \Delta H - T\Delta S$
$c = 2.998 \times 10^8\ \mathrm{m\ s^{-1}}$ (speed of light)	$\gamma_\pm^{(\nu_+ + \nu_-)} = \gamma_+^{\nu_+}\gamma_-^{\nu_-}$
$\varepsilon_o = 8.854 \times 10^{-12}\ \mathrm{C^2 N^{-1} m^{-2}}$ $\varepsilon = 78$ at 25 °C	$\mathrm{pH} = -\mathrm{Log}\,[H^+]$ $K_w = [OH^-][H^+]$
$e = 1.602 \times 10^{-19}\ \mathrm{C}$	$\Delta G^o{}_{solvation} = (1/\varepsilon_r - 1)z^2e^2N_A/(8\pi\varepsilon_o r)$
$E^\circ = (RT/zF)\ln(k^o)$	$\kappa = [2e^2N_A(1000\ \mathrm{L\ m^{-3}})/(\varepsilon_o k_B T)]^{1/2}\,[\rho_{sol}\,I/\varepsilon_r]^{1/2}$
$aa' = t_+ Q/FcA$ (travelled distance)	$\Delta G = RT\ln(c_1/c_2)$

Hydrogen Electrode: $H^+(aq) + e^-(g) \rightarrow \frac{1}{2}H_2$ $E^\circ = 0\ \mathrm{V}$

Silver-Silver Chloride: $e^- + AgCl(s) \rightarrow Ag(s) + Cl^-(aq)$ $E^\circ = 0.22233\ \mathrm{V}$

Calomel Electrode: $e^- + \frac{1}{2}Hg_2Cl_2(s) \rightarrow Cl^-(aq) + Hg(l)$ $E^\circ = 0.13337\ \mathrm{V}$

1. Consider the following cell at 25 °C:

   $$\text{Ag(s)|AgNO}_3\text{(aq)|AgI(s)|Ag(s)}$$

   Given the standard potentials: $E^\circ_{Ag^+/Ag} = 0.799V$ and $E^\circ_{AgI/Ag} = 0.061V$, calculate pK_{sp} of AgI.
   A) 14.5
   B) -14.5
   C) –12.5
   D) 3.352×10^{-13}
   E) 12.5

2. Determine the cell voltage for the following electrochemical reaction at 25 °C:

   $$\text{Sn(s)} + 2\ \text{Ag}^+\text{(aq)} \longrightarrow \text{Sn}^{2+}\text{(aq)} + 2\ \text{Ag(s)} \quad E^\circ_{cell} = 0.94\ \text{V}$$

   given that aqueous 0.10 M $AgNO_3$ and aqueous 0.050 M $Sn(NO_3)_2$ solutions are used to set up the cell.
   A) –0.92 V
   B) –0.97 V
   C) 0.86 V
   D) 0.92 V
   E) 0.97 V

3. An electrochemical cell is made by connecting an aluminum strip in 0.40 M $Al_2(SO_4)_3$ solution to a copper strip in 1.00 M $CuSO_4$ solution at 25 °C. Given the standard potentials: $E^\circ_{Cu^{2+}/Cu} = 0.34$ V and $E^\circ_{Al^{3+}/Al} = -1.67$ V, determine the cell voltage, assuming that the copper strip is gaining mass and that the aluminum strip is losing mass.
   A) 0.00 V
   B) 2.20 V
   C) 2.01 V
   D) 1.11 V
   E) 1.02 V

4. For fluorine, F_2, the standard potential is $E^{\circ}_{F2/F^-} = 2.87$ V. Given that

$$E^{\circ}_{Zn^{2+}/Zn} = -0.761 \text{ V}, E^{\circ}_{Ag^{+}/Ag} = 0.800, \text{ and } E^{\circ}_{Au^{+}/Au} = 1.68 \text{ V}$$

and assuming a fluorine electrode is made from fluorine bubbling over an inert metal surface, what will happen in a cell made of this fluorine electrode and one of the above mentioned metals in the standard state?

A) Flourine oxidizes Zn and Ag, but not Au.
B) Fluorine oxidizes Zn, but not Ag and Au.
C) Fluorine oxidizes Zn, Ag, and Au.
D) Fluorine oxidizes none of these metals.
E) Fluorine reduces all those metals.

5. Consider the cell

$$Pt(s)|Cl_2(g)|ClO_2^-(aq)||Cr_2O_7^{2-}(aq)|Cr(s).$$

In acidic medium, how many electrons are exchanged in this cell reaction (balanced with the smallest possible set of integer coefficients)?

A) 3
B) 9
C) 12
D) 6
E) 15

6. Consider the following cell at 25 °C.

$$Co(s)|Co^{2+}(aq, a = 0.832)||Cr^{3+}(aq, a = 0.342)|Cr(s)$$

Using the standard potentials: $E^{\circ}_{Co^{2+}/Co} = -0.280$ V and $E^{\circ}_{Cr^{3+}/Cr} = -0.744$ V, what happens spontaneously in the cell?

A) Chromium dissolves.
B) Cobalt dissolves.
C) Cannot be determined.
D) Electrons flow from Cobalt to Chromium
E) Chromium is deposited.

7. Calculate the mean ionic molality and the mean ionic activity of a 0.115 m K_3PO_4 solution for which the mean ionic activity coefficient is 0.125.

A) 0.105 m and 0.0215
B) 0.295 m and 0.0411
C) 0.262 m and 0.0328
D) 0.0531 m and 0.108
E) 0.155 m and 0.0819

8. Assume that the following reaction has a zero voltage (by definition as new standard):

$$Fe^{2+}(aq) + 2\ e^- \longrightarrow Fe(s)$$

What will be the voltage of the following reaction versus this new standard:

$$I_2(s) + 2\ e^- \longrightarrow 2\ I^-(aq)$$

given: $E^\circ_{Fe^{2+}/Fe} = -0.447$ V and $E^\circ_{I2/I-} = 0.536$ V versus standard hydrogen electrode?

A) -0.536 V
B) 0.447 V
C) 0.259 V
D) 0.931 V
E) 0.983 V

9. With respect to the mean ionic activity coefficient variation, $\gamma_\pm$, with the square root of the ionic strength, $\sqrt{I}$, for an electrolyte which of the following statements is **CORRECT**?

A) The $\gamma_\pm$ decreases as $\sqrt{I}$ increases, at all electrolyte concentrations.
B) The $\gamma_\pm$ decreases as $\sqrt{I}$ increases, and in turn solubility must decrease resulting in the salting out effect.
C) The $\gamma_\pm$ increases as $\sqrt{I}$ increases, at all electrolyte concentrations.
D) At high ionic strength $\gamma_\pm > 1$, solubility increases to keep the solubility product constant, resulting in the salting in effect.
E) At high ionic strength $\gamma_\pm > 1$, solubility decreases to keep the solubility product constant, resulting in the salting out effect.

10. Which of the following statements is **NOT CORRECT**?

A) The attractive and repulsive interactions between ions depend only on their chemical identity.
B) Henry's law is obeyed up to concentrations of unit molality according to its hypothetical standard state.
C) Deviations from ideal behavior begin at lower concentrations for electrolyte solutions than for nonelectrolyte solutions.
D) The attractive and repulsive interactions between ions depend on their charge and size.
E) In electrolyte solutions the main interaction is the long-range electrostatic Coulomb interaction between ions.

11. Which of the following inert electrolytes produces the largest increase in the degree of dissociation of acetic acid (using DHLL)?
    - A) 0.10 m $CsCl$
    - B) 0.01 m $CaCl_2$
    - C) 0.10 m $CuCl_2$
    - D) 0.001 m $NaCl$
    - E) 0.001 m KBr

12. The correct Nernst equation for the reaction

$$Al(s) + OH^-(aq) + 3\ H_2O(l) \longrightarrow Al(OH)_4^-(aq) + 3/2\ H_2(g)$$

is (do not use activities in the reaction ratio Q):

- A) $E = E^\circ - (RT/4F)\ \ln Q$ with $Q = (P(H_2))^{3/2}\ [Al(OH)_4^-]/[OH^-]$
- B) $E = E^\circ - (RT/3F)\ \ln Q$ with $Q = [H_2]^{3/2}\ [Al(OH)_4^-]/\{[Al(s)][OH^-]\}$
- C) $E = E^\circ - (RT/3F)\ \ln Q$ with $Q = (P(H_2))^{3/2}\ [Al][(OH)^-]/[Al(s)]$
- D) $E = E^\circ - (RT/4F)\ \ln Q$ with $Q = [Al(OH)_4^-]P(OH^-)/\{OH^-]$
- E) $E = E^\circ - (RT/3F)\ \ln Q$ with $Q = (P(H_2))^{3/2}[Al(OH)_4^-]/[OH^-]$

13. Enough of the salt $AB(s)$ is dissolved in a certain amount of water to bring it into equilibrium with the ions $A^{2+}(aq)$ and $B^{2-}(aq)$. If the equilibrium concentration of A^{2+} is $7.6\times10^{-5}\ mol\ kg^{-1}$, and the Debye Hückel Limiting Law (DHLL) is obeyed at this concentration, K_{sp} for the salt is:
    - A) 4.90×10^{-9}
    - B) 5.22×10^{-9}
    - C) 8.46×10^{-8}
    - D) 5.78×10^{-9}
    - E) 4.59×10^{-9}

14. Which statement is **TRUE**?
    A) The sum of the stoichiometric coefficients multiplied by the charges of each reactant and product in an electrochemical reaction is always negative.
    B) The Gibbs energy change of an electrochemical reaction at equilibrium is equal to zero.
    C) The sign of the Gibbs energy change of an electrochemical reaction at equilibrium can be changed by changing the ionic strength.
    D) The Gibbs energy change of an electrochemical reaction at equlibrium can be changed by an applied electric potential.
    E) The Gibbs energy change of a spotaneous electrochemical reaction at equilibrium is negative.

