G	A	D	D

Exam 1
Chem 12
Feb 28, 2011

Name Gaddafi's Crazy Brother

page **1** (20) _____
2 (25) _____
3 (30) _____
4 (25) _____
5 (35) _____
6 (20) _____

_____ total (150)

___ chk

The Management will appreciate your not writing in this space.

1. (20 points) Calculate the pH of each solution below. Assume all values are sufficiently precise that you can calculate pH to two decimal places.

6 (a) 0.516 mol of triethylamine, $(CH_3CH_2)_3N$, dissolved in water to a final volume of 700 mL.

$Et_3N + H_2O \rightleftharpoons Et_3\overset{\oplus}{N}H + HO^{\ominus}$

$\frac{.516\ mol}{0.700\ L} = 0.737M - x \qquad \propto \qquad x$

$K_b = 4.0 \times 10^{-4} = \frac{x^2}{(0.737 - x)} \Rightarrow x = 0.0172M = [HO^-]$

solve as usual... that's small ✓

$pH = 12.23$

8 (b) 0.0270 mol of chlorous acid, HO–Cl=O dissolved in water to a final volume of 500 mL.

$HOClO + H_2O \rightleftharpoons H_3O^{\oplus} + {}^{\ominus}OClO$

$\frac{.0270\ mol}{0.500\ L} = 0.0540M - x \qquad \propto \qquad x$

$K_a = 1.2 \times 10^{-2} = \frac{x^2}{.0540 - x} \Rightarrow x = 0.0255$

solve as usual... that's not small! 47% dissoc!

iterate... $x = 0.0185$ ⇒ again... $x = 0.0206$ again... $x = 0.0200$ ✓

6 (c) An aqueous solution containing 0.15 M benzoic acid ($PhCO_2H$) and 0.30 M potassium benzoate ($PhCO_2K$) in 763 mL of water.

$K_a = 6.4 \times 10^{-5}$

$pK_a = 4.19$

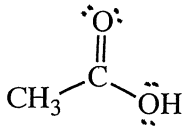
$pH = 4.19 + \log\left(\frac{0.30}{0.15}\right)$

$= 4.49$

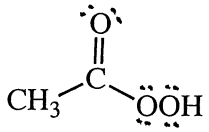
$pH = 1.70$

20

2. (12 points) Acetic acid (**AA**) has $K_a = 1.8 \times 10^{-5}$. Peroxyacetic acid (**PAA**) has $K_a = 6.3 \times 10^{-9}$.



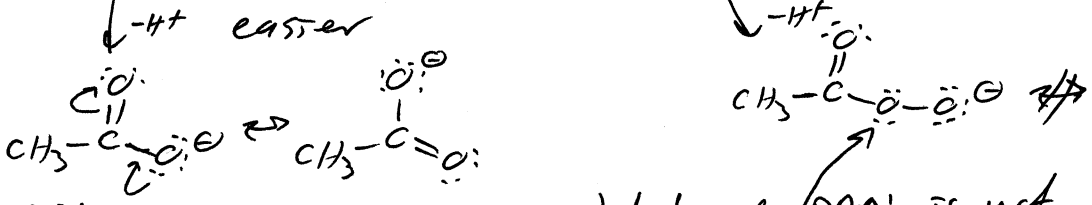
acetic acid (**AA**)



peroxyacetic acid (**PAA**)

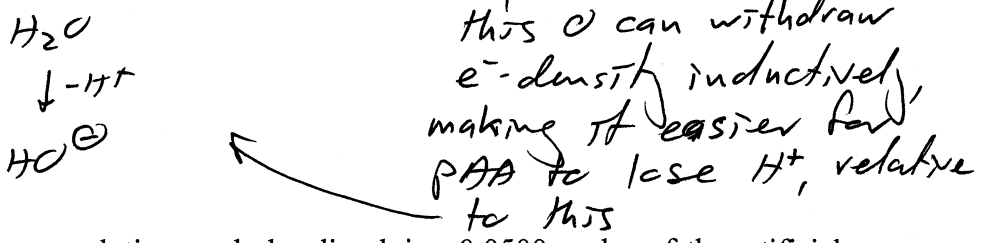
(a) Explain briefly, in terms of *structures*, why the acidities of these compounds are so different.

