

CH302H – Principles of Chemistry II: Honors
Spring 2014, Unique 51880

Exam 4
29 April 2014

Name: _____

You may use any material you wish provided it does not have a heartbeat nor does it connect to a wireless or cellular network.

Honor Code:

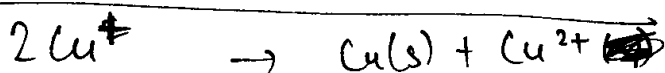
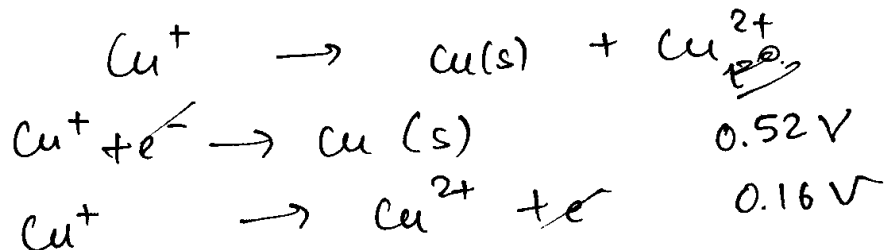
“The core values of the University of Texas at Austin are learning, discovery, freedom, leadership, individual opportunity, and responsibility. Each member of the University is expected to uphold these values through integrity, honesty, trust, fairness, and respect toward peers and community.”

I certify that the work on this exam is entirely my own.

Signature

Date

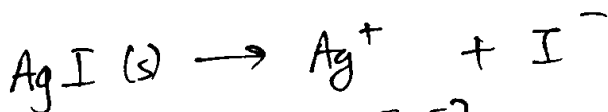
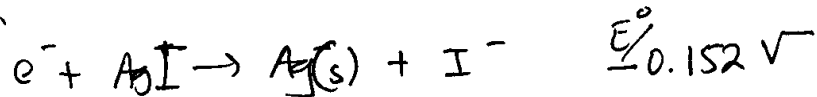
1. Someone said that Cu^+ is not that stable in solution unless complexed with particular ligands. Prove to me (as a scientist) that this instability is real and that Cu(s) and Cu^{2+} will dominate in the solution even if CuCl(s) were dissolved in water. (8 pts)



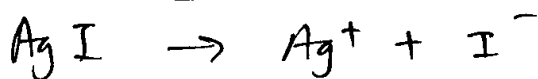
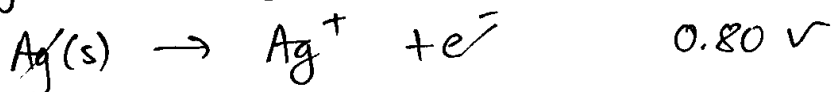
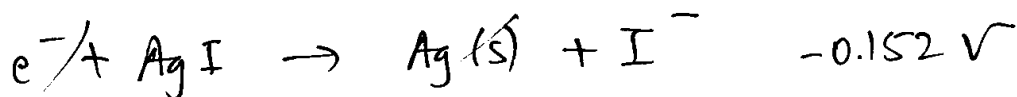
$$\begin{aligned} E^\circ_{\text{cell}} &= E_{\text{cathode}} - E_{\text{anode}} \\ &= 0.52 \text{ V} - 0.16 \text{ V} \\ &= 0.36 \text{ V} \end{aligned}$$

$E^\circ_{\text{cell}} > 0$, $\Delta G < 0$ and the reaction is spontaneous.
So, the Cu^+ will spontaneously dissociate into Cu(s) and Cu^{2+}

2. Using Standard Potential E° data, determine K_{sp} for AgI . (8 pts)



$$K_{\text{sp}} = [\text{Ag}^+][\text{I}^-]$$



$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.059}{n} \log Q$$

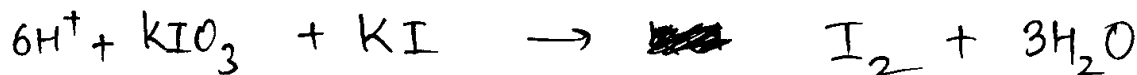
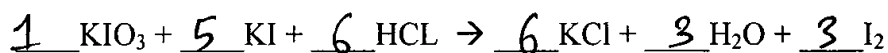
At equilibrium, $E_{\text{cell}} = 0$ and