15. Using activities, calculate the solubility of Ag_2SO_4 (silver sulfate) in 0.025 M aqueous KNO_3 solution at 25°C. You may ignore the contribution of Ag^+ and SO_4^{2-} to the ionic strength. [K_{sp} of $Ag_2SO_4 = 1.5 \times 10^{-5}$]
    A) 0.052 M
    B) 0.011 M
    C) 0.0041 M
    D) 0.023 M
    E) 0.0018 M

16. In the relation $\mu_{Fe_2(SO_4)_3} = \mu_\pm^\circ + \nu RT \ln\left(\frac{m}{m^\circ}\right) + \nu RT \ln \gamma_\pm$ the value of ν is:
    A) 4
    B) 1
    C) 3
    D) 2
    E) 5

17. Calculate the mean activity coefficient for a 0.002 M aqueous K_2SO_4 solution assuming complete dissociation and that DHLL is valid.
    A) 0.711
    B) 0.621
    C) 0.781
    D) 0.834
    E) 0.918

18. In an electrochemical cell the oxidation of oxalic acid (HOOCCOOH) to carbon dioxide and water by permanganate ions, MnO_4^-, in acidic solution has an equilibrium for which $\ln K = 778$. What can be concluded from that fact?
    - A) Carbon dioxide and water are reduced to oxalic acid.
    - B) Almost complete conversion from reactants into products happens.
    - C) No reaction happens.
    - D) Almost only reactants can be found in the cell.
    - E) Permanganate cannot oxidize oxalic acid.

19. Which of the following statements is **NOT CORRECT**?
    - A) The activities γ_+ and γ_- for the positive and negative ions of an electrolyte cannot be measured experimentally.
    - B) The mean ionic activity coefficient of an electrolyte $\gamma_\pm$ may be experimentally measured.
    - C) At very low electrolyte concentrations, the experimentally measured mean ionic activity coefficient, $\gamma_\pm$, is close to the $\gamma_\pm$ value calculated using the Debye-Huckel limiting law (DHLL).
    - D) At very high electrolyte concentrations, the mean ionic activity coefficient $\gamma_\pm$ may reach values greater than 1.
    - E) At all electrolyte concentrations, the mean ionic activity coefficient $\gamma_\pm$ is less than 1.

0,150

20. What is the pH of a buffer solution that is ~~0.250~~ *m* in CH_3COOH and 0.150 *m* in CH_3COONa, using the Davies equation (ignore the contributions from acetic acid dissociation in the ionic strength) to calculate $\gamma_\pm$? [pK_a of acetic acid = 4.76]
    - A) 4.63
    - B) 4.81
    - C) 4.21
    - D) 4.52
    - E) 4.39

Answer Key

1. E
2. D
3. C
4. C
5. C
6. A
7. C
8. E
9. E
10. A
11. C
12. E
13. A
14. B
15. D
16. E
17. D
18. B
19. E
20. D

CHEM 311 (132) **First Major Exam** **2 HOURS**

Wednesday, Oct. 22, 2014

STUDENT NAME: ....

STUDENT ID NUMBER: ....

Test Code (003)

(20 Questions)

Dr. Mazen Khaled	Section 1
Dr.Mohamed Morsy	Section 2
Dr. G. Oweimreen	Section 3
Dr. W Forner	Section 4

Useful Physical constants and Formula

PHYSICAL CONSTANTS:	**Useful Equations:**
$R = 8.314\ \mathrm{J\ mol^{-1}\ K^{-1}}$	$\Lambda = \kappa/c,\ G = 1/R = \kappa(A/l)$
$R = 0.08314\ \mathrm{L\ bar\ K^{-1}\ mol^{-1}}$	$\Lambda = \lambda_+ + \lambda_-$
$k_B = 1.381 \times 10^{-23}\ \mathrm{J\ K^{-1}}$	$\alpha = \Lambda/\Lambda_o$
$1\ \mathrm{J} = 1\ \mathrm{kg\ m^2\ s^{-2}}$	$K = c\alpha^2/(1 - \alpha)$
$1\ \mathrm{atm} = 1.101325 \times 10^5\ \mathrm{Pa}$	$\Lambda_m = \Lambda^\circ_m - K\ (c/c_o)^{1/2}$ $1/\Lambda_m = 1/\Lambda^\circ_m + c\Lambda_m/[(\Lambda^\circ_m)^2 K_a]$
$1\ \mathrm{atm} = 1.01325 \times 10^5\ \mathrm{Pa};\ 1\ \mathrm{bar} = 10^5\ \mathrm{Pa};$	DHLL: $\log \gamma_\pm = -z_+ \lvert z_- \rvert B\sqrt{I}$ Davies Eq.: $\log \gamma_\pm = -B \lvert z_+z_- \rvert [(\sqrt{I})/\{1 + (\sqrt{I})\} - 0.30\ I]$ in water at 25 °C: $B = 0.51\ \mathrm{M^{-1/2}}$
$1\ \mathrm{Torr} = 1\ \mathrm{mmHg} = 133.322\ \mathrm{Pa}$	$I = \frac{1}{2}\sum_i c_i z_i^2$
$g = 9.81\ \mathrm{m\ s^{-2}}$	$\Delta\Phi = RT/zF \ln(c_1/c_2)$ $RT/F = 0.0257$ at 298 K
$0\ ^\circ\mathrm{C} = 273.15\ \mathrm{K}$	$E = E^\circ - (RT/z F) \ln(Q)$
$L = 6.022 \times 10^{23}\ \mathrm{mol^{-1}}$ (Avogadro's number)	$\Delta G = -zFE$
$h = 6.626 \times 10^{-34}\ \mathrm{J\ s}$	$\Delta S = z F (\partial E/\partial T)_p$
$F = 96500\ \mathrm{C\ mol^{-1}}$	$\Delta G = \Delta H - T\Delta S$
$c = 2.998 \times 10^8\ \mathrm{m\ s^{-1}}$ (speed of light)	$\gamma_\pm^{(\nu_+ + \nu_-)} = \gamma_+^{\nu_+}\gamma_-^{\nu_-}$
$\varepsilon_o = 8.854 \times 10^{-12}\ \mathrm{C^2 N^{-1} m^{-2}}$ $\varepsilon = 78$ at 25°C	$\mathrm{pH} = -\mathrm{Log}\ [H^+]$ $K_w = [OH^-][H^+]$
$e = 1.602 \times 10^{-19}\ \mathrm{C}$	$\Delta G^\circ_{solvation} = (1/\varepsilon_r - 1)z^2e^2N_A/(8\pi\varepsilon_o r)$
$E^\circ = (RT/z F)\ln(k^\circ)$	$\kappa = [2e^2N_A(1000\ \mathrm{L\ m^{-3}})/(\varepsilon_o k_B T)]^{1/2}\ [\rho_{sol}\ I/\varepsilon_r]^{1/2}$
$aa' = t_+ Q/FcA$ (travelled distance)	$\Delta G = RT \ln(c_1/c_2)$

Hydrogen Electrode: $H^+ (aq) + e^- (g) \rightarrow \frac{1}{2}H_2$ $E^\circ = 0$ V

Silver-Silver Chloride: $e^- + AgCl (s) \rightarrow Ag (s) + Cl^- (aq)$ $E^\circ = 0.22233$ V

Calomel Electrode: $e^- + \frac{1}{2}Hg_2Cl_2(s) \rightarrow Cl^- (aq) + Hg (l)$ $E^\circ = 0.13337$ V

1. The correct Nernst equation for the reaction

$$Al(s) + OH^-(aq) + 3\ H_2O(l) \longrightarrow Al(OH)_4^-(aq) + 3/2\ H_2(g)$$

is (do not use activities in the reaction ratio Q):

A) $E = E^o - (RT/4F) \ln Q$ with $Q = [Al(OH)_4^-]P(OH^-)/[OH^-]$

B) $E = E^o - (RT/4F) \ln Q$ with $Q = (P(H_2))^{3/2} [Al(OH)_4^-]/[OH^-]$

C) $E = E^o - (RT/3F) \ln Q$ with $Q = (P(H_2))^{3/2}[Al(OH)_4^-]/[OH^-]$

D) $E = E^o - (RT/3F) \ln Q$ with $Q = (P(H_2))^{3/2} [Al][(OH)^-]/[Al(s)]$

E) $E = E^o - (RT/3F) \ln Q$ with $Q = [H_2]^{3/2} \{Al(OH)_4^-]/\{[Al(s)][OH^-]\}$

2. Which of the following statements is **NOT CORRECT**?

A) Deviations from ideal behavior begin at lower concentrations for electrolyte solutions than for nonelectrolyte solutions.

B) In electrolyte solutions the main interaction is the long-range electrostatic Coulomb interaction between ions.

C) The attractive and repulsive interactions between ions depend on their charge and size.

