

CHEMISTRY 1B – Fall, 2015
EXAM 3 – VERSION A - KEY

Use Scantron Form SC982-E and select the letter corresponding to the correct answer. Make sure to put **your full name, lab section number, and exam version** (under test no.) on the Scantron Form.

Equations and constants that you could need: $0^{\circ}\text{C} = 273\text{ K}$; $R = \text{Universal Gas Constant} = 8.314\text{ J mol}^{-1}\text{ K}^{-1}$ $F = \text{Faraday's constant} = 96,485\text{ C/mol e}^{-}$

The Nernst Equation and related constants are given below:

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0592}{n} \log Q \quad (\text{valid at } 298\text{K only}) \quad \Delta G^{\circ} = -nFE^{\circ}$$

$$1\text{ A (amp)} = 1\text{ C (Coulomb)}/\text{s} \quad 1\text{ V} = 1\text{ J/C} \quad \Delta G = \Delta G^{\circ} - RT \log Q \quad n = \text{moles e}^{-}$$

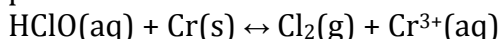
Part I. Multiple Choice Section. All questions have only one correct answer. Each question is worth 4 points. Unless otherwise specified, assume reactions occur at 25°C .

1. The oxidation state of C in $\text{C}_2\text{O}_4^{2-}$ is:

- a) +4 **b) +3** c) +2 d) 0 e) -2

$$2x + 4(-2) = -2 \text{ or } 2x = +6 \text{ or } x = +3$$

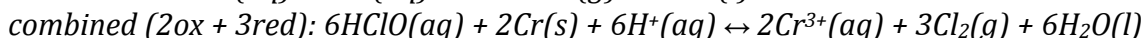
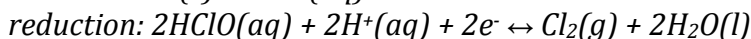
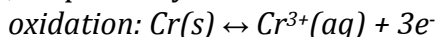
2. The following reaction is an UNBALANCED reaction showing reactants and products of a redox reaction:



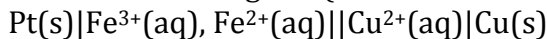
When balanced and with no fractional coefficients in the equation, the coefficients in front of HClO and Cr(s) are:

- a) 1 and 1 b) 2 and 1 c) 3 and 1 d) 3 and 2 **e) 6 and 2**

, respectively.



3. In the following cell (in which $E_{\text{cell}} > 0$), what material is used to make the cathode?



- a) Pt b) Fe c) Fe^{2+} d) $\text{NaCl}(\text{aq})$ **e) Cu**

4. In cell notation, the symbol “||” refers to:

- a) a phase boundary b) a double phase boundary **c) a salt bridge**
d) an anode e) a cathode

5. If an external power supply provides voltage to two electrodes in a beaker to drive a reaction, the cell formed in the beaker is called a(n):

- a) battery cell b) voltaic cell c) Faraday cell d) galvanic cell **e) electrolytic cell**

For the questions 6 to 11, consult the table below giving standard electrode reduction potentials:

Reaction	E° (V)
$\text{PbO}_2(\text{s}) + 4\text{H}^+(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O}(\text{l})$	+1.69
$\text{Cl}_2(\text{g}) + 2\text{e}^- \leftrightarrow 2\text{Cl}^-(\text{aq})$	+1.36
$\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \leftrightarrow 2\text{H}_2\text{O}(\text{l})$	+1.23
$\text{Br}_2(\text{l}) + 2\text{e}^- \leftrightarrow 2\text{Br}^-(\text{aq})$	+1.09
$\text{Ag}^+(\text{aq}) + \text{e}^- \leftrightarrow \text{Ag}(\text{s})$	+0.80
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Cu}(\text{s})$	+0.34
$2\text{H}^+(\text{aq}) + 2\text{e}^- \leftrightarrow \text{H}_2(\text{g})$	0.00
$\text{Cd}^{2+}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Cd}(\text{s})$	-0.40
$2\text{H}_2\text{O}(\text{l}) + 2\text{e}^- \leftrightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$	-0.83
$\text{Na}^+(\text{aq}) + \text{e}^- \leftrightarrow \text{Na}(\text{s})$	-2.71

6. Which compound is the best oxidizing agent?

- a) $\text{Ag}^+(\text{aq})$ **b) $\text{PbO}_2(\text{s})$** c) $\text{PbSO}_4(\text{s})$ d) $\text{Na}^+(\text{aq})$ e) $\text{Na}(\text{s})$
greatest reducer (highest E° value) is best