$$E^\circ_{\text{cell}} = -\frac{0.059}{n} \log K_{\text{sp}}$$

$$-(-0.152 \text{ V} - 0.80) = -\frac{0.059}{1} \log K_{\text{sp}}$$

$$K_{\text{sp}} = \cancel{1.7 \times 10^{-17}} \quad 7.32 \times 10^{-17}$$

3. Balance the following chemical equations: (8 pts)



4. For the famous $A + B \rightarrow C$ reaction, an initial concentration of $[A] = [B] = 2.1 \times 10^{-2} \text{ M}$ yielded $[C] = 1.3 \times 10^{-3} \text{ M}$ after 1 hour. A second reaction was run holding $[B]$ at $2.1 \times 10^{-2} \text{ M}$ but increasing $[A]$ to $3.4 \times 10^{-2} \text{ M}$. This yielded $[C] = 2.1 \times 10^{-3} \text{ M}$ after 1 hour. (Note: The stoichiometry shown is not necessarily the reaction mechanism for this reaction.)

a) If the reaction is first order in $[B]$, what is the order dependence on $[A]$? (8 pts)

	$\frac{[A]}{[A]}$	$\frac{[B]}{[B]}$	$\frac{[C]}{[C]}$	Rate
①	0.021 M	0.021 M	0.0013 M	0.0013 M/hr
②	0.034 M	0.021 M	0.0021 M	0.0021 M/hr

$$\boxed{\text{Rate} = -\frac{\partial[A]}{\partial t} = -\frac{\partial[B]}{\partial t} = \frac{\partial[C]}{\partial t}}$$

$$\frac{\text{Rate 1}}{\text{Rate 2}} = \frac{0.0013}{0.0021} = \frac{k[0.021]^m [0.021]}{k[0.034]^m [0.021]}$$

$$m \log 0.619 = \log 0.618$$

$$m = 1$$

\therefore The reaction is 1st order on A .

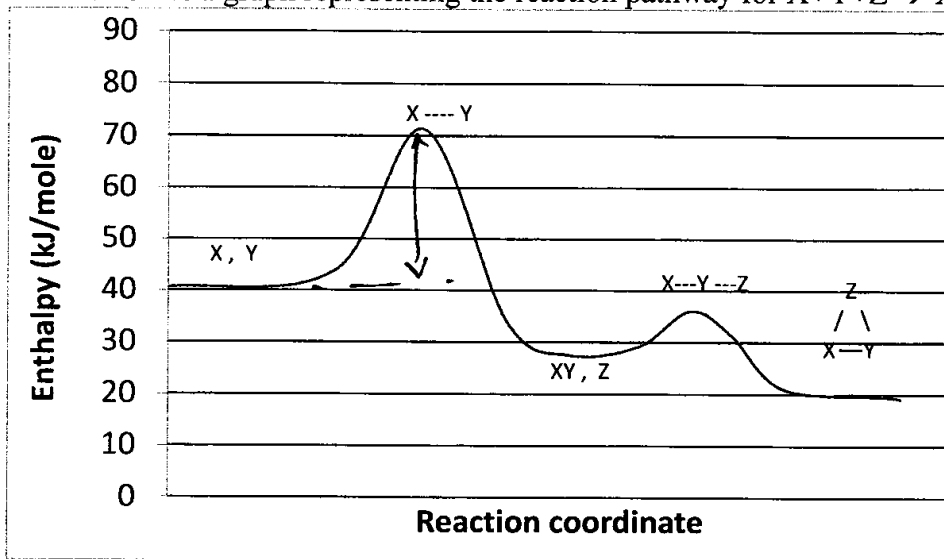
b) If the reaction is first order in $[B]$, what is the rate constant, k ? (8 pts)

$$\text{Rate} = k [A]^1 [B]^1$$

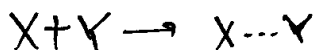
$$0.0013 \text{ M/hr} = k (0.021) (0.021) \text{ M}^2$$

$$k = 2.95 \text{ M}^{-1} \text{ hr}^{-1}$$

5. Shown below is a graph representing the reaction pathway for $X+Y+Z \rightarrow XYZ$



a) What is the rate limiting step, i.e., write the reaction? (6 pts)



b) What set of experiments might you perform to determine the activation energy, E_a ? (6 pts)

Measure rate constant as a function of temperature and use.