D) Henry's law is obeyed up to concentrations of unit molality according to its hypothetical standard state.

E) The attractive and repulsive interactions between ions depend only on their chemical identity.

3. Consider the cell

$$Pt(s)|Cl_2(g)|ClO_2^-(aq)||Cr_2O_7^{2-}(aq)|Cr(s).$$

In acidic medium, how many electrons are exchanged in this cell reaction (balanced with the smallest possible set of integer coefficients)?

A) 6

B) 15

C) 3

D) 9

E) 12

4. What is the pH of a buffer solution that is ~~0.250~~ 0.150 *m* in CH_3COOH and 0.150 *m* in CH_3COONa, using the Davies equation (ignore the contributions from acetic acid dissociation in the ionic strength) to calculate $\gamma_\pm$? [pK_a of acetic acid = 4.76]
   A) 4.39
   B) 4.21
   C) 4.52
   D) 4.63
   E) 4.81

5. Calculate the mean ionic molality and the mean ionic activity of a 0.115 m K_3PO_4 solution for which the mean ionic activity coefficient is 0.125.
   A) 0.0531 m and 0.108
   B) 0.155 m and 0.0819
   C) 0.105 m and 0.0215
   D) 0.295 m and 0.0411
   E) 0.262 m and 0.0328

6. Using activities, calculate the solubility of Ag_2SO_4 (silver sulfate) in 0.025 M aqueous KNO_3 solution at 25°C. You may ignore the contribution of Ag^+ and SO_4^{2-} to the ionic strength. [K_{sp} of $Ag_2SO_4 = 1.5 \times 10^{-5}$]
   A) 0.0018 M
   B) 0.0041 M
   C) 0.023 M
   D) 0.052 M
   E) 0.011 M

7. Which of the following statements is **NOT CORRECT**?
   - A) At all electrolyte concentrations, the mean ionic activity coefficient $\gamma_\pm$ is less than 1.
   - B) At very low electrolyte concentrations, the experimentally measured mean ionic activity coefficient, $\gamma_\pm$, is close to the $\gamma_\pm$ value calculated using the Debye-Huckel limiting law (DHLL).
   - C) At very high electrolyte concentrations, the mean ionic activity coefficient $\gamma_\pm$ may reach values greater than 1.
   - D) The activities γ_+ and γ_- for the positive and negative ions of an electrolyte cannot be measured experimentally.
   - E) The mean ionic activity coefficient of an electrolyte $\gamma_\pm$ may be experimentally measured.

8. In the relation $\mu_{Fe_2(SO_4)_3} = \mu_\pm^\circ + \nu\, RT \ln\left(\frac{m}{m^\circ}\right) + \nu\, RT \ln \gamma_\pm$ the value of V is:
   - A) 1
   - B) 3
   - C) 2
   - D) 5
   - E) 4

9. Assume that the following reaction has a zero voltage (by definition as new standard):

$$Fe^{2+}(aq) + 2\,e^- \longrightarrow Fe(s)$$

What will be the voltage of the following reaction versus this new standard:

$$I_2(s) + 2\,e^- \longrightarrow 2\,I^-(aq)$$

given: $E^\circ_{Fe^{2+}/Fe} = -0.447$ V and $E^\circ_{I2/I-} = 0.536$ V versus standard hydrogen electrode?
   - A) 0.259 V
   - B) 0.931 V
   - C) 0.983 V
   - D) -0.536 V
   - E) 0.447 V

10. Which of the following inert electrolytes produces the largest increase in the degree of dissociation of acetic acid (using DHLL)?
    A) 0.01 m $CaCl_2$
    B) 0.001 m NaCl
    C) 0.001 m KBr
    D) 0.10 m $CuCl_2$
    E) 0.10 m CsCl

11. Calculate the mean activity coefficient for a 0.002 M aqueous K_2SO_4 solution assuming complete dissociation and that DHLL is valid.
    A) 0.621
    B) 0.834
    C) 0.918
    D) 0.781
    E) 0.711

12. With respect to the mean ionic activity coefficient variation, $\gamma_{\pm}$, with the square root of the ionic strength, $\sqrt{I}$, for an electrolyte which of the following statements is **CORRECT**?
    A) At high ionic strength $\gamma_{\pm} > 1$, solubility increases to keep the solubility product constant, resulting in the salting in effect.
    B) The $\gamma_{\pm}$ increases as $\sqrt{I}$ increases, at all electrolyte concentrations.
    C) The $\gamma_{\pm}$ decreases as $\sqrt{I}$ increases, at all electrolyte concentrations.
    D) At high ionic strength $\gamma_{\pm} > 1$, solubility decreases to keep the solubility product constant, resulting in the salting out effect.
    E) The $\gamma_{\pm}$ decreases as $\sqrt{I}$ increases, and in turn solubility must decrease resulting in the salting out effect.

13. Consider the following cell at 25 °C.

$$Co(s)|Co^{2+}(aq, a = 0.832)||Cr^{3+}(aq, a = 0.342)|Cr(s)$$

Using the standard potentials: $E^\circ_{Co^{2+}/Co} = -0.280$ V and $E^\circ_{Cr^{3+}/Cr} = -0.744$ V, what happens spontaneously in the cell?

A) Chromium is deposited.
B) Chromium dissolves.
C) Electrons flow from Cobalt to Chromium
D) Cobalt dissolves.
E) Cannot be determined.

14. Determine the cell voltage for the following electrochemical reaction at 25 °C:

$$Sn(s) + 2\ Ag^{+}(aq) \longrightarrow Sn^{2+}(aq) + 2\ Ag(s) \quad E^\circ_{cell} = 0.94\ V$$

given that aqueous 0.10 M $AgNO_3$ and aqueous 0.050 M $Sn(NO_3)_2$ solutions are used to set up the cell.

A) 0.92 V
B) 0.97 V
C) –0.97 V
D) 0.86 V
E) –0.92 V

15. In an electrochemical cell the oxidation of oxalic acid (HOOCCOOH) to carbon dioxide and water by permanganate ions, MnO_4^-, in acidic solution has an equilibrium for which $\ln K = 778$. What can be concluded from that fact?

A) No reaction happens.
B) Permanganate cannot oxidize oxalic acid.
C) Almost only reactants can be found in the cell.
D) Almost complete conversion from reactants into products happens.
E) Carbon dioxide and water are reduced to oxalic acid.

16. Enough of the salt $AB(s)$ is dissolved in a certain amount of water to bring it into equilibrium with the ions $A^{2+}(aq)$ and $B^{2-}(aq)$. If the equilibrium concentration of A^{2+} is $7.6\times10^{-5}\ mol\ kg^{-1}$, and the Debye Hückel Limiting Law (DHLL) is obeyed at this concentration, K_{sp} for the salt is:

A) 8.46×10^{-8}

B) 5.78×10^{-9}

C) 5.22×10^{-9}

D) 4.59×10^{-9}

E) 4.90×10^{-9}

17. An electrochemical cell is made by connecting an aluminum strip in 0.40 M $Al_2(SO_4)_3$ solution to a copper strip in 1.00 M $CuSO_4$ solution at 25 °C. Given the standard potentials: $E^{\circ}_{Cu^{2+}/Cu} = 0.34$ V and $E^{\circ}_{Al^{3+}/Al} = -1.67$ V, determine the cell voltage, assuming that the copper strip is gaining mass and that the aluminum strip is losing mass.

A) 2.20 V

B) 2.01 V

C) 1.02 V

D) 0.00 V

E) 1.11 V

18. Which statement is **TRUE**?

A) The sign of the Gibbs energy change of an electrochemical reaction at equilibrium can be changed by changing the ionic strength.

B) The Gibbs energy change of a spotaneous electrochemical reaction at equilibrium is negative.

C) The Gibbs energy change of an electrochemical reaction at equlibrium can be changed by an applied electric potential.

D) The Gibbs energy change of an electrochemical reaction at equilibrium is equal to zero.

E) The sum of the stoichiometric coefficients multiplied by the charges of each reactant and product in an electrochemical reaction is always negative.

19. For fluorine, F_2, the standard potential is $E^o_{F2/F^-} = 2.87$ V. Given that

$$E^o_{Zn^{2+}/Zn} = -0.761 \text{ V},\ E^o_{Ag^+/Ag} = 0.800, \text{ and } E^o_{Au^+/Au} = 1.68 \text{ V}$$

and assuming a fluorine electrode is made from fluorine bubbling over an inert metal surface, what will happen in a cell made of this fluorine electrode and one of the above mentioned metals in the standard state?

A) Fluorine oxidizes Zn, but not Ag and Au.
B) Fluorine oxidizes Zn, Ag, and Au.
C) Flourine oxidizes Zn and Ag, but not Au.
D) Fluorine oxidizes none of these metals.
E) Fluorine reduces all those metals.

20. Consider the following cell at 25 °C:

$$Ag(s)|AgNO_3(aq)|AgI(s)|Ag(s)$$

Given the standard potentials: $E^o_{Ag^+/Ag} = 0.799$V and $E^o_{AgI/Ag} = 0.061$V, calculate pK_{sp} of AgI.

A) –12.5
B) 3.352×10^{-13}
C) -14.5
D) 12.5
E) 14.5

Answer Key

1. C
2. E
3. E
4. C
5. E
6. C
7. A
8. D
9. C
10. D
11. B
12. D
13. B
14. A
15. D
16. E
17. B
18. D
19. B
20. D

CHEM 311 (132) **First Major Exam** **2 HOURS**

Wednesday, Oct. 22, 2014

STUDENT NAME: ....

