Chemistry 271, Section 22xx

Your Name: _Key_

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University of Maryland, College Park

Your SID #: _____

General Chemistry and Energetics

Your Section #: _____

Exam I (100 points total)

February 29, 2012

$N = 185 + 3 = 188$

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:

$K_a = [H^+][A^-]/[HA]$ $pH = -\log([H^+])$ $K_b = [BH^+][HO^-]/[B]$

$F = ma$ $e^{i\pi} + 1 = 0$ $PV = nRT$

$K_w = [H^+][HO^-] = 10^{-14}$ $pH = pK_a + \log([A^-]/[HA])$ $pH\ (e.p.) = (pK_{a1} + pK_{a2})/2$

$R = 0.08206\ L \cdot atm/mole\ K$ $0\,°C = 273.15\ K$ $pK_a = -\log(K_a)$

$K_p = K_c(RT)^{\Delta n}$ $P^2/a^3 = 4\pi^2/MG$ $x = \dfrac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

(+1) point extra credit for filling in this box

+1 for the honor pledge

1. (30 pts) Short Answer

(a; 2 pts) pH of 0.1 M HCl _____ **1**   (+2) $-\log(10^{-1}) = 1$

(b; 2 pts) pOH of 0.001 M NaOH _____ **3** (+2) $-\log(10^{-3}) = 3$ (or $H_2O \rightleftharpoons H^+ + HO^-$)

(c; 4 pts) The water self-dissociation equilibrium is $2H_2O \rightleftharpoons H_3O^+ + HO^-$, its equilibrium (+2)

constant is symbolized by _____ K_w (+1) _____ , and the numerical value of the equilibrium constant at

25 °C is _____ 10^{-14} (M^2). $= $ (+1)

(d; 2 pts) [H⁺] at pH 5.5 _____ $10^{-5.5} = 3.2 \times 10^{-6}$ (or 3×10^{-6})   (+2)   (in scientific notation).

(e; 2 pts) [OH⁻] at pH 10.3 _____ $10^{-(14-10.3)} = 10^{-3.7}$ _____ (in scientific notation).

         $= 2.0 \times 10^{-4}$ (+2)   (or 2×10^{-4})   typo → g

(f; 4 pts) Write down Q in terms of partial pressures for the reaction C (s) + H₂O (g) ⇌ CO (s) + H₂ (g) :

(+4) $Q = \dfrac{P_{CO} \cdot P_{H_2}}{P_{H_2O}}$ or $Q = \dfrac{P_{H_2}}{P_{H_2O}}$ $\left[\text{if you believed the}\right.$ typo $\left.\right]$

[+2 for Q in []'s, +1 for any attempt]

(g; 4 pts) We can use the Henderson-Hasselbach relationship as a shortcut for calculating pH if and only if

(+4) the concentrations of [HA] and [A⁻] are >> [H⁺] and [HO⁻] .

or (+2) for " " " " are large enough not to change upon

equilibration " he ratio of A⁻ and HA doesn't change " → Why?

(h; 3 pts) The pI is equal to the pH at the equivalence point of a polyprotic acid titration for which

the +2 if no mention of "average"

(+3) the average charge on the species of interest is zero .

[(+2) for " the molecule doesn't move in an electric field "]

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

     (circle one):   zero   (equal)   unrelated
                           (+2)

(j; 5 pts) Circle the correct choice in each pair: Real gases approach ideal behavior as the temperature goes

(up) down   and the pressure goes   up   (down) because under these conditions intermolecular

interactions are (minimized) stabilized   and the total excluded volume is   larger   (smaller) The
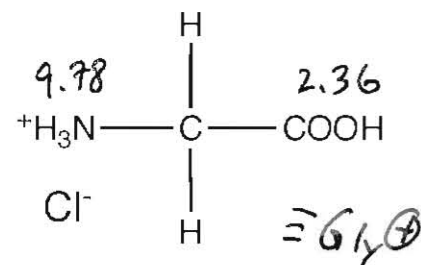
formula for the ideal gas law is _____ $PV = nRT$ _____ .