6



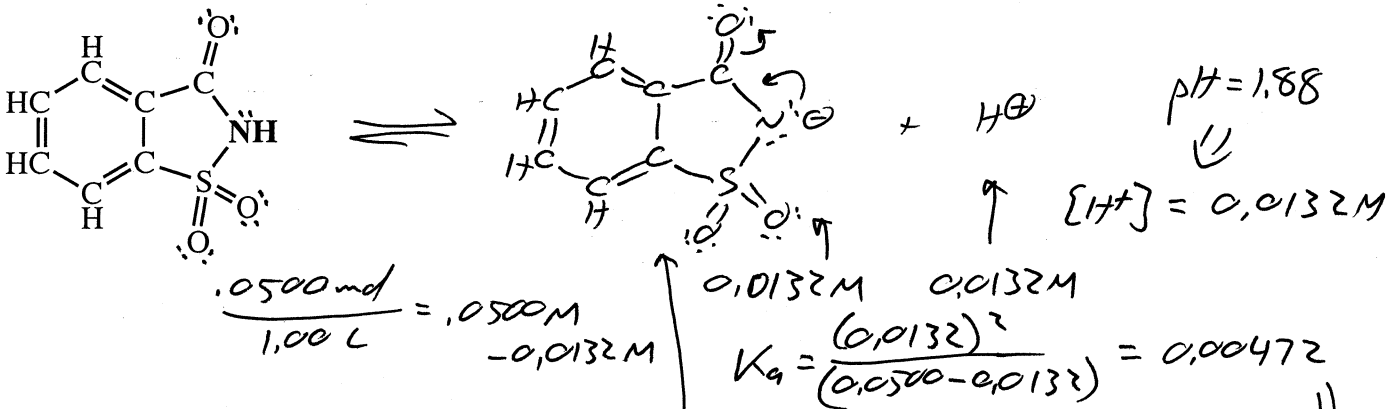
(b) Explain briefly, in terms of *structures*, why peroxyacetic acid is a stronger acid than water.

6



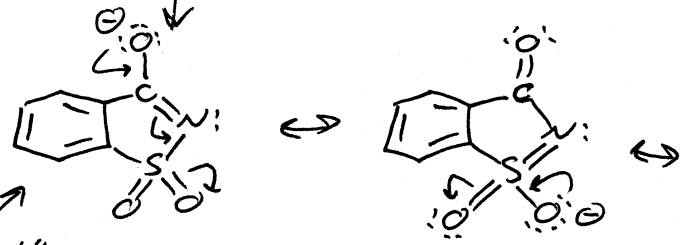
3. (13 points) (a) A 1.00-L aqueous solution made by dissolving 0.0500 moles of the artificial sweetener saccharin (below) in water has a pH of 1.88. What is the pK_a of saccharine?

7



(b) Hs attached to neutral Ns are not normally very acidic. (For example, the pK_a of NH_3 is about 38.) Explain briefly, what it is about the *structure* of saccharine that makes that H so acidic.

6



Saccharin's conjugate base is resonance-stabilized by extensive delocalization of the negative charge! ("skeletal" notation)

25

4. (30 points) Under certain conditions, carbon dioxide will establish an equilibrium with carbon monoxide and oxygen, as shown below. The reaction as written has $K = 2.00 \times 10^{-6}$ M.

$$2\ CO_2 \rightleftharpoons 2\ CO + O_2$$

(a) 1.00 mol of CO_2 is placed in a 2.00-L container. What are the concentrations of CO_2, CO, and O_2 present after equilibrium has been established? (Find the correct concentrations to three significant figures.)

8

0,500M − 2x +2x +x

$K = \frac{[CO]^2[O_2]}{[CO_2]^2}$

$2,00 \times 10^{-6} = \frac{(2x)^2 x}{(0,500-2x)^2}$ ← assume 2x small, as usual

⇓

$x = 0,0050$ ~1% of initial conc. close enough ⇐ (iteration ⇒ $x = 0,0049$)

$[CO_2] = 0,490\ M$

$[CO] = 0,010\ M$

$[O_2] = 0,005\ M$

(b) The container used in part a has a movable piston that is suddenly pulled back to increase the volume by a factor of 10 (i.e. to a volume of 20.0 L). How would you expect the reaction to shift in response to this volume change? should shift right

2

(c) Calculate the new equilibrium concentrations of the three species.

10

same procedure as above, but initial $[CO_2] = 0,0500$

$2,00 \times 10^{-6} = \frac{(2x)^2 x}{(0,0500-2x)^2}$ ← assume small ⇒

$x = 0,00108$ ok

~2% of init. conc.

