Chemistry 277, Spring 2019 **Your Name:** – Key –

Prof. Jason Kahn

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

General Chemistry and Energetics

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

May 16, 2019

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:

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

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

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

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

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

$Absorbance = \varepsilon c \ell$ $\quad$ $PV = nRT$ $\quad$ $N(E) = N_0\ \omega\ \exp(-E/k_BT)$

$pK_a = -\log(K_a)$ $\quad$ $\mathrm{pH(e.p.)} = \frac{1}{2}(pK_{a1} + pK_{a2})$ $\quad$ $S = k_B \ln W$

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. Redox titration (25 pts)

In Lab 7B, we used iodate IO_3^- + excess iodide to generate triiodide according to:

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

then used the triiodide in excess to oxidize ascorbic acid, as in:

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

(a; 6 pts) Fill in the blanks:

…and then back-titrated with (word): (Na) thiosulfate (+3) to find out how much triiodide was still left according to this reaction: $I_3^- + 2$ ($S_2O_3^{2-}$, +3) $\rightarrow 3\ I^- + S_4O_6^{2-}$.

(b; 4 pts) If you Google for ascorbic acid titration, you can find a few undergraduate labs that do an acid-base titration to determine the purity of commercial vitamin C tablets. Why is this inferior to the redox titration that we and most others use?

(+2 for idea of diff ingredients) Vitamin C tablets have excipients that are probably there for buffering to make it less acidic for the mouth and stomach. Any such agents would interfere with an acid/base titration. Using the redox properties of AA is more specific. oops (+2 for idea of specificity of redox)

(c; 3 pts) Why is iodate used as the primary concentration standard in this lab, as opposed to triiodide or thiosulfate?

Iodate is a stable, presumably pure solid – the triiodide and thiosulfate are not stable upon storage. (+3 for either/both)

(d; 3 pts) What result would you have obtained if the supplier had a QC problem and supplied KIO_3 at 90% purity, with the remainder being entirely soluble and inert? Circle the best answer:

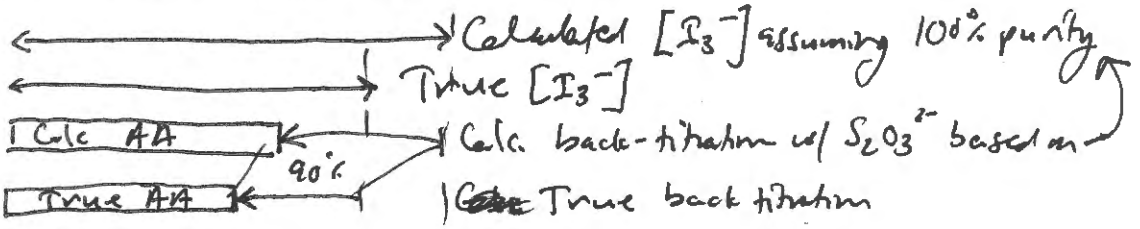
(*i*) There would have been no change in the experiment.

(*ii*) The calculated ascorbic acid concentration would be 10 % too low.

(+3) (*iii*) The calculated ascorbic acid concentration would be 10 % too high.

(*iv*) The experiment would have failed completely.

(e; 3 pts) Briefly explain your answer to (d).



The true graph is just 90% of calculated in every (horizontal) line.

Calc. [AA] ∝ [IO_3^-]

(+3 for idea consistent w/ (d))

Score for the page 19

(f; 6 pts) Briefly discuss how/why a truly terrible KIO_3 purity of ~15 % would have made (*iv*) the correct answer to part (d), and state what you could have done to recover.

(+3) yes – If the I_3^- is not in excess there is nothing to back-titrate!

(+3) for either one – Use a much smaller portion of the Vitamin C tablet and then multiply to get the [AA]

– will need some other primary standard to measure $[IO_3^-]$.

2. Acid-base and methods development (16 pts)

Ammonia gas (NH_3) dissolves in water and is in equilibrium with ammonium hydroxide, but the pKb of NH_3 is about 4.75 so the concentration of ammonium cation is low:

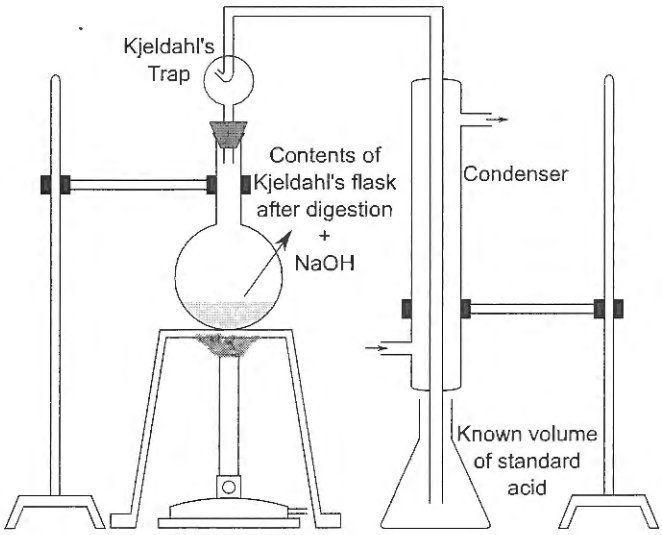
$$NH_3\,(g) + H_2O\,(l) \rightleftharpoons NH_3\,(aq) + H_2O\,(l) \rightleftharpoons NH_4^+\,(aq) + HO^-\,(aq)$$