STUDENT ID NUMBER: ....

Test Code (004)

(20 Questions)

Dr. Mazen Khaled	Section 1
Dr.Mohamed Morsy	Section 2
Dr. G. Oweimreen	Section 3
Dr. W Forner	Section 4

Useful Physical constants and Formula

PHYSICAL CONSTANTS:	**Useful Equations:**
$R = 8.314\ \mathrm{J\ mol^{-1}\ K^{-1}}$	$\Lambda = \kappa / c$, $G = 1/R = \kappa(A/l)$
$R = 0.08314\ \mathrm{L\ bar\ K^{-1}\ mol^{-1}}$	$\Lambda = \lambda_+ + \lambda_-$
$k_B = 1.381 \times 10^{-23}\ \mathrm{J\ K^{-1}}$	$\alpha = \Lambda / \Lambda_o$
$1\ \mathrm{J} = 1\ \mathrm{kg\ m^2\ s^{-2}}$	$K = c\alpha^2/(1 - \alpha)$
$1\ \mathrm{atm} = 1.101325 \times 10^5\ \mathrm{Pa}$	$\Lambda_m = \Lambda^o{}_m - K\ (c/c_o)^{1/2}$ $1/\Lambda_m = 1/\Lambda^o{}_m + c\Lambda_m / [(\Lambda^o{}_m)^2\ K_a]$
$1\ \mathrm{atm} = 1.01325 \times 10^5\ \mathrm{Pa}$; $1\ \mathrm{bar} = 10^5\ \mathrm{Pa}$;	DHLL: $\log \gamma_\pm = -z_+ \lvert z_- \rvert B\sqrt{I}$ Davies Eq.: $\log \gamma_\pm = -B \lvert z_+ z_- \rvert [(\sqrt{I})/\{1 + (\sqrt{I})\} - 0.30\ I]$ in water at 25 °C: $B = 0.51\ \mathrm{M^{-1/2}}$
$1\ \mathrm{Torr} = 1\ \mathrm{mmHg} = 133.322\ \mathrm{Pa}$	$I = \frac{1}{2}\sum_i c_i z_i^2$
$g = 9.81\ \mathrm{m\ s^{-2}}$	$\Delta\Phi = RT/zF\ \ln(c_1/c_2)$ $RT/F = 0.0257$ at 298 K
$0\ °\mathrm{C} = 273.15\ \mathrm{K}$	$E = E° - (RT/z\ F)\ \ln(Q)$
$L = 6.022 \times 10^{23}\ \mathrm{mol^{-1}}$ (Avogadro's number)	$\Delta G = -zFE$
$h = 6.626 \times 10^{-34}\ \mathrm{J\ s}$	$\Delta S = z\ F\ (\partial E/\partial T)_p$
$F = 96500\ \mathrm{C\ mol^{-1}}$	$\Delta G = \Delta H - T\Delta S$
$c = 2.998 \times 10^8\ \mathrm{m\ s^{-1}}$ (speed of light)	$\gamma_\pm^{(\nu_+ + \nu_-)} = \gamma_+^{\nu_+} \gamma_-^{\nu_-}$
$\varepsilon_o = 8.854 \times 10^{-12}\ \mathrm{C^2 N^{-1} m^{-2}}$ $\varepsilon = 78$ at 25°C	$\mathrm{pH} = -\mathrm{Log}\ [H^+]$ $K_w = [OH^-]\ [H^+]$
$e = 1.602 \times 10^{-19}\ \mathrm{C}$	$\Delta G°_{solvation} = (1/\varepsilon_r - 1) z^2 e^2 N_A / (8\pi\varepsilon_o r)$
$E° = (RT/z\ F) \ln(k°)$	$\kappa = [2e^2 N_A (1000\ \mathrm{L\ m^{-3}})/(\varepsilon_o k_B T)]^{1/2}\ [\rho_{sol}\ I/\varepsilon_r]^{1/2}$
$aa' = t_+\ Q/FcA$ (travelled distance)	$\Delta G = RT\ \ln(c_1/c_2)$

Hydrogen Electrode: $H^+\ (aq) + e^-\ (g) \rightarrow \frac{1}{2}H_2$ $E° = 0\ \mathrm{V}$

Silver-Silver Chloride: $e^- + AgCl\ (s) \rightarrow Ag\ (s) + Cl^-\ (aq)$ $E° = 0.22233\ \mathrm{V}$

Calomel Electrode: $e^- + \frac{1}{2}Hg_2Cl_2(s) \rightarrow Cl^-\ (aq) + Hg\ (l)$ $E° = 0.13337\ \mathrm{V}$

1. Assume that the following reaction has a zero voltage (by definition as new standard):

$$Fe^{2+}(aq) + 2\ e^- \longrightarrow Fe(s)$$

What will be the voltage of the following reaction versus this new standard:

$$I_2(s) + 2\ e^- \longrightarrow 2\ I^-(aq)$$

given: $E^o_{Fe^{2+}/Fe} = -0.447$ V and $E^o_{I2/I-} = 0.536$ V versus standard hydrogen electrode?

A) 0.983 V
B) 0.447 V
C) -0.536 V
D) 0.931 V
E) 0.259 V

2. The correct Nernst equation for the reaction

$$Al(s) + OH^-(aq) + 3\ H_2O(l) \longrightarrow Al(OH)_4^-(aq) + 3/2\ H_2(g)$$

is (do not use activities in the reaction ratio Q):

A) $E = E^o - (RT/4F) \ln Q$ with $Q = (P(H_2))^{3/2}\ [Al(OH)_4^-]/[OH^-]$
B) $E = E^o - (RT/3F) \ln Q$ with $Q = [H_2]^{3/2}\ [Al(OH)_4^-]/\{[Al(s)][OH^-]\}$
C) $E = E^o - (RT/4F) \ln Q$ with $Q = [Al(OH)_4^-]P(OH^-)/[OH^-]$
D) $E = E^o - (RT/3F) \ln Q$ with $Q = (P(H_2))^{3/2}[Al(OH)_4^-]/[OH^-]$
E) $E = E^o - (RT/3F) \ln Q$ with $Q = (P(H_2))^{3/2}\ [Al][(OH)^-]/[Al(s)]$

3. Which of the following inert electrolytes produces the largest increase in the degree of dissociation of acetic acid (using DHLL)?

A) 0.001 m NaCl
B) 0.001 m KBr
C) 0.10 m $CuCl_2$
D) 0.10 m CsCl
E) 0.01 m $CaCl_2$

4. Consider the following cell at 25 °C:

$$Ag(s)|AgNO_3(aq)|AgI(s)|Ag(s)$$

Given the standard potentials: $E^o_{Ag^+/Ag} = 0.799V$ and $E^o_{AgI/Ag} = 0.061V$, calculate pK_{sp} of AgI.

A) 14.5
B) −12.5
C) 12.5
D) 3.352×10^{-13}
E) -14.5

5. Using activities, calculate the solubility of Ag_2SO_4 (silver sulfate) in 0.025 M aqueous KNO_3 solution at 25°C. You may ignore the contribution of Ag^+ and SO_4^{2-} to the ionic strength. [K_{sp} of $Ag_2SO_4 = 1.5 \times 10^{-5}$]

A) 0.0041 M
B) 0.023 M
C) 0.052 M
D) 0.011 M
E) 0.0018 M

6. For fluorine, F_2, the standard potential is $E^o_{F2/F^-} = 2.87$ V. Given that

$$E^o_{Zn^{2+}/Zn} = -0.761 \text{ V}, E^o_{Ag^+/Ag} = 0.800, \text{ and } E^o_{Au^+/Au} = 1.68 \text{ V}$$

and assuming a fluorine electrode is made from fluorine bubbling over an inert metal surface, what will happen in a cell made of this fluorine electrode and one of the above mentioned metals in the standard state?

A) Flourine oxidizes Zn and Ag, but not Au.
B) Fluorine oxidizes Zn, but not Ag and Au.
C) Fluorine oxidizes Zn, Ag, and Au.
D) Fluorine oxidizes none of these metals.
E) Fluorine reduces all those metals.

7. Calculate the mean ionic molality and the mean ionic activity of a 0.115 m K_3PO_4 solution for which the mean ionic activity coefficient is 0.125.

A) 0.262 m and 0.0328
B) 0.105 m and 0.0215
C) 0.295 m and 0.0411
D) 0.0531 m and 0.108
E) 0.155 m and 0.0819

8. Consider the following cell at 25 °C.

$$\text{Co(s)}|\text{Co}^{2+}(\text{aq}, a = 0.832)||\text{Cr}^{3+}(\text{aq}, a = 0.342)|\text{Cr(s)}$$

Using the standard potentials: $E^\circ_{Co^{2+}/Co} = -0.280$ V and $E^\circ_{Cr^{3+}/Cr} = -0.744$ V, what happens spontaneously in the cell?

A) Chromium dissolves.
B) Electrons flow from Cobalt to Chromium
C) Cobalt dissolves.
D) Cannot be determined.
E) Chromium is deposited.