7. Which of the metals (in oxidation state of zero) in the list above are oxidized by H^+ ?

- a) Na and Cd** b) Na only c) Cd only d) Cu and Ag e) Cu only
 $E^\circ < 0$

8. A voltaic cell is made **under standard conditions** by $\text{Br}_2(\text{l})$, $\text{NaBr}(\text{aq})$, and a platinum electrode (an inert electrode) in one half cell and $\text{CdCl}_2(\text{aq})$ and $\text{Cd}(\text{s})$ in another half cell (with the two half cells connected by a salt bridge). The voltage measured from the platinum (+) to the cadmium electrode (-) will be:

- a) -0.69 V b) -0.27 V c) +0.27 V d) +0.69 V **e) +1.49 V**

$$E^\circ_{\text{cell}} = E^\circ_{\text{red. rxn}} - E^\circ_{\text{ox. rxn}} = 1.09 \text{ V} - (-0.40 \text{ V}) = +1.49 \text{ V}$$

9. A beaker contains 1.0 M HCl and 1.0 M NaBr, and is subject to electrolysis with inert electrodes (assume no gases present at start and any gases formed are at 1 atm). At the anode, the expected reaction (must be in direction shown) is:

- a) $2\text{H}_2\text{O}(\text{l}) + 2\text{e}^- \leftrightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$ b) $\text{H}_2(\text{g}) \leftrightarrow 2\text{H}^+(\text{aq}) + 2\text{e}^-$
c) $2\text{Br}^-(\text{aq}) \leftrightarrow \text{Br}_2(\text{l}) + 2\text{e}^-$ d) $2\text{H}_2\text{O}(\text{l}) \leftrightarrow \text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^-$
e) $2\text{Cl}^-(\text{aq}) \leftrightarrow \text{Cl}_2(\text{l}) + 2\text{e}^-$

The oxidation with the lowest E° is the most likely to occur, but we can rule out a) (reduction) and b) (no $\text{H}_2(\text{g})$ present). This leaves c) with the lowest remaining E°

10. Which of the above reactions is a common coupling reaction for corrosion (oxidation) of a variety of solid metals in contact with water?

- a) $\text{Cl}_2(\text{g}) + 2\text{e}^- \leftrightarrow 2\text{Cl}^-(\text{aq})$ **b) $\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \leftrightarrow 2\text{H}_2\text{O}(\text{l})$**
c) $2\text{H}^+(\text{aq}) + 2\text{e}^- \leftrightarrow \text{H}_2(\text{g})$ d) $2\text{H}_2\text{O}(\text{l}) + 2\text{e}^- \leftrightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$

A reduction reaction is needed to couple with oxidation. a) has the highest E value, but Cl is not commonly present. b) is next highest and O_2 is from air.

BONUS 11. A cell is made containing 0.10 M NaBr(aq), Ag(s), and AgBr(s) in a half-cell coupled with another half-cell with Cu²⁺(1.0 M)/Cu(s) with Cu(s) in the cathode, the measured voltage is 0.25 V. The equilibrium constant of AgBr(s) ↔ Ag⁺(aq) + Br⁻(aq) is:

- a) 2.9×10^{-16} **b) 1.0×10^{-13}** c) 1.7×10^{-8} d) 2.8×10^{-4} e) 3.5×10^4

$K_{sp} = [Ag^+][Br^-]$ and $[Br^-] = 0.10 M$ (given) We can use information given to determine $[Ag^+]$.

The cell has $Cu^{2+}(aq) + 2e^- \leftrightarrow Cu(s)$ and $Ag(s) \leftrightarrow Ag^+(aq) + e^-$ or combined as

$Cu^{2+}(aq) + 2Ag(s) \leftrightarrow Cu(s) + 2Ag^+(aq)$ and $E^\circ_{cell} = 0.34 V - 0.80 V = -0.46 V$ and

$E_{cell} = E^\circ_{cell} - (0.0592/2)\log\{[Ag^+]^2/[Cu^{2+}]\}$ or $0.25 V = -0.46 V - (0.0592/2)\log[Ag^+]^2$

or $(0.71 V)(2/-0.0592) = \log[Ag^+]^2$ or $[Ag^+]^2 = 10^{-24.0}$ or $[Ag^+] = 1.0 \times 10^{-12}$ and $K_{sp} = 1.0 \times 10^{-13}$

Alternative: we combine 1) $Ag^+(aq) + e^- \leftrightarrow Ag(s)$ and 2) $AgBr(s) \leftrightarrow Ag^+(aq) + Br^-(aq)$

to make 3) $AgBr(s) + e^- \leftrightarrow Ag(s) + Br^-(aq)$ So $E_3^\circ = E_1^\circ + E_2^\circ$ or $E_2^\circ = E_3^\circ - E_1^\circ$