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \text{ to find } E_a.$$

c) Approximately what would find for the activation energy for this reaction? (6 pts)

$$\sim 30 \text{ kJ/mole}$$

d) Write the rate law for the formation of species XYZ. (6 pts)

$$\text{Rate} = k [X][Y]$$

6. ^{131}I is a radioactive isotope of iodine and iodine is preferentially concentrated in the thyroid gland. As a consequence, it can be the cause of cancer if exposed to nuclear event where ^{131}I is created. However, its greatest use is in the treatment of thyrotoxicosis (hyperthyroidism) and some types of thyroid cancer as well as serving as an enhancing agent for medical imaging. It has a half-life of 8.02 days. How long will it take to reduce the activity to 0.1% of its initial level if a patient were to receive an injection for imaging purposes?

(8 pts) Assuming first order decay,

$$t_{1/2} = \frac{\ln 2}{k}$$

$$k = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{8.02 \text{ days}} = 0.0864 \text{ days}^{-1}$$

$$[^{131}\text{I}] = [^{131}\text{I}_0] \exp(-kt)$$

$$0.1\% = 100\% \cdot \exp(-0.0864 \text{ days}^{-1} \times t)$$

$$-6.908 = -0.0864 \text{ days}^{-1} \times t$$

$$t \approx 80 \text{ days} //$$

7. From an EPA web site: "The half-life of CO₂ emissions is roughly 100 years (5 to 200 years: IPCC, 2001), but about a quarter of emissions today will still be in the atmosphere after hundreds of years and about one-tenth for hundreds of thousands of years (Archer and Ganopolski, 2005; Archer et al., 1998)".

[parenthetic references can be found in the article at

<http://cfpub.epa.gov/eroe/index.cfm?fuseaction=detail.viewPDF&ch=46&lShowInd=0&subtop=342&lv=list.listByChapter&r=239797>]

From these comments, argue for or against the fact that CO₂ loss is approximately first order in CO₂. (8 pts)

Assuming first order decay,

$$t_{1/2} = \frac{\ln 2}{k}$$

$$k = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{100 \text{ yrs}} = 0.0069 \text{ yrs}^{-1}$$

let's find out how long will it take for $\frac{1}{4}$ th ^{and $\frac{1}{10}$ th} of CO₂ emission to remain using k calculated above.

$$\frac{1}{4} = \exp(-0.0069 \text{ yrs}^{-1} \times t)$$

$$t \approx 200 \text{ yrs.}$$

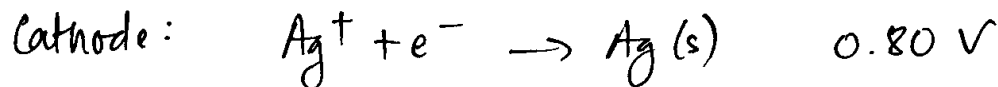
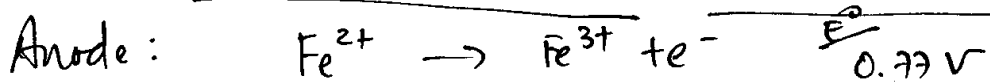
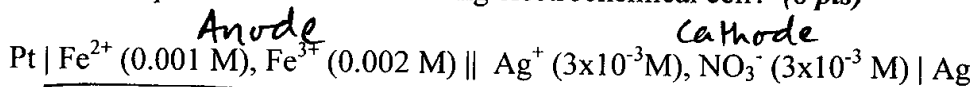
$$\frac{1}{10} = \exp(-0.0069 \text{ yrs}^{-1} \times t)$$

$$t \approx 300 \text{ yrs}$$

Not 100's of 1000's of years

SO **NO**

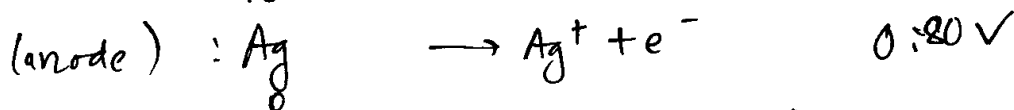
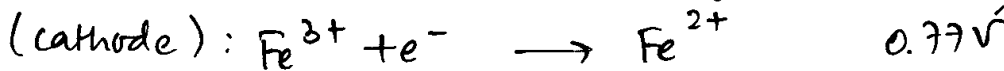
8. a) What is the cell potential for the following electrochemical cell? (8 pts)



$$\begin{aligned} E_{\text{cell}} &= E^\circ_{\text{cell}} - \frac{0.059}{n} \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}][\text{Ag}^+]} \\ &= (0.80 - 0.77) - \frac{0.059}{1} \log \frac{(0.002)}{(0.001)(0.003)} \\ &= -0.137 \text{ V} \end{aligned}$$

b) Is a solution of Fe^{3+} capable of oxidizing a significant amount of $\text{Ag}(\text{s})$? Justify your answer. (8 pts)

