Chemistry 271, Section 22xx
Prof. Jason Kahn
University of Maryland, College Park

General Chemistry and Energetics
Exam I (100 points total)

Your Name: ______________________________

Your SID #: ______________________________

Your Section # or day+time: ______________________________

October 15, 2012

You have 50 minutes for this exam.

Exams written in pencil or erasable ink will not be re-graded under any circumstances.

Explanations should be concise and clear. I have given you more space than you should need. There is extra space on the last page if you need it.

You will need a calculator for this exam. No other study aids or materials are permitted.

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

Useful Equations:

$K_a = [H^+][A^-]/[HA]$

$F = ma$

$K_w = [H^+][HO^-] = 10^{-14}$

$R = 0.08206$ L·atm/mole K

$K_p = K_c(RT)^{\Delta n}$

$\text{pH} = -\log([H^+])$

$e^{i\pi} + 1 = 0$

$\text{pH} = \text{pK}_a + \log([A^-]/[HA])$

$0\ °C = 273.15\ K$

$P^2/a^3 = 4\pi^2/MG$

$K_b = [BH^+][HO^-]/[B]$

$PV = nRT$

$\text{pH (e.p.)} = (\text{p}K_{a1} + \text{p}K_{a2})/2$

$\text{p}K_a = -\log(K_a)$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

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 point extra credit for filling in this box

1. (25 pts) Short Answer

(a; 2 pts) pOH of 0.1 M HCl_____________

(b; 2 pts) pH of 0.001 M NaOH___________

(c; 4 pts) The water self-dissociation equilibrium is ______________________________, its equilibrium constant is symbolized by____________________, and the numerical value of the equilibrium constant at 25 °C at low ionic strength is__________________. The K_{eq} doesn't really have units, but if we wrote the units for clarity, they would be ________________.

(d; 2 pts) $[H^+]$ at pH 4.2________________________(in scientific notation).

(e; 2 pts) $[OH^-]$ at pH 9.7_______________________(in scientific notation).

(f; 4 pts) Write down *Q* in terms of partial pressures and in terms of concentrations for the reaction

$N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2\,NH_3\,(g)$:

(g; 3 pts) The numerical values of K_c and K_p in Part f are (circle one) the same different because…

(i; 2 pts) At equilibrium the rates of the forward and reverse reactions are

(circle one): zero equal unrelated maximal

(j; 4 pts) The hemoglobin cube that we drew in class represents the multiple equilibria that describe R/T interconversion and also the binding of __________________ and _____________________.