$E_1^\circ = 0.80$ and $E_3 = E_3^\circ - 0.0592\log[Br^-]$ or $E_3^\circ = E_3 + 0.0592\log[Br^-]$ and $E_{cell} = E_{Cu^\circ} - E_3$ (since

Cu is under standard conditions) or $E_3 = E_{cell} - E_{Cu^\circ}$ or $E_3 = 0.34 - 0.25 = 0.09 V$

$E_3^\circ = 0.09 V + 0.0592\log(0.1) = 0.031 V$. $E_2^\circ = E_3^\circ - E_1^\circ = 0.031 - 0.80 = -0.769 V$

and at equilibrium $E = 0 = E_2^\circ - 0.0592\log K$ or $\log K = E_2^\circ/0.0592 = -12.99$ and $K = 1.0 \times 10^{-13}$

12. In a battery, 10.0 g. of Zn (Atomic weight = 65.39 g mol⁻¹) is oxidized to Zn²⁺. If Zn is the limiting reagent, how many Coulombs of charge is stored in the battery?

- a) 0.153 C b) 7.380 C c) 14,800 C **d) 29,500 C** e) 193,000 C

oxidation requires 2 mol e/mol Zn ($Zn(s) \leftrightarrow Zn^{2+}(aq) + 2e^-$)

$q = nF = (10.0 g. Zn)(1 mol Zn/65.39 g Zn)(2 mol e/1 mol Zn)(96486 C/mol e) = 29,500 C$

13. In a voltaic cell,

a) the oxidation occurs on the anode which is positive

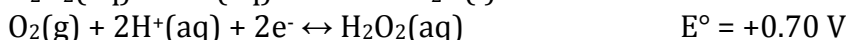
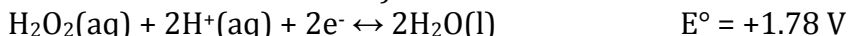
b) the oxidation occurs on the cathode which is positive

c) the oxidation occurs on the anode which is negative

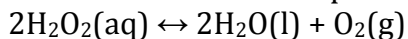
d) the oxidation occurs on the cathode which is negative

e) only reduction reactions occur in voltaic cells, oxidation occurs in electrolytic cells

14. Hydrogen peroxide, H₂O₂, can react with itself through oxidation and reduction half reactions (both shown as reductions below):



Based on the reduction potentials listed above, what is ΔG° for the reaction:



- a) -479 kJ/mol b) -343 kJ/mol **c) -208 kJ/mol** d) -104 kJ/mol e) +343 kJ/mol

Based on the E° values, we see that the 2nd reaction must be oxidation. Then net reaction is the one shown below and $E^\circ_{cell} = 1.78 - 0.70 = 1.08 V$

$\Delta G^\circ = -nFE^\circ = -(2 mole e/mol)(96485 C/mol e)(1.08 V)(1 V/1 J/C)(1 kJ/1000 J) = -208 kJ/mol$

15. The electron configuration of Pd²⁺ is:

- a) [Ar]3d⁸ **b) [Kr]4d⁸** c) [Kr]5s²4d⁶ d) [Kr]3f¹⁴4d⁸ e) [Kr]5d⁸

Pd is [Kr]5s²4d⁸ and s electrons are removed first on oxidation

16. The maximum oxidation state of Ti is:

- a) + 1 b) +2 c) + 3 **d) + 4** e) +5

elements to the left of Mn can lose all s and d electrons

Questions 17 and 18 involve $\text{Na}[\text{Cr}(\text{H}_2\text{O})_2(\text{ox})_2]$. Note that the Latin root for Cr is the same as in English and “ox” stands for $\text{C}_2\text{O}_4^{2-}$ or oxalate, a bidentate ligand.