Fe^{3+} reduces and $\text{Ag}(\text{s})$ oxidizes. E°



$$E_{\text{cell}} = 0.77 \text{ V} - 0.80 \text{ V} = -0.03 \text{ V}$$

$E^\circ_{\text{cell}} < 0$, $\Delta G > 0$, not spontaneous. The answer is NO

c) In (b) above, I use the phrase "significant amount". Why didn't I simply ask, "Is X capable of oxidizing Y?" ... regardless of what chemical systems I select for X and Y? (4 pts)

When we mix any redox species, X and Y, there is always a redox reaction occurring. The extent of the reaction ~~is~~ depends on how strong the oxidizing and reducing agents are (E° values) and the concentration of the species available.

Standard Reduction Potentials at 25°C (298 K) for Many Common Half-reactions

Half-reaction	E° (V)	Half-reaction	E° (V)
$F_2 + 2e^- \rightarrow 2F^-$	2.87	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	0.40
$Ag^+ + e^- \rightarrow Ag$	1.99	$Cu^{2+} + 2e^- \rightarrow Cu$	0.34
$Co^{3+} + e^- \rightarrow Co^{2+}$	1.82	$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$	0.27
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.78	$AgCl + e^- \rightarrow Ag + Cl^-$	0.22
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	1.70	$SO_4^{2-} + 4H^+ + 2e^- \rightarrow H_2SO_3 + H_2O$	0.20
$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$	1.69	$Cu^{2+} + e^- \rightarrow Cu^+$	0.16
$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$	1.68	$2H^+ + 2e^- \rightarrow H_2$	0.00
$IO_4^- + 2H^+ + 2e^- \rightarrow IO_3^- + H_2O$	1.60	$Fe^{3+} + 3e^- \rightarrow Fe$	-0.03
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	1.51	$Pb^{2+} + 2e^- \rightarrow Pb$	-0.13
$Au^{3+} + 3e^- \rightarrow Au$	1.50	$Sn^{2+} + 2e^- \rightarrow Sn$	-0.14
$PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O$	1.46	$Ni^{2+} + 2e^- \rightarrow Ni$	-0.23
$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.36	$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$	-0.35
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	1.33	$Cd^{2+} + 2e^- \rightarrow Cd$	-0.40
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.23	$Fe^{2+} + 2e^- \rightarrow Fe$	-0.44
$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	1.21	$Cr^{3+} + e^- \rightarrow Cr^{2+}$	-0.50
$IO_3^- + 6H^+ + 5e^- \rightarrow \frac{1}{2}I_2 + 3H_2O$	1.20	$Cr^{3+} + 3e^- \rightarrow Cr$	-0.73
$Br_2 + 2e^- \rightarrow 2Br^-$	1.09	$Zn^{2+} + 2e^- \rightarrow Zn$	-0.76
$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$	1.00	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	-0.83
$AuCl_4^- + 3e^- \rightarrow Au + 4Cl^-$	0.99	$Mn^{2+} + 2e^- \rightarrow Mn$	-1.18
$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$	0.96	$Al^{3+} + 3e^- \rightarrow Al$	-1.66
$ClO_2 + e^- \rightarrow ClO_2^-$	0.954	$H_2 + 2e^- \rightarrow 2H^-$	-2.23
$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$	0.91	$Mg^{2+} + 2e^- \rightarrow Mg$	-2.37
$Ag^+ + e^- \rightarrow Ag$	0.80	$La^{3+} + 3e^- \rightarrow La$	-2.37
$Hg_2^{2+} + 2e^- \rightarrow 2Hg$	0.80	$Na^+ + e^- \rightarrow Na$	-2.71
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.77	$Ca^{2+} + 2e^- \rightarrow Ca$	-2.76
$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	0.68	$Ba^{2+} + 2e^- \rightarrow Ba$	-2.90
$MnO_4^- + e^- \rightarrow MnO_4^{2-}$	0.56	$K^+ + e^- \rightarrow K$	-2.92
$I_2 + 2e^- \rightarrow 2I^-$	0.54	$Li^+ + e^- \rightarrow Li$	-3.05
$Cu^+ + e^- \rightarrow Cu$	0.52		

SCE: $Hg_2Cl_2 + 2e \rightarrow 2Hg + 2Cl^-$ (sat'd KCl) $E^\circ = +0.241$ V