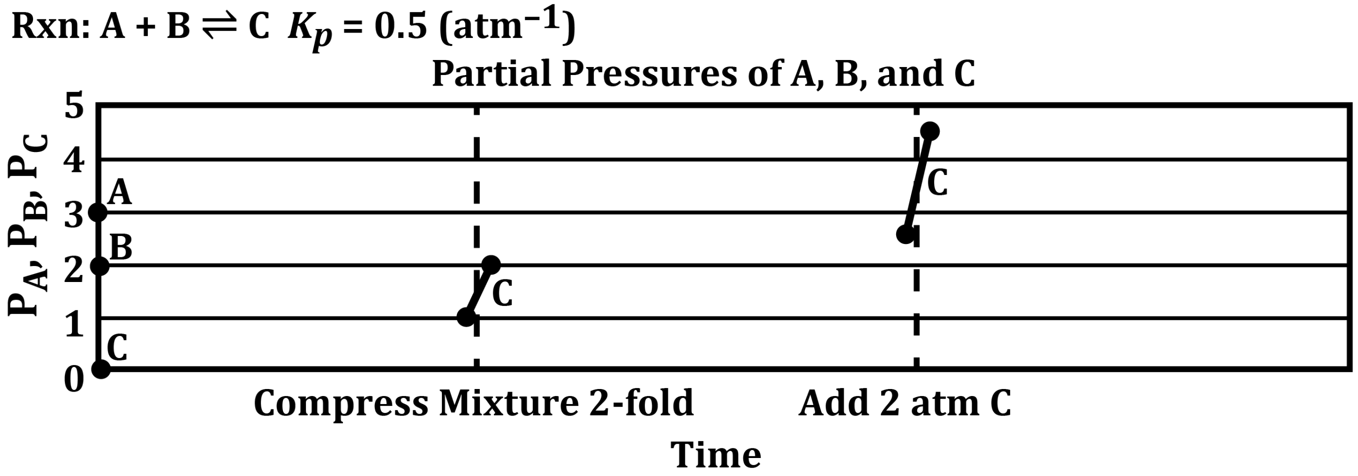
Score for the page____________

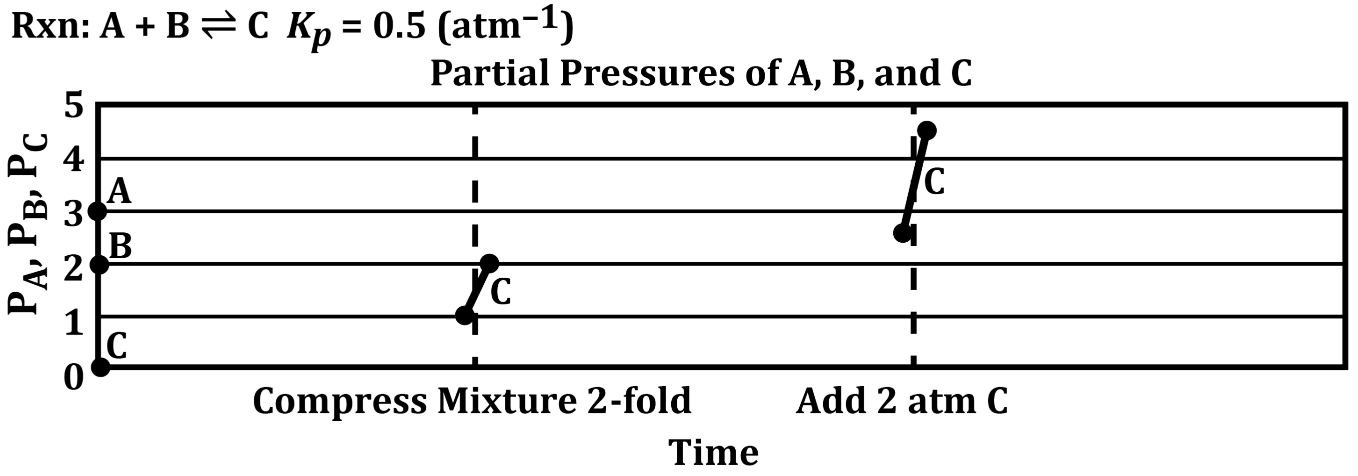
2. (15 pts) LeChatelier and Dynamic Equilibrium

Consider the reaction A(*g*) + B(*g*) ⇌ C(*g*), with $K_p = 0.5$ (atm^{-1}). We start the reaction with $P_A = 3$ atm, $P_B = 2$ atm, and $P_C = 0$. After it has come to equilibrium (first dashed line below), we compress the container to half its original volume and allow the mixture to equilibrate again (until the second dashed line). Then we inject an additional 2 atm of C and allow the mixture to equilibrate a third time.

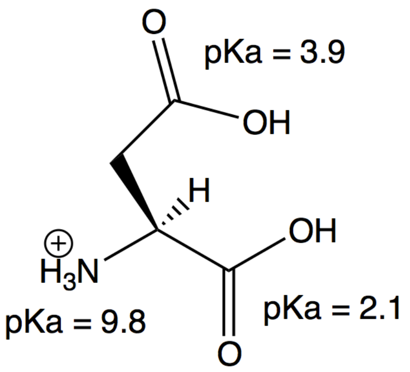
Sketch the time course for the concentrations P_A, P_B, and P_C on the graph below. You should be able to give precise partial pressures at the first dashed line (since I give you $P_C = 1$ atm at that point), but after that point don't worry about exact concentrations, just relative numbers.

I give you two copies in case you mess one up. Circle the one you want graded.





3. (35 pts) Acid-Base Equilibria and Titrations



Consider a titration of aspartic acid. The structure of the fully protonated form is given at the right. We are starting with a C_0 = 100 mM solution of this form.

