Chemistry 277
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University of Maryland, College Park
General Chemistry and Energetics
Final Exam (100 points)

Your Name: Key

Your SID #:

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:

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

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

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

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

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

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

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

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."

Tara

1. Back titration (25 pts)

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

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

I used 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 thiosulfate (+2) to find out how much triiodide was still there:

$$I_3^- + 2\ \underbrace{S_2O_3^{-2}}_{(+2)} \rightarrow 3\ I^- + S_4O_6^{2-}.$$

(+2) (+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) (+2)) makes with starch (+3).

(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:

(+3) (i) There would have been no change in the experiment.

(ii) The forward titration would have been slower.

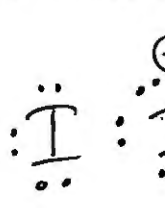
(iii) The back titration would have been slower.

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

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

(+3) The iodide is in excess – we don't detect it, we only detect triiodide, whose [ ] is independent of how much (+2) excess iodide is present. Using more iodate would change everything.

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



(+3) for anything reasonable and linear

(linear by VSEPR)

Score for the page 25

Renee

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)

(+2) (+1) (+1)) for leaving b+c blank

(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.

+2

If you run the experiment very slowly, then during the titration of HCO_3^- w/ HCl you will get (+2) CO_2 bubbling out as H_2CO_3 is produced, and the pH will drift up - the measured pKa will be too high. (+2)

3. Presentations (12 pts)

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

- introduction to the general area and its importance
- methods / experimental design
- results / interpretation
- discussion of relevance
- acknowledgments
- future directions

(+3) each for any four

Score for the page 22

JDK

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?

- Adding $NaBH_4$ dropwise means that each ~~small local~~ $H^{\ominus}$ ion "sees" a constant excess $[Ag^+]$ that can be reduced to Ag°, so there is a small + consistent pulse of Ag° to nucleate into a seed nanoparticle that is hopefully small + consistent in size. Otherwise we would see just metallic silver plating out or aggregating. (+3) (+2) (+3)

(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.

+4 for ~~each~~ each. –

what did you do?

what happened?

what you would do differently?

Score for the page 20/20

Devyn

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?

If $\Delta\varepsilon$ is small the color change will be hard (+2) to see and therefore there will be more uncertainty in the volume where it actually occurs. (+3)

+3 for either

or → we will need to use a lot of indicator and this alters the $[Zn^{+2}]$.

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

If too much of the Zn^{+2} remains bound to endogenous ligands then we may never see the indicator light up. The experiment could fail completely, or the EDTA can grab Zn^{+2} from either and blur out the endpoint. (+3)

+3 for either (+3)

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

If K_b(indicator) $\simeq$ K_b(EDTA) then as the titration ends the EDTA complex, free EDTA, indicator complex, and free indicator may all coexist and it will be hard to tell when the endpoint actually is reached. (+3)

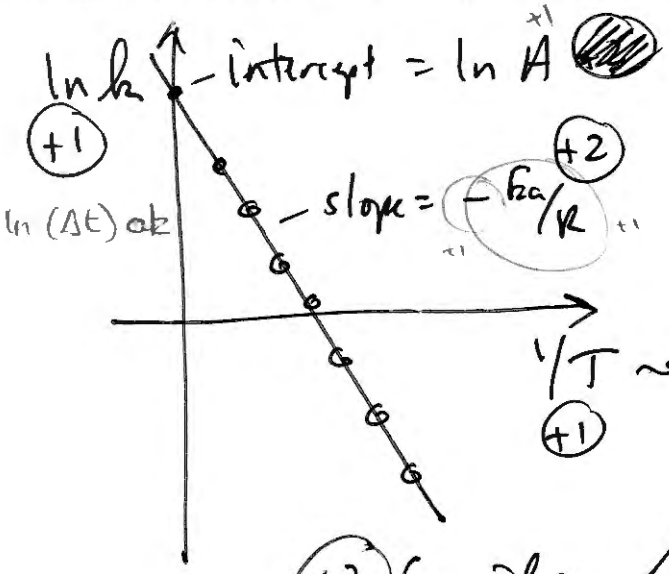
(+2)

Score for the page 15

A2

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.



Arrhenius: $k = Ae^{-E_a/RT}$

$\ln k = \ln A - \left(\frac{E_a}{R}\right)\cdot\frac{1}{T}$ (+1)

(+2) for idea of an Arrhenius plot – in fact for anything with a line of a ⊖ slope.

(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?

(+3) – the enzyme is probably dying during the reaction, so the reaction slows down more than expected simply from the reaction progress (+3)

– Test by allowing the reaction to progress ~~and then~~ until it is very slow, then (+3) add more enzyme and see if there is another pulse of reaction. Repeat. (+3)

+3 each for max of 10.

[OR: temperature could change during the rxn and cause rxn to slow down

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

Score for the page 18/18