(+1) each

                                              Score for the page _____ **30**

2. (45 pts) Acid-Base Equilibria and Titrations

Consider a titration of the diprotic acid glycine, with pKa's of 2.36 and 9.78. The structure of the fully protonated form as the chloride salt is given at the right. We are starting with a $C_0 = 75$ mM solution of this form.

9.78   2.36

^+H_3N——C——$COOH$

Cl^-

(a; 10 pts) Calculate the initial pH assuming "x" is small relative to C_0. Physically, why does this turns out to be a fairly lousy assumption? The actual pH is 1.79.

$$Gly^{\oplus} \rightleftharpoons Gly + H^+$$

$$K_a = 10^{-2.36} = \frac{[Gly][H^+]}{[Gly^{\oplus}]} = \frac{x \cdot x}{(75mM - x)} \approx \frac{x^2}{0.075} = 4.365 \times 10^{-3}$$

assumed negligible   (+2)

$$x = \sqrt{0.075 \times 4.365 \times 10^{-3}} = 1.809 \times 10^{-2} \ (+2)$$

$$pH = -\log(x) = \boxed{1.74} \ (+2) \qquad \rightarrow = 0.018$$

(+2)

— The Glycin is a relatively strong weak acid — it's ~25% dissociated (+1)

(b; 12 pts) What is the pH after addition of NaOH to 50 mM, ignoring dilution? At this pH, what fraction of the $-NH_3^+$ groups are found in the $-NH_2$ form? Why is the precise numerical value of the second pK_a (i.e. 9.78 as opposed to ~8 or ~11) irrelevant to the pH at this point in the titration?

$$[Gly = H_3\overset{+}{N}\diagdown_{CO_2^-}] = 50 \ mM \ \text{after addition of NaOH}$$

$$[Gly^{\oplus}] = (75 - 50) \ mM = 25 \ mM$$

(+3) $\left[pH = pK_a + \log \frac{[Gly]}{[Gly\ H^+]} = 2.36 + \log \frac{(50)}{(25)} = 2.66 \right.$ (+2)

$$-NH_2$$

$$= 2.66 = 9.78 + \log \frac{[Gly^{\ominus}]}{[Gly]} \quad (+3)$$

$$-NH_3 \qquad (+2)$$

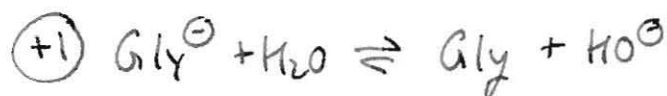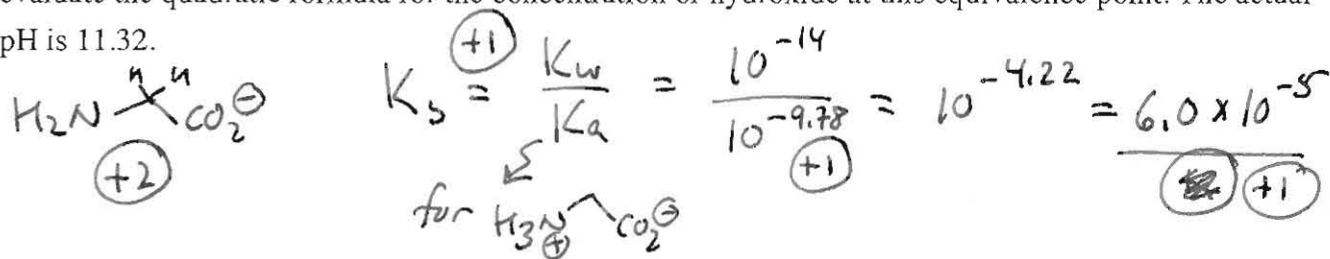$$\frac{[-NH_2]}{[-NH_3^+]} = 10^{-(9.78 - 2.66)} = 10^{-7.12} = 7.58 \times 10^{-8} \ or \ 7.6 \times 10^{-6} \ \%$$

essentially

— The $-NH_3^{\oplus}$ group would be completely protonated at any pKa (+2) above ~7 so it does not donate any protons at ~pH 2.66