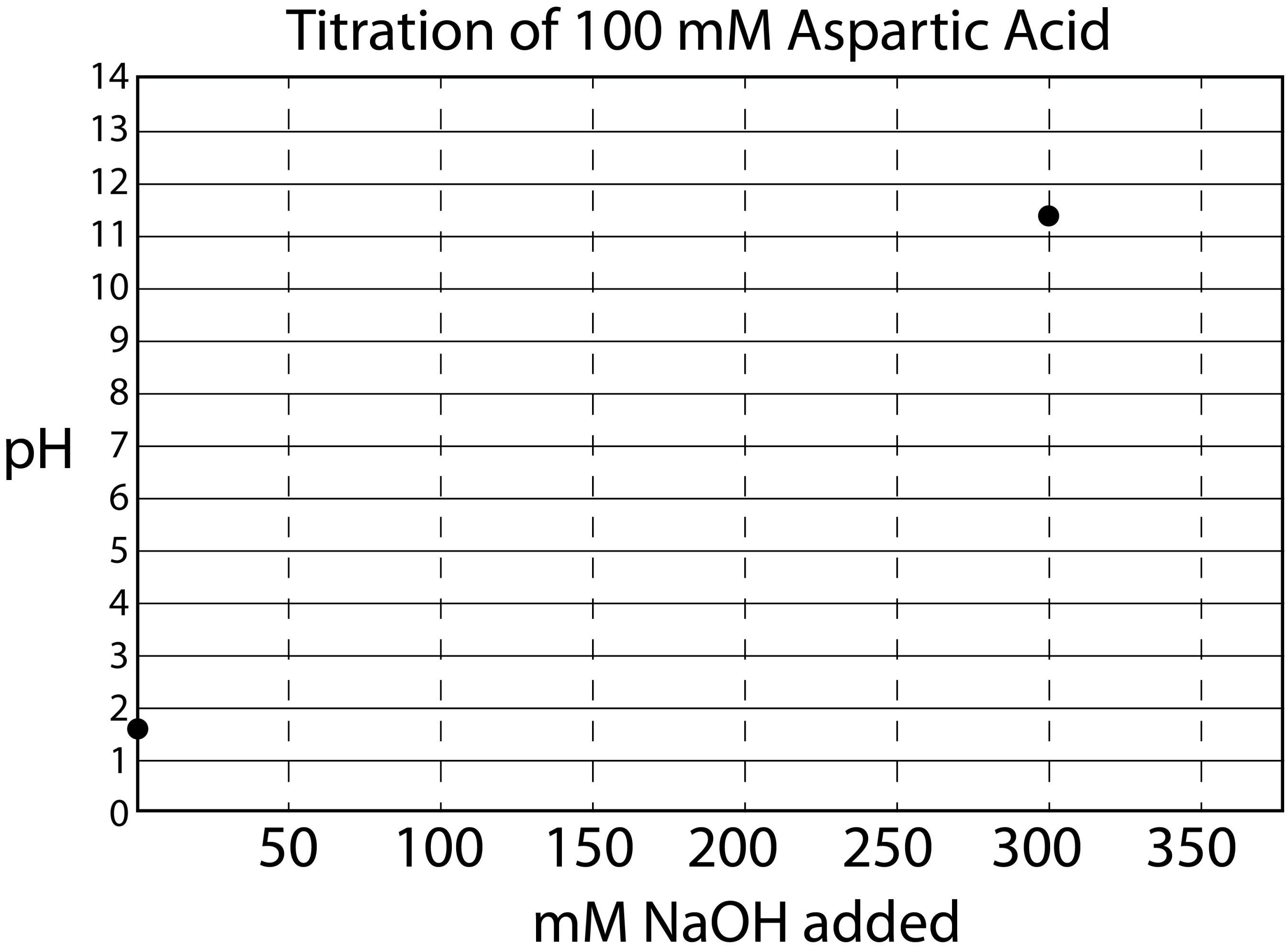
(a; 8 pts) Calculate the initial pH considering only the first pK_a (2.1) and assuming "x" is small relative to C_0. (The actual pH is 1.61.)

(b; 7 pts) At pH 1.61, what is the % dissociation of the side chain carboxylic acid, with its pK_a of 3.9? Why doesn't this second dissociation have any material effect on the initial pH?

Score for the page____________

(c; 8 pts) Draw the dominant ionic form of aspartic acid at its pI (isoelectric point, the pH at which the average net charge = 0.), and calculate the numerical value of the pI.

(d; 12 pts) Sketch the titration curve for titration of100 mM aspartic acid with NaOH on the axes below, ignoring dilution. Label the half-equivalence points and the equivalence points.



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4. (25 pts) Multiple Equilibria

Fluoride, usually as either NaF = sodium fluoride or H_2SiF_6 = hexafluorosilicic acid, is frequently added to drinking water. The EPA is therefore interested in the chemical forms of fluorine present in aqueous solution, as a function of pH. The bifluoride ion HF_2^- or $[F\text{-}H\text{-}F]^-$ is one such species. Fun fact: it has the world's strongest hydrogen bond. Bifluoride is used to etch glass, so we hope there isn't too much of it in drinking water. Consider the two equilibria below:

$$HF \rightleftharpoons H^+ + F^- \qquad K_a = 10^{-2.89}$$

$$2\,F^- + H^+ \rightleftharpoons HF_2^- \qquad K_2 = 10^{+3.87}$$

(a; 6 pts) Calculate the equilibrium constant for the reaction below:

$$F^- + HF \rightleftharpoons HF_2^- \qquad K_3 = ?$$

(b; 9 pts) If the concentration of fluoride ion $[F^-]$ is measured to be 12 μM at pH 6.52, calculate the concentrations of HF and HF_2^-. There's not much HF_2^-. At what pH would the concentration of HF_2^- be maximized? (No calculation needed for this second question. Look at the equilibria at hand and think Henderson-Hasselbach).

Score for the page____________

(c; 10 pts) A more difficult and realistic problem is to calculate the concentrations of all of the relevant species knowing only input concentrations. Assume we make a solution in water starting with known concentrations of [HF] = C_A and [NaF] = C_B, where the NaF is assumed to dissociate completely. We would like to calculate [H^+], [OH^-], [HF], [F^-], and [HF_2^-]. Write down five independent equations that would have to be satisfied to give the answer, but do not solve (unless you feel like it).

(d; 2 pts) Extra credit: Draw a dodecahedron.

Page	Score
1	/1
2	/25
3	/15
4	/15
5	/20
6	/15
7	/12
Total	**/103**

Score for the page____________