9. Enough of the salt $AB(s)$ is dissolved in a certain amount of water to bring it into equilibrium with the ions $A^{2+}(aq)$ and $B^{2-}(aq)$. If the equilibrium concentration of A^{2+} is 7.6×10^{-5} $mol\ kg^{-1}$, and the Debye Hückel Limiting Law (DHLL) is obeyed at this concentration, K_{sp} for the salt is:

A) 5.22×10^{-9}
B) 8.46×10^{-8}
C) 4.90×10^{-9}
D) 5.78×10^{-9}
E) 4.59×10^{-9}

0.150

10. What is the pH of a buffer solution that is ~~0.250~~ m in CH_3COOH and 0.150 m in CH_3COONa, using the Davies equation (ignore the contributions from acetic acid dissociation in the ionic strength) to calculate $\gamma_\pm$? [pK_a of acetic acid = 4.76]

A) 4.52
B) 4.39
C) 4.63
D) 4.81
E) 4.21

11. In the relation $\mu_{Fe_2(SO_4)_3} = \mu_{\pm}^{\circ} + \nu\, RT \ln\left(\frac{m}{m^{\circ}}\right) + \nu\, RT \ln \gamma_{\pm}$ the value of V is:

A) 2
B) 4
C) 3
D) 1
E) 5

12. Determine the cell voltage for the following electrochemical reaction at 25 °C:

$$Sn(s) + 2\ Ag^{+}(aq) \longrightarrow Sn^{2+}(aq) + 2\ Ag(s) \quad E^{\circ}_{cell} = 0.94\ V$$

given that aqueous 0.10 M $AgNO_3$ and aqueous 0.050 M $Sn(NO_3)_2$ solutions are used to set up the cell.

A) –0.97 V
B) 0.86 V
C) –0.92 V
D) 0.92 V
E) 0.97 V

13. Which of the following statements is **NOT CORRECT**?

A) The attractive and repulsive interactions between ions depend only on their chemical identity.
B) Henry's law is obeyed up to concentrations of unit molality according to its hypothetical standard state.
C) In electrolyte solutions the main interaction is the long-range electrostatic Coulomb interaction between ions.
D) Deviations from ideal behavior begin at lower concentrations for electrolyte solutions than for nonelectrolyte solutions.
E) The attractive and repulsive interactions between ions depend on their charge and size.

14. Which statement is **TRUE**?
    A) The Gibbs energy change of an electrochemical reaction at equilibrium is equal to zero.
    B) The Gibbs energy change of an electrochemical reaction at equlibrium can be changed by an applied electric potential.
    C) The sum of the stoichiometric coefficients multiplied by the charges of each reactant and product in an electrochemical reaction is always negative.
    D) The Gibbs energy change of a spotaneous electrochemical reaction at equilibrium is negative.
    E) The sign of the Gibbs energy change of an electrochemical reaction at equilibrium can be changed by changing the ionic strength.

15. Which of the following statements is **NOT CORRECT**?
    A) At very high electrolyte concentrations, the mean ionic activity coefficient $\gamma_\pm$ may reach values greater than 1.
    B) The activities γ_+ and γ_- for the positive and negative ions of an electrolyte cannot be measured experimentally.
    C) At very low electrolyte concentrations, the experimentally measured mean ionic activity coefficient, $\gamma_\pm$, is close to the $\gamma_\pm$ value calculated using the Debye-Huckel limiting law (DHLL).
    D) The mean ionic activity coefficient of an electrolyte $\gamma_\pm$ may be experimentally measured.
    E) At all electrolyte concentrations, the mean ionic activity coefficient $\gamma_\pm$ is less than 1.

16. With respect to the mean ionic activity coefficient variation, $\gamma_\pm$, with the square root of the ionic strength, $\sqrt{I}$, for an electrolyte which of the following statements is **CORRECT**?
    A) The $\gamma_\pm$ decreases as $\sqrt{I}$ increases, and in turn solubility must decrease resulting in the salting out effect.
    B) The $\gamma_\pm$ decreases as $\sqrt{I}$ increases, at all electrolyte concentrations.
    C) At high ionic strength $\gamma_\pm > 1$, solubility decreases to keep the solubility product constant, resulting in the salting out effect.
    D) At high ionic strength $\gamma_\pm > 1$, solubility increases to keep the solubility product constant, resulting in the salting in effect.
    E) The $\gamma_\pm$ increases as $\sqrt{I}$ increases, at all electrolyte concentrations.

17. In an electrochemical cell the oxidation of oxalic acid (HOOCCOOH) to carbon dioxide and water by permanganate ions, MnO_4^-, in acidic solution has an equilibrium for which $\ln K = 778$. What can be concluded from that fact?
    A) Almost complete conversion from reactants into products happens.
    B) Carbon dioxide and water are reduced to oxalic acid.
    C) No reaction happens.
    D) Permanganate cannot oxidize oxalic acid.
    E) Almost only reactants can be found in the cell.

18. Consider the cell

$$Pt(s)|Cl_2(g)|ClO_2^-(aq)||Cr_2O_7^{2-}(aq)|Cr(s).$$

In acidic medium, how many electrons are exchanged in this cell reaction (balanced with the smallest possible set of integer coefficients)?
    A) 15
    B) 12
    C) 6
    D) 3
    E) 9

19. Calculate the mean activity coefficient for a 0.002 M aqueous K_2SO_4 solution assuming complete dissociation and that DHLL is valid.
    A) 0.918
    B) 0.781
    C) 0.834
    D) 0.711
    E) 0.621

20. An electrochemical cell is made by connecting an aluminum strip in 0.40 M $Al_2(SO_4)_3$ solution to a copper strip in 1.00 M $CuSO_4$ solution at 25 °C. Given the standard potentials: $E^\circ_{Cu^{2+}/Cu} = 0.34$ V and $E^\circ_{Al^{3+}/Al} = -1.67$ V, determine the cell voltage, assuming that the copper strip is gaining mass and that the aluminum strip is losing mass.
    A) 1.11 V
    B) 2.20 V
    C) 2.01 V
    D) 1.02 V
    E) 0.00 V

Answer Key

1. A
2. D
3. C
4. C
5. B
6. C
7. A
8. A
9. C
10. A
11. E
12. D
13. A
14. A
15. E
16. C
17. A
18. B
19. C
20. C

CHEM 311 (132) First Major Exam 2 HOURS
Wednesday, Oct. 22, 2014

STUDENT NAME: ....

STUDENT ID NUMBER: ....

Test Code (000)

(20 Questions)

Dr. Mazen Khaled	Section 1
Dr.Mohamed Morsy	Section 2
Dr G. Oweimreen	Section 3
Dr. W Forner	Section 4

Useful Physical constants and Formula

PHYSICAL CONSTANTS:	**Useful Equations:**
$R = 8.314\ \text{J mol}^{-1}\ \text{K}^{-1}$	$\Lambda = \kappa/c$, $G = 1/R = \kappa(A/l)$
$R = 0.08314\ \text{L bar K}^{-1}\ \text{mol}^{-1}$	$\Lambda = \lambda_+ + \lambda_-$
$k_B = 1.381 \times 10^{-23}\ \text{J K}^{-1}$	$\alpha = \Lambda/\Lambda_o$
$1\ \text{J} = 1\ \text{kg m}^2\ \text{s}^{-2}$	$K = c\alpha^2/(1-\alpha)$
1 atm = 1.101325×10^5 Pa	$\Lambda_m = \Lambda^\circ_m - K\,(c/c_o)^{1/2}$ $1/\Lambda_m = 1/\Lambda^\circ_m + c\Lambda_m/[(\Lambda^\circ_m)^2 K_a]$
1 atm = 1.01325×10^5 Pa; 1 bar = 10^5 Pa;	DHLL: $\log \gamma_\pm = -z_+ \lvert z_- \rvert B\sqrt{I}$ Davies Eq.: $\log \gamma_\pm = -B\,\lvert z_+ z_- \rvert\,[(\sqrt{I})/\{1 + (\sqrt{I})\} - 0.30\,I]$ in water at 25 °C: B = ~~$0.5092\ \text{M}^{-1/2}$~~ $0.51\ \text{M}^{-1/2}$
1 Torr = 1 mmHg = 133 322 Pa	$I = \frac{1}{2}\sum_i c_i z_i^2$
$g = 9.81\ \text{m s}^{-2}$	$\Delta\Phi = RT/zF \ln(c_1/c_2)$ $RT/F = 0.0257$ at 298 K
0 °C = 273.15 K	$E = E^\circ - (RT/z F)\ln(Q)$
$L = 6.022 \times 10^{23}\ \text{mol}^{-1}$ (Avogadro's number)	$\Delta G = -zFE$
$h = 6.626 \times 10^{-34}\ \text{J s}$	$\Delta S = z F\,(\partial E/\partial T)_p$
$F = 96500\ \text{C mol}^{-1}$	$\Delta G = \Delta H - T\Delta S$
$c = 2.998 \times 10^8\ \text{m s}^{-1}$ (speed of light)	$\gamma_\pm^{(\nu_+ + \nu_-)} = \gamma_+^{\nu_+} \gamma_-^{\nu_-}$
$\varepsilon_o = 8.854 \times 10^{-12}\ \text{C}^2\text{N}^{-1}\text{m}^{-2}$ $\varepsilon = 78$ at 25°C	$\text{pH} = -\text{Log}\,[\text{H}^+]$ $K_w = [\text{OH}^-]\,[\text{H}^+]$
$e = 1.602 \times 10^{-19}\ \text{C}$	$\Delta G^\circ_{solvation} = (1/\varepsilon_r - 1)z^2e^2N_A/(8\pi\varepsilon_o r)$
$E^\circ = (RT/z F)\ln(k^\circ)$	$\kappa = [2e^2N_A(1000\ \text{L m}^{-3})/(\varepsilon_o k_B T)]^{1/2}\,[\rho_{sol}\,1/\varepsilon_r]^{1/2}$
$aa' = t_+ Q/FcA$ (travelled distance)	$\Delta G = RT \ln(c_1/c_2)$