Score for the page_____

(c; 11 pts) Draw the dominant ionic form of glycine at the second equivalence point, i.e. after the addition of NaOH to 150 mM. Calculate the K_b for this relatively strong weak base. Write down but do not evaluate the quadratic formula for the concentration of hydroxide at this equivalence point. The actual pH is 11.32.

$$H_2N \overset{H\ H}{\diagup\!\!\diagdown} CO_2^{\ominus} \quad (+2)$$

$$K_b \overset{(+1)}{=} \frac{K_w}{K_a} = \frac{10^{-14}}{10^{-9.78}} = 10^{-4.22} = 6.0 \times 10^{-5} \quad (+1)$$

for $H_3\overset{\oplus}{N} \diagdown CO_2^{\ominus}$

$(+1)$ $Gly^{\ominus} + H_2O \rightleftharpoons Gly + HO^{\ominus}$

$$K_b = \frac{[Gly][HO^-]}{(+2)\ [Gly^{\ominus}]} = \frac{[HO^-]^2}{0.075m - [HO^-]} \quad (+1) \quad \text{at the equivalence point}$$
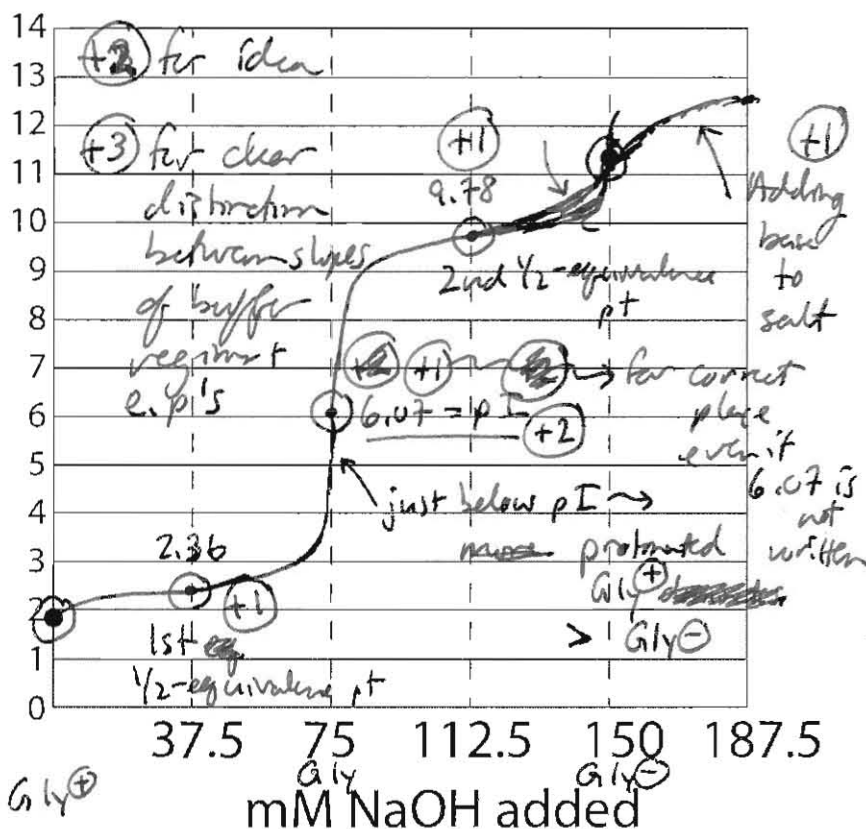
$$[HO^-]^2 + [HO^-](K_b) - K_b(0.075\,m) = 0$$

$(+2)$ for either

$$[HO^-] = \frac{-6.0 \times 10^{-5} + \sqrt{(6.0 \times 10^{-5})^2 + 4 \cdot 0.075 \times 6.0 \times 10^{-5}}}{2}$$

— evaluates to 2.096×10^{-3} ✓

(d; 12 pts) Sketch the titration curve for 75 mM glycine on the axes at the right, ignoring dilution. Label the two half-equivalence points, the pI, and the part of the curve where we are just "adding base to salt." At a pH just below the pI, draw the second most abundant form of glycine below.

