Chemistry 277 **Your Name:** _____

Prof. Jason Kahn

University of Maryland, College Park **Your SID #:** _____

General Chemistry and Energetics

Final Exam (100 points) **Your Section # or time:** _____

May 12, 2018

You have 50 minutes for this exam.

Explanations should be concise and clear. There is extra space on the last page if you need it.

You will not need a calculator for this exam. No other study aids or materials are permitted.

Generous partial credit will be given, *i.e.*, if you don't know, guess.

Useful Equations:

$\sigma_Y{}^2 = \lim_{N\to\infty} \frac{1}{N}\left[\sum_i (Y_i - \overline{Y})^2\right]$ $\quad$ $\mathrm{pH} = -\log([\mathrm{H}^+])$ $\quad$ $\sigma_Y{}^2 = \left(\frac{\partial Y}{\partial u}\right)^2 \sigma_u{}^2 + \left(\frac{\partial Y}{\partial v}\right)^2 \sigma_v{}^2 + \cdots$

$\mathrm{R} = 0.08206\ \mathrm{L\cdot atm/mole\ K}$ $\quad$ $T^2 = 4\pi^2 a^3/GM$ $\quad$ $\ln K_{eq} = -\Delta H°/(\mathrm{R}T) + \Delta S°/\mathrm{R}$

$\mathrm{R} = 8.314\ \mathrm{J/mole\ K} = 1.987\ \mathrm{cal/mole\ K} = \mathrm{N_A}k_B$ $\quad$ $SEM = \frac{\sigma}{\sqrt{n}}$

$°\mathrm{C} = °\mathrm{K} - 273.15$ $\quad$ $P(v)dv = Cv^2 exp(-mv^2/2kT)$ $\quad$ $\ln k = (-\mathrm{E_a}/\mathrm{RT}) + \ln \mathrm{A}$

$\mathrm{pH} = \mathrm{p}K_a + \log([\mathrm{A}^-]/[\mathrm{HA}])$ $\quad$ $K_p = K_c(\mathrm{R}T)^{\Delta \mathrm{n}}$ $\quad$ $K_w = [\mathrm{H}^+][\mathrm{OH}^-] = 10^{-14}$

$Absorbance = \varepsilon c \ell$ $\quad$ $PV = n\mathrm{R}T$ $\quad$ $\left[\frac{-\hbar^2}{2\mu}\nabla^2 + V(\mathbf{r})\right]\Psi(\mathbf{r}) = E\Psi(\mathbf{r})$

$\mathrm{p}K_a = -\log(K_a)$ $\quad$ $\mathrm{pH(e.p.)} = \frac{1}{2}(\mathrm{p}K_{a1} + \mathrm{p}K_{a2})$

Honor Pledge: At the end of the examination time, please write out the following sentence and sign it, or talk to me about it:

"I pledge on my honor that I have not given or received any unauthorized assistance on this examination."

1. Back titration (25 pts)

In Lab 7B, we used iodate + excess iodide to generate triiodide

$$IO_3^- + 8\ I^- + 6\ H^+ \rightarrow 3\ I_3^- + 3\ H_2O,$$

tused the triiodide to titrate ascorbic acid

$$\text{ascorbic acid} + I_3^- \rightarrow \text{dehydroascorbic acid} + 3I^- + 2H^+,$$

(a; 6 pts) Fill in the blanks:
…and then back-titrated with _____ to find out how much triiodide was still there:

$$I_3^- + 2\ \_\_\_\_\_ \rightarrow 3\ I^- + S_4O_6^{2-}.$$

(b; 2 pts) Circle one: Iodide I^- is (oxidized / reduced) to make triiodide I_3^-.

(c; 5 pts) Circle one and fill in the blank: We detected the end of the back titration using the complex that (iodide / triiodide) makes with _____.

(d; 3 pts) What would have happened if we had made a mistake and used twice the specified amount of iodide in the first place? Choose the best answer:

(i) There would have been no change in the experiment.

(ii) The forward titration would have been slower.

(iii) The back titration would have been slower.

(iv) The measured amount of ascorbic acid would have been wrong.

(e; 5 pts) Briefly explain your answer to (d).

(f; 4 pts) Draw the Lewis dot structure of triiodide.

Score for the page_____

2. Acid-base (10 pts)

In lab 7A, you measured the pH while titrating soda ash (mostly Na_2CO_3) with HCl to determine (a) the concentration of carbonate in soda ash, and along the way (b) the pKa of bicarbonate and (c) the pKa of carbonic acid.

(a; 4 pts) If you made an error in the HCl concentration, which measurement(s) would be affected?:

Circle correct answer(s): (a) (b) (c)

(b 6 pts) If you ran the experiment much too slowly, which measurement would be the most affected?:

Circle correct answer: (a) (b) (c). Briefly explain your answer.

3. Presentations (12 pts)

List four elements (other than a title slide) that are almost always included in a scientific presentation:

Score for the page_____

4. Nanoparticles (20 pts)

(a; 8 pts) In Lab 5, why did we add $NaBH_4$ dropwise in making seed particles for nanoparticles? Why not just add it all at once?

(b; 12 pts) Explain in one or so sentences each what you planned for Lab 8, what you learned, and what you would do differently if you could do it over.

Score for the page_____

5. Complexometric titrations (15 pts)

In doing the Cold-Eeze complexometric titration, we added indicator Xylenol Orange to a sample containing the analyte Zn^{+2} and then titrated in EDTA and measured the disappearance of color. We didn't measure them, but binding constants (Kbs) are important here, where for example Kb(indicator+analyte) is defined as the equilibrium constant for the reaction below:

$$\text{Indicator} + \text{Analyte} \rightleftharpoons \text{Indicator}\bullet\text{Analyte}$$

The accuracy and precision of the experiment depend on using an indicator that meets several criteria:

(1) The indicator should show a large change in extinction coefficient upon binding the analyte.

The indicator should show the following relationships of binding constants or Kb values:

(2) Kb(endogenous ligands+analyte) << Kb(indicator+analyte), and

(3) Kb(indicator+analyte) << Kb(EDTA+analyte).

[Criteria (2) and (3) are a quantitative way of saying that ideally the indicator should bind to Zn^{+2} much more tightly than any of the complexing agents in the sample but much less tightly than EDTA.]

(a; 5 pts) Why does an indicator that fails criterion (1) give a less precise value for analyte concentration?

(b; 5 pts) Why does an indicator that fails criterion (2) give a less accurate value for analyte concentration?

(c; 5 pts) Why does an indicator that fails criterion (3) give a less precise value for analyte concentration?

Score for the page_____

6. Miscellaneous (18 pts)

(a; 8 pts) In the notes for the wrap-up lab lecture, I typed "measure the activation energy by measuring rate constants as a function of time." Oops. Sketch the plot we use to determine activation energy.

(b; 10 pts) If you are observing a time course for an enzymatic reaction, and you know the correct rate law for the reaction, but you calculate a rate constant that changes with time, what is likely to be the source of error? How could you test this theory?

Page	Score
2	/25
3	/22
4	/20
5	/15
6	/18
Total	**/100**

Score for the page_____