Hydrogen Electrode: $H^+ (aq) + e^- (g) \rightarrow \frac{1}{2}H_2$ $E^\circ = 0$ V

Silver-Silver Chloride: $e^- + AgCl (s) \rightarrow Ag (s) + Cl^- (aq)$ $E^\circ = 0.22233$ V

Calomel Electrode: $e^- + \frac{1}{2}Hg_2Cl_2(s) \rightarrow Cl^- (aq) + Hg (l)$ $E^\circ = 0.13337$ V

$$I = \frac{1}{2} \cdot 0.025M\left(1\cdot(+1)^2 + 1\cdot(-1)^2\right) = 0.025M$$

$$\log_{10} \gamma_I = -0.51 \cdot |1 \cdot (-2)| \cdot \sqrt{0.025} = -0.161276$$

$$\underset{Ag^+}{\uparrow} \quad \underset{SO_4^{2-}}{\uparrow}$$

$$\gamma_I = 10^{-0.161276} = 0.68980$$

solubility : s

Ag_2SO_4 :

$[Ag^+] = 2 \cdot s$

$[SO_4^{2-}] = s$

$s = [Ag_2SO_4]$

1. Using activities, calculate the solubility of Ag_2SO_4 (silver sulfate) in 0.025 M aqueous KNO_3 solution at 25°C. You may ignore the contribution of Ag^+ and SO_4^{2-} to the ionic strength. [K_{sp} of Ag_2SO_4 = 1.5 x 10^{-5}]
   - $\boxed{\text{A) 0.023 M}}$
   - B) 0.052 M
   - C) 0.011 M
   - D) 0.0018 M
   - E) 0.0041 M

$$K_{sp} = a_{Ag^+}^2 \cdot a_{SO_4^{2-}} = [Ag^+]^2[SO_4^{2-}]\gamma_I^3$$

$$K_{sp} = (2s)^2 \cdot s \cdot \gamma_I^3 = 4s^3\gamma_I^3$$

$$s = \frac{1}{\gamma_I}\sqrt[3]{\frac{1}{4}K_{sp}} = \frac{1}{0.68980}\sqrt[3]{\frac{1}{4}\cdot 1.5\cdot 10^{-5}}\,M = 0.0225\,M$$
$$= 0.023\,M$$

2. Which of the following inert electrolytes produces the largest increase in the degree of dissociation of acetic acid (using DHLL)? see next page!
   - $\boxed{\text{A) 0.10 m CuCl}_2}$ $I = \frac{1}{2} \cdot 0.1m(4+2) = 0.3\,m$ largest I, largest α
   - B) 0.001 m NaCl — $I = \frac{1}{2}\, 0.001m(1+1) = 0.001\,m$
   - C) 0.001 m KBr — $I = \frac{1}{2} \cdot 0.001m(1+1) = 0.001\,m$
   - D) 0.10 m CsCl — $I = \frac{1}{2} \cdot 0.1m(1+1) = 0.10\,m$
   - E) 0.01 m $CaCl_2$ — $I = \frac{1}{2}\, 0.01m(4+2) = 0.03\,m$

$c_{K^+} = 2c_{K_2SO_4}$

$c_{SO_4^{2-}} = c_{K_2SO_4}$

$I = \frac{1}{2}\left[(+1)^2 c_{K^+} + (-2)^2 \cdot c_{SO_4^{2-}}\right]$

$= \frac{1}{2}(1 \cdot 0.004 + 4 \cdot 0.002M)$

$= \frac{1}{2}(2+4)\cdot 0.002M = 0.006\,M$

3. Calculate the mean activity coefficient for a 0.002 M aqueous K_2SO_4 solution assuming complete dissociation and that DHLL is valid.
   - $\boxed{\text{A) 0.834}}$
   - B) 0.918
   - C) 0.711
   - D) 0.621
   - E) 0.781

$$\log_{10}\gamma_\pm = -0.51\,|z_+ z_-|\sqrt{I/M}$$
$$= -0.51 \cdot 2 \cdot \sqrt{0.006} = -0.079009$$
$$\gamma_\pm = 10^{-0.079009} = 0.83366$$
$$= 0.834$$

4. What is the pH of a buffer solution that is 0.150 *m* in CH_3COOH and 0.150 *m* in CH_3COONa, using the Davies equation (ignore the contributions from acetic acid dissociation in the ionic strength) to calculate $\gamma_\pm$? [pK_a of acetic acid = 4.76]
   - A) ~~4.52~~ ~~4.39~~ $\boxed{4.52}$
   - B) 4.63
   - C) 4.21
   - D) 4.81
   - E) 4.39

see page after next page

2. $K_a = \text{const.} = \frac{a_{H^+} a_{Ac^-}}{a_{HAc}} = \frac{[H^+][Ac^-]}{[HAc]} \gamma_\pm^2$

$\gamma(HAc) \approx 1$ Ac = Acetate

degree of dissociation ~ $x = [H^+] = [Ac^-]$

$$K_a = \frac{x^2}{c^0 - x} \gamma_\pm^2$$

c^0 : [HAc] before dissociation

dissociated : x

K_a small ⇒ $c^0 - x \approx c$

$$K_a = \frac{x^2}{c} \gamma_\pm^2$$

$$\sqrt{\gamma_\pm^2} = |\gamma_\pm|$$

$$x = \sqrt{K_a c}\, |\gamma_\pm|^{-1}$$

⇒ largest $|\gamma_\pm|$ → ~~largest~~ smallest x

$$\log_{10} \gamma_\pm = -0.51 |z_+ z_-| \sqrt{I}$$

$$\gamma_\pm = 10^{\log_{10} \gamma_\pm}$$

⇒ largest I → smallest $\gamma_\pm$ ($\log \gamma_\pm$ negative)

largest I → smallest $|\gamma_\pm|$ → ~~smallest~~ largest x

→ largest degree of dissociation α

$$\alpha = x/c = \frac{1}{|\gamma_\pm|}\left(\sqrt{cK_a}/c\right) = \frac{1}{\gamma_\pm} \sqrt{\frac{K_a}{c}}$$

smallest $|\gamma_\pm|$ (largest I) ⇒ largest α

$|\gamma_\pm| = \gamma_\pm$ since $\gamma_\pm > 0$

4)

$$K_a = \frac{m_{H^+}\, m_{Ac^-}}{m_{HAc}}\, \gamma_I^{\,2}$$

$$\gamma(HAc) \approx 1 \, , \quad m_{H^+} = x$$

$$K_a = \gamma_I^{\,2}\, \frac{x\,(m^0_{Ac^-} + x)}{(m^0_{HAc} - x)} \qquad K_a = 10^{-4{,}76} = 1{,}7378 \cdot 10^{-5}$$

$$= (\gamma_I^{\,2}) \times \frac{m_0^{Ac^-}}{m_0\, HAc}\, x = \; m_{H^+} = \frac{K_a}{\gamma_I^{\,2}}\, \frac{m^0_{HAc}}{m^0_{Ac^-}} = \frac{K_a}{\gamma_I^2}\, \frac{0{,}15}{0.15} = \frac{K_a}{\gamma_\pm^2}$$

$$\Rightarrow \quad m^0_{Ac^-} = 0.15\,m \gg x \; , \; m^0_{HAc} = 0.15\,m \gg x$$

x very small $\Rightarrow$ I from NaAc alone!

$$I = \tfrac{1}{2} \cdot 0.15\,m \left(1 \cdot (+1)^2 + 1 \cdot (-1)^2\right) = 0.15\,m$$

$$\log_{10} \gamma_I = -0{,}51 \cdot |1 \cdot (-1)| \left[\frac{\sqrt{I}}{1 + \sqrt{I}} - 0{,}3 \cdot I\right]$$

$$= -0{,}51 \left[\frac{\sqrt{0.15}}{1 + \sqrt{0{,}15}} - 0{,}3 \cdot 0{,}15\right]$$

$$= -0{,}11943$$

$$\gamma_\pm = 10^{-0{,}11943} = 0{,}75957$$

$$\cancel{x = \frac{1{,}7378 \cdot 10^{-5}}{(0{,}75957)^2}\, m = 3{,}0121 \cdot 10^{-5}\, m}$$

$$\cancel{pH = -\log_{10}(3{,}0121 \cdot 10^{-5}) = 4{,}52}$$

$$x = \frac{1{,}7378 \cdot 10^{-5}}{(0.75957)^2}\, m \cdot \cancel{1{,}67} = \overset{3{,}01206 \cdot 10^{-5}}{\cancel{5{,}0301 \cdot 10^{-5}\, m}}$$

$$pH = -\log_{10}\left(\overset{3{,}01206}{\cancel{5{,}0301}} \cdot 10^{-5}\right) = \cancel{4{,}30}\ \cancel{4{,}229}\ 4{,}521$$

$$= \cancel{4{,}30}\ 4{,}52$$

$m_\pm^{\nu} = m_+^{\nu_+} \cdot m_-^{\nu_-}$ $\nu = \nu_+ + \nu_- = 3+1 = 4$

$m_+ = 3 \cdot m^\circ$, $m_- = m^\circ$

$m_\pm^4 = (3 \cdot 0,115)^3 \cdot 0,115 = 4,7223 \cdot 10^{-3}$ m°

5. Calculate the mean ionic molality and the mean ionic activity of a 0.115 m K_3PO_4 solution for which the mean ionic activity coefficient is 0.125.
   - $\boxed{\text{A) 0.262 m and 0.0328}}$
   - B) 0.155 m and 0.0819
   - C) 0.0531 m and 0.108
   - D) 0.295 m and 0.0411
   - E) 0.105 m and 0.0215