In the Kjeldahl assay for determining protein concentration, a sample is reacted completely with strong acid to convert all organic nitrogen to NH_4^+ (*aq*). The solution is then made basic, and whatever is volatile (i.e. not ions) is distilled into a receiving flask containing an acid, often the weak acid boric acid $B(OH)_3$.

$$B(OH)_3\,(aq) + H_2O \rightleftharpoons B(OH)_4^-\,(aq) + H^+\,(aq)$$

Then the ammonia and/or ammonium content in the receiving flask is measured.

(Not fun at all fact: The Kjeldahl assay can be fooled by the nitrogen-rich but non-nutritious and poisonous compound melamine, which was used in 2007-2008 by unscrupulous pet food and baby formula manufacturers to simulate protein in their products, killing dogs and babies.)



Picture credit: By Roshan220195 - Own work, CC BY-SA 3.0, https://commons.wikimedia.org/w/index.php?curid=18937792

(a; 4 pts) Why is it necessary to raise the pH before doing the distillation?

The NH_3/NH_4^+ must be in the volatile NH_3 form or it will not distill over → go to high pH to deprotonate all NH_4^+.

(+2) for idea of volatility

(+2) for idea of NH_3 @ high pH, implicit OK

Score for the page 10/10

(b; 6 pts) Why is it necessary to collect the distillate in an acidic receiving solution? What are the products of bubbling ammonia into boric acid?

(+4) – If the NH_3 went into a neutral or basic solution, it could evaporate away – here we trap it as NH_4^+ (+2)

$$H_2O + NH_3 + B(OH)_3 \longrightarrow \underset{(+2)}{NH_4^+} + \underset{(+2)}{B(OH)_4^-}$$

(c; 6 pts) Experimentally, how could you determine the amount of ammonia that ended up in the collection flask?

– There is some mixture of NH_4^+ and $B(OH)_4^-$ and $B(OH)_3$ in the flask.

(+4 for either) – Titrate w/ HCl or other acid (like $B(OH)_2^-$...) to convert all $B(OH)_4^-$ back to $B(OH)_3$ → that is the amount of NH_4^+

– or titrate w/ NaOH to measure amt of $NH_4^+ + B(OH)_3$

(+2 for recognizing this done) – Either way you need to know the initial $[B(OH)_3]$ or be prepared to disentangle 2 equivalence points

3. SDL (12 pts)

Describe an unexpected finding from your SDL, why it was a surprise or disappointment, and how you would either make the issue go away by improving your methods or else investigate it further.

(+4) for the finding "NP's were grey instead of colored"

(+4) for why the surprise "wanted beautiful color as in the literature"

(+4) for next step. "Do TEM to see if the particles are polydisperse"

"Reflux the way the prep said"

"Try a different capping agent"

Score for the page 24/24

4. Nanoparticles and Chelators (22 pts)

(a; 6 pts) Write the name of the physical phenomenon that causes nanoparticles of different sizes to be different colors: Surface plasmon resonance (+3). What technique provided the calibration curve we used to estimate size from λ_{max}? transmission electron microscopy (+3) (TEM +2)

(b; 3 pts) What color do you get if all wavelengths are absorbed equally? gray (or black ok) (+3)

In Lab 6, we used EDTA to rip Zn^{+2} away from a xylenol orange indicator.

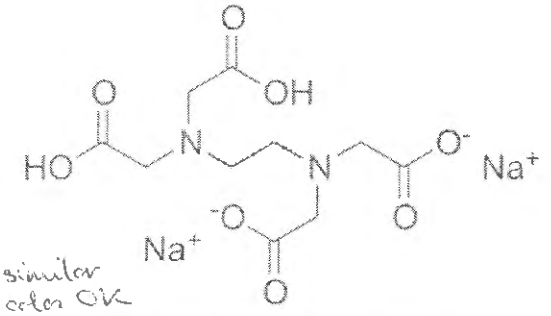


Figure 1: The Chemical Structure of Disodium EDTA

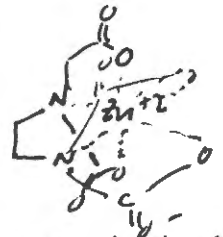
https://pediaa.com/difference-between-disodium-edta-and-tetrasodium-edta/

(c; 4 pts) Explain why we used EDTA in this lab instead of just titrating directly with xylenol orange until no further color change was observed.