Titration of 75 mM Glycine

pH

$(+2)$ for idea
$(+3)$ for clear distinction between slopes of buffer region & e. pI's
9.78
$(+1)$
2nd ½-equivalence pt
$6.07 = pI$ $(+2)$
for correct place, even if 6.07 is not written

Adding base to salt

just below pI → most protonated $Gly^{\oplus}$ > $Gly^{\ominus}$

2.36
1st eq.
½-equivalence pt

$Gly^{\oplus}$ Gly $Gly^{\ominus}$

37.5   75   112.5   150   187.5

mM NaOH added

1st equivalence point
$\swarrow$ pH $= \frac{2.36 + 9.78}{2} = 6.07 = pI$

Don't need a # here.

pH of xs 37.5 mM NaOH
$= 14 + \log(0.0375) = 12.57$

2nd most abundant form at pH 6 —

$$H_3\overset{+}{N} \diagdown COOH \quad (+1)$$
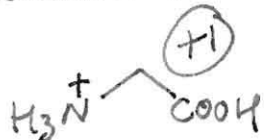
Score for the page_____

4.   (25 pts) Chemical Equilibrium (Problem adapted from Oxtoby)

The equilibrium constant for the reaction $H_2 (g) + I_2 (s) \rightleftharpoons 2\, HI (g)$ at 25 °C is $K_p = 0.345$ ~~at 25 °C~~.

(a; 8 pts) If the partial pressure of H_2 is $P_{H2} = 1.00$ atm and solid iodine is present, what is the equilibrium partial pressure of HI at 25 °C?

$$K_p = \frac{P_{HI}^2}{P_{H_2}} \quad so \quad P_{HI}^2 = K_p\, P_{H_2}$$

(+3)

$$P_{HI} = \sqrt{K_p\, P_{H_2}} = \sqrt{0.345 \cdot 1.00} = 0.587 \text{ atm}$$

(+2)   (+3)

(too many points...)

(b; 9 pts) An excess of solid I_2 is added to a container initially filled with 4.00 atm of H_2 at 25 °C. Calculate the partial pressures of H_2 and HI reached at equilibrium.

	I_2	H_2	HI
I	(xs)	4.00	0
C	−x	−x	+2x
E	(xs)	4.00 − x	2x

(+2)
for table

$$0.345 = \frac{(2x)^2}{4.00 - x} \quad \text{(+1) for eq'n}$$

$P_{H_2} = 3.45$ atm   (+2)

$P_{HI} = \cancel{1.28}$ atm   (+2)
       1.09

Check: $\dfrac{P_{HI}^2}{P_{H_2}} = \dfrac{1.09^2}{3.45} = 0.345 \checkmark$

$$4x^2 = 0.345(4-x) = 1.380 - 0.345x \qquad \underset{a}{4x^2} + \underset{b}{0.345x} - \underset{c}{1.380} = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-0.345 + \sqrt{0.345^2 + 4 \cdot 4 \cdot 1.38}}{8} = 0.5458$$

(+2)
for plugging in #5

Score for the page_____

(c; 4 pts) If the volume of the container is increased at constant temperature, which way will the equilibrium
shift and why?

$Q = \dfrac{P_{HI}^2}{P_{H_2}}$ will decrease if $V \uparrow$, so the reaction will

shift to the right (+2) to raise $Q \rightarrow K$ or to (+2)

respond to the stress of decreased pressure by increasing

the gas pressure (Le Chatelier). (+2)

(d; 4 pts) Why might Hilary Clinton be excited about the prospect of a hydrogen economy? In other words,
describe a geopolitical consequence of running the cars in the US on hydrogen.

— the (+2) Hydrogen can be produced domestically from
coal, natural gas, or eventually other sources.

→ (+2) So we could choose which problems in the Middle
East to deal with rather than being held over
a barrel by our need for oil.

Page	Score
1	/1
2	/30
3	/22
4	/23
5	/17
6	/8
Total	/101

Score for the page_____