$m_\pm = \sqrt[4]{4,7223 \cdot 10^{-3}}$

$= 0,2621\ m = 0,262\ m$

$a_\pm^4 = m_\pm^4 \gamma_\pm^4$ $a_\pm = m_\pm \gamma_\pm$

$a_\pm = 0,2621 \cdot 0,125 = 0,03276 = 0,0328$

6. An electrochemical cell is made by connecting an aluminum strip in 0.40 M $Al_2(SO_4)_3$ solution to a copper strip in 1.00 M $CuSO_4$ solution at 25 °C. Given the standard potentials, $E^\circ_{Cu^{2+}/Cu} = 0.34$ V and $E^\circ_{Al^{3+}/Al} = -1.67$ V, determine the cell voltage, assuming that the copper strip is gaining mass and that the aluminum strip is losing mass.
   - $\boxed{\text{A) 2.01 V}}$
   - B) 2.20 V
   - C) 1.02 V
   - D) 1.11 V
   - E) 0.00 V

mass gain of Cu:

$Cu^{2+} + 2e^- \rightarrow Cu \,|\cdot 3$

mass loss of Al:

$Al \rightarrow Al^{3+} + 3e^- \,|\cdot 2$

$3Cu^{2+} + 2Al \rightarrow 3Cu + 2Al^{3+}$

$\underline{n = 6}$

$E^\circ = (0,34 + 1,67)\ V = 2,01\ V$

$E = E^\circ - \frac{RT}{6F} \ln \frac{[Al^{3+}]^2}{[Cu^{2+}]^3} = 2,01V - \frac{25,7mV}{6} \ln \frac{(0,8)^2}{(1,00)^3}$

$= 2,01\ V - 4,2833 \cdot 10^{-3}\ V \cdot \ln 0,64$

$[Al^{3+}] = 0,8\ M$ $= 2,01V - 4,2833 \cdot 10^{-3}\ V\,(-0,44629) = 2,0119\ V = 2,01\ V$

$E^\circ = E^\circ_{ox} + E^\circ_{red}$, $E^\circ_{ox} = -E^\circ_{Al^{3+}/Al}$, $E^\circ = E^\circ_{Cu^{2+}/Cu} - E^\circ_{Al^{3+}/Al}$

7. Determine the cell voltage for the following electrochemical reaction at 25 °C:

$$Sn(s) + 2\ Ag^+(aq) \longrightarrow Sn^{2+}(aq) + 2\ Ag(s) \quad E^\circ_{cell} = 0.94\ V \quad \underline{n = 2}$$

given that aqueous 0.10 M $AgNO_3$ and aqueous 0.050 M $Sn(NO_3)_2$ solutions are used to set up the cell.
   - $\boxed{\text{A) 0.92 V}}$
   - B) 0.97 V
   - C) 0.86 V
   - D) –0.92 V
   - E) –0.97 V

$E = E^\circ - \frac{25,7\ mV}{2} \ln \frac{[Sn^{2+}]}{[Ag^+]^2}$

$= 0,94V - 12,85\ mV \ln \frac{0,05}{(0,1)^2}$

$= 0,94\ V - 12,85\ mV \ln 5 = 0,919\ V$

$= 0,92\ V$

8. The correct Nernst equation for the reaction $Al \rightarrow Al^{3+} + 3e^-$ $n = 3!$

$$Al(s) + OH^-(aq) + 3\ H_2O(l) \longrightarrow Al(OH)_4^-(aq) + 3/2\ H_2(g)$$

is (do not use activities in the reaction ratio Q):
   - $\boxed{\text{A)}}$ $E = E^\circ - (RT/3F) \ln Q$ with $Q = (P(H_2))^{3/2}[Al(OH)_4^-]/[OH^-]$ correct
   - B) $E = E^\circ - (RT/3F) \ln Q$ with $Q = [H_2]^{3/2}[Al(OH)_4^-]/\{[Al(s)][OH^-]\}$ wrong : $P(H_2)$
   - C) $E = E^\circ - (RT/4F) \ln Q$ with $Q = [Al(OH)_4^-]P(OH^-)/[OH^-]$ wrong $n = 3$
   - D) $E = E^\circ - (RT/3F) \ln Q$ with $Q = (P(H_2))^{3/2}[Al][(OH)^-]/[Al(s)]$ wrong $[Al(OH)_4^-]$ missing
   - E) $E = E^\circ - (RT/4F) \ln Q$ with $Q = (P(H_2))^{3/2}[Al(OH)_4^-]/[OH^-]$ wrong $n = 3$

$Al \rightarrow Al^{3+} + 3e^-$

$H^+ + e^- \rightarrow \frac{1}{2} H_2 \,|\cdot 3$ $\underline{n = 3}$

$Al + 3H^+ \rightarrow Al^{3+} + \frac{3}{2} H_2$

9. Assume that the following reaction has a zero voltage (by definition as new standard):

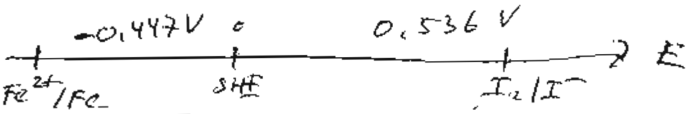
$$Fe^{2+}(aq) + 2\ e^- \rightarrow Fe(s)$$

What will be the voltage of the following reaction versus this new standard

$$I_2(s) + 2\ e^- \rightarrow 2\ I^-(aq)$$

given: $E^0_{Fe^{2+}/Fe} = -0.447$ V and $E^0_{I_2/I^-} = 0.536$ V versus standard hydrogen electrode? (SHE)

[✓ A) 0.983 V]
B) -0.536 V
C) 0.447 V
D) 0.259 V
E) 0.931 V



(0.447 + 0.536) V = 0.983 V

10. Which statement is **TRUE**?

[✓ A)] The Gibbs energy change of an electrochemical reaction at equilibrium is equal to zero. correct
B) The Gibbs energy change of a spotaneous electrochemical reaction at equilibrium is negative. wrong
C) The sign of the Gibbs energy change of an electrochemical reaction at equilibrium can be changed by changing the ionic strength. wrong
D) The Gibbs energy change of an electrochemical reaction at equlibrium can be changed by an applied electric potential. wrong
E) The sum of the stoichiometric coefficients multiplied by the charges of each reactant and product in an electrochemical reaction is always negative. wrong

11. Which of the following statements is **NOT CORRECT?**

[✓ A)] The attractive and repulsive interactions between ions depend only on their chemical identity not correct (also on distance!)
B) Deviations from ideal behavior begin at lower concentrations for electrolyte solutions than for nonelectrolyte solutions. correct
C) In electrolyte solutions the main interaction is the long-range electrostatic Coulomb interaction between ions. correct
D) The attractive and repulsive interactions between ions depend on their charge and size. correct (no "only")
E) Henry's law is obeyed up to concentrations of unit molality according to its hypothetical standard state. correct;

definition of Henry's law
standard state

12. In the relation $\mu_{Fe_2(SO_4)_3} = \mu_\pm + \nu RT \ln\left(\frac{m}{m}\right) + \nu RT \ln \gamma_\pm$ the value of V is:

- [✓ A) 5]
- B) 2
- C) 1
- D) 4
- E) 3

$\nu_+ = 2 \quad \nu_- = 3$

$\nu = \nu_+ + \nu_- = 2 + 3 = 5$

$[A^{2+}] = [B^{2-}] \quad K_{sp} = [A^{2+}][B^{2-}]\gamma_\pm^2 = [A^{2+}]^2 \gamma_\pm^2$

13. Enough of the salt $AB(s)$ is dissolved in a certain amount of water to bring it into equilibrium with the ions $A^{2+}(aq)$ and $B^{2-}(aq)$. If the equilibrium concentration of A^{2+} is $7.6\times10^{-5}\ mol\ kg^{-1}$, and the Debye Hückel Limiting Law (DHLL) is obeyed at this concentration, K_{sp} for the salt is

- [✓ A) 4.90×10^{-9}]
- B) 5.22×10^{-9}
- C) 5.78×10^{-9}
- D) 4.59×10^{-9}
- E) 8.46×10^{-8}

10^{-9}

$I = 7{,}6 \cdot 10^{-5} m \, (1 \cdot (2)^2 + 1 \cdot (-2)^2) \cdot \frac{1}{2}$

$= 4 \cdot 7{,}6 \cdot 10^{-5} m = 3{,}04 \cdot 10^{-4} m$

$\log_{10} \gamma_\pm = -0{,}51 \cdot |2 \cdot (-2)| \sqrt{I/m}$

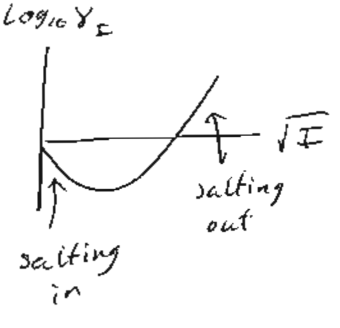
$= -0.51 \cdot 4 \cdot \sqrt{3{,}04 \cdot 10^{-4}} = -0.035569$

$\gamma_\pm = 0{,}92136$

$K_{sp} = (7{,}6 \cdot 10^{-5})^2 \cdot (0{,}92136)^2 = 4{,}903 \cdot 10^{-9} = 4{,}90 \cdot 10^{-9}$

14. With respect to the mean ionic activity coefficient variation, $\gamma_\pm$, with the square root of the ionic strength, $\sqrt{I}$, for an electrolyte which of the following statements is **CORRECT**?