(+2 for any reason for) It is hard to tell the difference between more of a yellow color and a change to an orange color (any similar color ok) – the end point would not be obvious. (+2)

(d; 3 pts) Explain why EDTA has such a strong binding affinity for Zn^{+2} (and many other metal ions).

Chelation (+3) – it can make multiple non-covalent interactions with the ligand. or +3 for some words



or +3 for just a picture that gets the idea across

(e; 6 pts) Explain why EDTA is used in the treatment of lead and mercury poisoning, but why large doses should be avoided unless one has actually been poisoned.

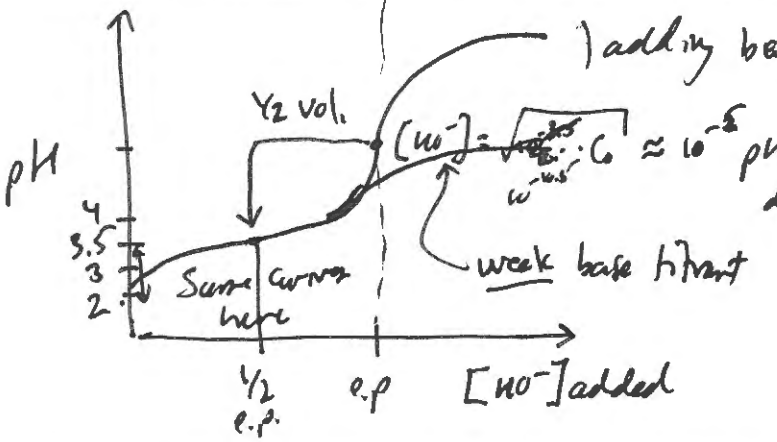
(+3) – EDTA can chelate Pb^{+2} or Hg^{+2} so it can be removed from the body.

(+3) – But it can also remove useful metal ions like Ca^{+2} and Mg^{+2}, so taking too much can be dangerous.

Score for the page 22/22

5. Using the computer as if it were a piece of apparatus (25 pts)

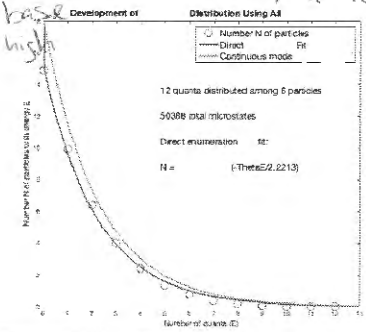
(a; 12 pts) Sketch a ~~curve~~ graph showing pH vs. volume of base added with two titration curves, one curve for an acid with a pKa of 3.5 with strong base, and the other curve for the same acid at the same concentration with the same concentration of a weak base. Indicate how you would measure the pKa of the acid.



+3 for idea of titration
+2 for pH = pKa at ½ e.p.
+3 for 2nd curve correct
+3 for indicating to log Y₂ the volume at the e.p.
↳ +2 for say ½ eq. pt

+1 - 2 wrong but different curves
+2 - weak base goes too high

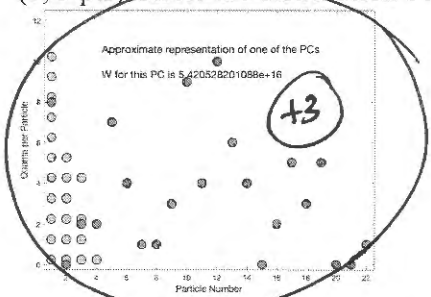
(b; 4 pts) What is the functional form of the curve that is fit to the observed number of particles that have a given number of quanta in the plot shown at the right, and whose distribution is shown?

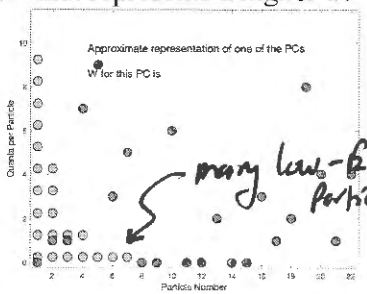


(decaying) exponential (+2) +1 for compare ideal to experimental

Boltzmann (+2)

(c; 3 pts) ~~Circle the distribution~~ below that represents a higher T:





Page	Score
2	/19
3	/10
4	/24
5	/22
6	/25
Total	**/100**

(d; 6 pts) How would you exercise the micro_movr3 program to see whether its toy model for entropy is an extensive state function (which is the idea that two moles of a pure substance at a given temperature has twice the entropy of one mole)?

- Run the program w/ e.g. $q = 30$ and $p = 20$, record the entropy (+3 for idea)
- Run the " w/ eg. $q = 60$ and $p = 40$ — same q/p ratio i.e. just 2× the same system → does the entropy double or not?

2/6 for a "you tried"

(+3) for looking at results for S

5/6 if ↑ p and q but not mention double

Score for the page 25


137
143
F
cresc.
148
f
153
dim.
158
sempre dim.
G
163
p
sempre
pp
II
169
pizz.
p