17. The name for this complex is:

- a) Sodium diaquadioxalatochromate(III)** b) Sodium biquabioxochromium(III)
c) Diaquadioxalatochromium(III) sodiate d) Sodium diaquadioxalatocrobalate(III)
e) Sodium bis(dihydromonoxide)dioxalatochromate(III)

18. The expected geometry about the Cr atom:

- a) linear b) square planar c) tetrahedral d) hexahedral **e) octahedral**
bidentate ligands for two bonds per ligand or 4 bonds + 2 for water so 6 total

19. In coordination complexes, electrons in bonds between ligands and metals almost always come from:

- a) metal s shells b) metal d shells **c) ligand lone pair electrons**
d) ligand inner shell electrons e) ligand sigma bonds

20. What do bidentate ligands and ligands capable of linkage isomerization have in common? (Note: asymmetrical means lacking in symmetry)

- a) negative charge **b) two or more sets of lone pair electron**
c) at least four atoms d) asymmetrical structure

21. Which of the following structures will have geometric isomers

- a) $[\text{Pt}(\text{NH}_3)_3\text{Cl}]^+$ (square planar structure)
b) $[\text{ZnCl}_2\text{Br}_2]^{2-}$ (tetrahedral structure)
c) $[\text{Co}(\text{H}_2\text{O})_4\text{Br}_2]$
d) $[\text{Fe}(\text{CN})_5\text{Cl}]^{3-}$
e) $[\text{Fe}(\text{EDTA})]^-$ (EDTA is a hexadentate ligand)

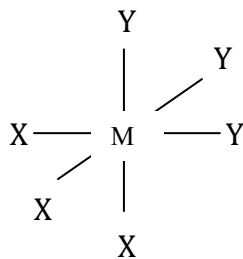
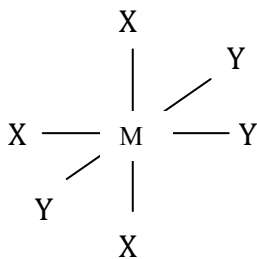
see examples in problem 23. All others have only one arrangement possible

22. Which type of isomers have nearly identical properties?

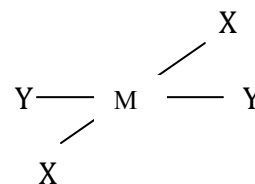
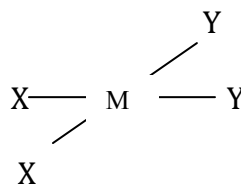
- a) coordination isomers b) linkage isomers
c) geometric isomers **d) optical isomers**
e) all isomers have the same properties

23. Which of the following sets of isomers illustrate cis- trans- isomers?

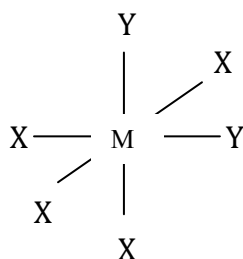
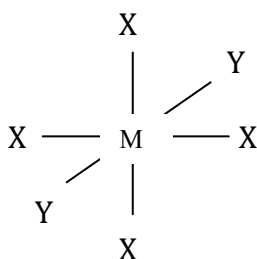
Set I



Set II



Set III



a) Sets II and III

b) Sets I and II

c) Set II only

d) Sets I and III

e) All sets

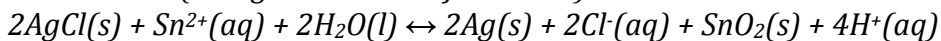
Set I are fac- mer- isomers

Work out Problem (12 pts) – **Answer on the back of the Scantron and show work**
An electrochemical cell (see notation below) is made to determine the concentration of tin (Sn^{2+}) in an industrial process stream:



The standard potentials for the reduction reactions are: for $\text{AgCl}(\text{s}) + \text{e}^- \leftrightarrow \text{Ag}(\text{s}) + \text{Cl}^- (\text{aq})$, $E^\circ = 0.222 \text{ V}$ and for $\text{SnO}_2(\text{s}) + 4\text{H}^+(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Sn}^{2+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$, $E^\circ = -0.094 \text{ V}$. Assume $T = 25^\circ\text{C}$. The cell voltage is measured and found to be 0.378 V . Determine $[\text{Sn}^{2+}]$ to 2 sig fig.

Net reaction (2X AgCl + reverse of SnO₂ rxn):



Nernst Equation: $E_{\text{cell}} = E^\circ_{\text{cell}} - (0.0592/2)\log\{[\text{Cl}^-]^2[\text{H}^+]^4/[\text{Sn}^{2+}]\}$ where $E^\circ_{\text{cell}} = 0.222 - (-0.094)$

$$E_{\text{cell}} = 0.378 \text{ V} = 0.316 \text{ V} - (0.0592/2)\log\{(0.1)^2(0.1)^4/[\text{Sn}^{2+}]\}$$

$$\log\{10^{-6}/[\text{Sn}^{2+}]\} = (0.378 - 0.316)/(2/-0.0592) \text{ or } 10^{-6}/[\text{Sn}^{2+}] = 10^{-2.095}$$

$$[\text{Sn}^{2+}] = 10^{-6}/10^{-2.095} = 1.2 \times 10^{-4} \text{ M}$$