- [✓ A)] At high ionic strength $\gamma_\pm > 1$, solubility decreases to keep the solubility product constant, resulting in the salting out effect. correct
- B) The $\gamma_\pm$ increases as $\sqrt{I}$ increases, at all electrolyte concentrations. wrong
- C) The $\gamma_\pm$ decreases as $\sqrt{I}$ increases, at all electrolyte concentrations. wrong
- D) The $\gamma_\pm$ decreases as $\sqrt{I}$ increases, and in turn solubility must decrease resulting in the salting out effect.
- E) At high ionic strength $\gamma_\pm > 1$, solubility increases to keep the solubility product constant, resulting in the salting in effect



Ⓐ high $I \Rightarrow \gamma_\pm$ increases $\Rightarrow$ solubility must decrease to keep K_{sp} = const.

Ⓓ wrong: salting in where $\gamma_\pm$ decreases with increasing $\sqrt{I}$

Ⓔ opposite of Ⓐ $\Rightarrow$ wrong

15 Which of the following statements is **NOT CORRECT**?

[✓ A)] At all electrolyte concentrations, the mean ionic activity coefficient $\gamma_\pm$ is less than 1. wrong

B) The mean ionic activity coefficient of an electrolyte $\gamma_\pm$ may be experimentally measured correct

C) At very low electrolyte concentrations, the experimentally measured mean ionic activity coefficient, $\gamma_\pm$, is close to the $\gamma_\pm$ value calculated using the Debye-Huckel limiting law (DHLL). correct

D) The activities γ_+ and γ_- for the positive and negative ions of an electrolyte cannot be measured experimentally. correct

E) At very high electrolyte concentrations, the mean ionic activity coefficient $\gamma_\pm$ may reach values greater than 1 correct

$$E^0 = E^0_{red} + E^0_{ox} = E^0_{Cr^{3+}/Cr} + E^0_{Co/Co^{2+}} = E^0_{Cr^{3+}/Cr} - E^0_{Co^{2+}/Co}$$

$$= (-0.744 + 0.280)\,V = -0.464\,V$$

right: red.
left: oxid

16. Consider the following cell at 25 °C.

Co(s)|Co^{2+}(aq, a = 0.832)||Cr^{3+}(aq, a = 0.342)|Cr(s)

Using the standard potentials, $E°_{Co^{2+}/Co}$ = -0.280 V and $E°_{Cr^{3+}/Cr}$ = -0.744 V, what happens spontaneously in the cell?

$2Cr^{3+} + 3Co \rightarrow$
$\rightarrow 2Cr + 3Co^{2+}$
$n = 6$

[✓ A)] Chromium dissolves.

B) Chromium is deposited.

C) Cobalt dissolves.

D) Electrons flow from Cobalt to Chromium

E) Cannot be determined.

$$E = E^0 - \frac{25.7\,mV}{6} \ln \frac{a^3_{Co^{2+}}}{a^2_{Cr^{3+}}}$$

$$= -0.464\,V - 4.2833\,mV \ln \frac{(0.832)^3}{(0.342)^2}$$

$$= -0.464\,V - 6.8231 \cdot 10^{-3}\,V = -0.47[illegible]\,V$$

→ reversed reaction → Cr dissolves, Co deposited

e^- flow left to right if $E > 0$, thus here Cr → Co e^- flow

17. Consider the following cell at 25 °C:

Ag(s)|AgNO$_3$(aq)|AgI(s)|Ag(s)

Given the standard potentials: $E°_{Ag^+/Ag}$ = 0.799V and $E°_{AgI/Ag}$ = 0.061V, calculate pK_{sp} of AgI.

[✓ A)] 12.5

B) −12.5

C) 14.5

D) -14.5

E) 3.352 x 10^{-13}

left oxidation: $Ag \rightarrow Ag^+ + e^-$

right reduction: $AgI + e^- \rightarrow Ag + I^-$

overall: $AgI \rightleftharpoons Ag^+ + I^-$

$$E = E^0 - 25.7\,mV \ln(a_{Ag^+} a_{I^-}) = E^0 - 25.7\,mV \ln K_{sp}$$

equilibrium: $Q = K_{sp}$, $E = 0$

$$\ln K_{sp} = \frac{E^0}{25.7\,mV} \qquad E^0 = E^0_{red} + E^0_{ox}$$

$$= E^0_{AgI/Ag} + E^0_{Ag/Ag^+} = E^0_{AgI/Ag} - E^0_{Ag^+/Ag} = E^0_{right} - E^0_{left} = (0.061 - 0.799)\,V$$

$$= -0.738\,V$$

$$\ln K_{sp} = \frac{-0.738\,V}{25.7 \cdot 10^{-3}\,V} = -28.71595, \quad K_{sp} = 3.3793 \cdot 10^{-13}$$

$Zn + F_2 \rightarrow Zn^{2+} + 2F^-$ $E^0 = E^0_{red} + E^0_{ox} = E^0_{F_2/F^-} + E^0_{Zn/Zn^{2+}}$

$= E^0_{F_2/F^-} - E^0_{Zn^{2+}/Zn} = (2.87 + 0.761)\,V = 3.631\,V > 0!$

$2Ag + F_2 \rightarrow 2Ag^+ + 2F^-$ $E^0 = E^0_{F_2/F^-} - E^0_{Ag^+/Ag} = (2.87 - 0.8)\,V$

$= 2.07\,V > 0!$

18. For fluorine, F_2, the standard potential is $E^0_{F_2/F^-} = 2.87$ V Given that $E^0_{Zn^{2+}/Zn} = -0.761$ V, $E^0_{Ag^+/Ag} = 0.800$, and $E^0_{Au^+/Au} = 1.68$ V and assuming a fluorine electrode is made from fluorine bubbling over an inert metal surface, what will happen in a cell made of this fluorine electrode and one of the above mentioned metals in the standard state?

$\boxed{A)}$ Fluorine oxidizes Zn, Ag, and Au.
B) Flourine oxidizes Zn and Ag, but not Au.
C) Fluorine oxidizes Zn, but not Ag and Au.
D) Fluorine oxidizes none of these metals
E) Fluorine reduces all those metals

$2Au + F_2 \rightarrow 2Au^+ + 2F^-$

$E^0 = E^0_{F_2/F^-} - E^0_{Au^+/Au}$

$= (2.87 - 1.68)\,V = 1.19\,V > 0!$

19. In an electrochemical cell the oxidation of oxalic acid (HOOCCOOH) to carbon dioxide and water by permanganate ions, MnO_4^-, in acidic solution has an equilibrium for which ln$K$ = 778. What can be concluded from that fact?

$K = e^{778} \gg 1$

A) Almost complete conversion from reactants into products happens correct
B) No reaction happens wrong
C) Almost only reactants can be found in the cell. wrong (it is products)
D) Permanganate cannot oxidize oxalic acid. wrong
E) Carbon dioxide and water are reduced to oxalic acid. wrong

20. Consider the cell

$Pt(s)|Cl_2(g)|ClO_2^-(aq)||Cr_2O_7^{2-}(aq)|Cr(s)$.

In acidic medium, how many electrons are exchanged in this cell reaction (balanced with the smallest possible set of integer coefficients)?

$\boxed{A)\ 12}$
B) 9
C) 6
D) 3
E) 15

left oxidation: $Cl_2 \rightarrow ClO_2^-$

$\overset{0}{Cl_2} + 4H_2O \rightarrow 2\overset{+3}{Cl}O_2^- + 8H^+ + 6e^-$ $|\cdot 2$

right reduction: $Cr_2O_7^{2-} \rightarrow Cr^{3+}$

$\overset{+6}{Cr_2}O_7^{2-} + 14H^+ + 12e^- \rightarrow 2\overset{0}{Cr} + 7H_2O$

$2Cl_2 + 8H_2O + Cr_2O_7^{2-} + 14H^+ \rightarrow 4ClO_2^- + 16H^+ + 2Cr + 7H_2O$

$2Cl_2 + H_2O + Cr_2O_7^{2-} \rightarrow 4ClO_2^- + 2H^+ + 2Cr$

$\Rightarrow$ 12 e^- cancel out $\Rightarrow n = 12$

Answer Key

1. A
2. A
3. A
4. A
5. A
6. A
7. A
8. A
9. A
10. A
11. A
12. A
13. A
14. A
15. A
16. A
17. A
18. A
19. A
20. A