Iterate ⇓

$x = 0,00106$ ~no change ✓

$[CO_2] = 0,0479\ M$

$[CO] = 0,00212\ M$

$[O_2] = 0,00106\ M$

(d) In a separate 1.00-L vessel, 0.470 mol of CO and 0.820 mol of O_2 are combined. What are the concentrations of all species present after equilibrium has been established?

10

$2CO_2 \rightleftharpoons 2CO + O_2$

0,470M 0,820M

← K very small, so stoichiometric shift gives better starting point.

new "initial": 0,470M 0 0,585M

fine-tune (i.e. "change"): −2x +2x +x

$2,00 \times 10^{-6} = \frac{(2x)^2(0,585+x)}{(0,470-2x)}$ usual approach ⇒

$x = 0,000434$

$= 4,34 \times 10^{-4}$

$[CO_2] = 0,469\ M$ $[CO] = 8,68 \times 10^{-4}\ M$ ⇐

$[O_2] = 0,585\ M$

30

5. (25 points) (a) What is the K_a value of anilinium bromide, $C_6H_5NH_3Br$ (aka $PhNH_3Br$)? (Use information in the attached data tables.)

2 $K_a = \frac{10^{-14}}{K_b \text{ for } PhNH_2,\ 3.8\times10^{-10}} = 2.63\times10^{-5}$

(b) What is the pH of 200 mL of a solution 0.250 M $PhNH_3Br$?

(I'll keep one extra sig fig to avoid rounding errors later)

5 $Ph\text{-}NH_3^{\oplus} \rightleftharpoons Ph\text{-}NH_2 + H^+$

$0.250 - x \qquad x \qquad x$

$2.63\times10^{-5} = \frac{x^2}{0.250 - x} \Rightarrow x = 0.00256\ M = [H^+]$

$pH = 2.59$

(c) How many moles of $PhNH_3Br$ are present in this solution?

2 ignoring the ~1% that dissociates,

$\frac{0.250\ mol}{L} \times 0.200\ L = 0.050\ mol$

Suppose you titrate this solution with 0.500 M aqueous NaOH.

(d) How many mL of aqueous NaOH solution is needed to reach the equivalence point?

2 need 0.050 mol HO^- (whether you considered the dissociation in part c or not)

$\times \frac{1\ L}{0.500\ mol} = 0.100\ L = 100\ mL$

(e) What is the pH of the solution at the equivalence point?

6 "all" $PhNH_3^{\oplus}$ converted to $PhNH_2$

$Ph\text{-}NH_2 + H_2O \rightleftharpoons PhNH_3^{\oplus} + HO^{\ominus}$

$\frac{0.050\ mol}{0.300\ L} = 0.1667\ M - x \qquad x \qquad x$

$3.8\times10^{-10} = \frac{x^2}{(0.1667 - x)}$

$\Rightarrow x = 7.96\times10^{-6} = [HO^-]$

$pH = 8.90$

(f) What is the pH when exactly half of the amount of NaOH needed to reach the equivalence point has been added?

2 $pH = pK_a = 4.58$

(g) How many mL of NaOH has been added when the pH of the solution is 5.00?

6 $5.00 = 4.58 + \log\left(\frac{[PhNH_2]}{[PhNH_3^+]}\right)$

$\frac{[PhNH_2]}{[PhNH_3^+]} = 2.63$

$[PhNH_2] = 2.63\,[PhNH_3^+]$

and we know that $[PhNH_2] + [PhNH_3^+] = 0.050\ mol$

$\Rightarrow$ 0.0362 mol $PhNH_2$ + 0.0138 mol $PhNH_3^+$

$\Rightarrow$ 72.4 mL of 9g NaOH

6. (15 points) Strontium fluoride, SrF_2, is very slightly soluble in water, with $K_{sp} = 7.9 \times 10^{-10}$. (Ignore any acid-base chemistry involving fluoride ion.)

(a) Calculate $[Sr^{2+}]$ in a solution saturated with strontium fluoride.

$SrF_2(s) \rightleftharpoons Sr^{2+}(aq) + 2F^-(aq)$

$K_{sp} = [Sr^{2+}][F^-]^2$

6

$7.9 \times 10^{-10} = (x)(2x)^2 = 4x^3$

$x = [Sr^{2+}] = 5.8 \times 10^{-4}\ M$

(b) How would you expect the addition of 0.50 M NaF to affect the $[Sr^{2+}]$?

3 added F^- will "push" rxn back to the left ⇒ decrease the Sr^{2+} conc.

(c) Calculate $[Sr^{2+}]$ in a saturated SrF_2 solution containing 0.50 M NaF.

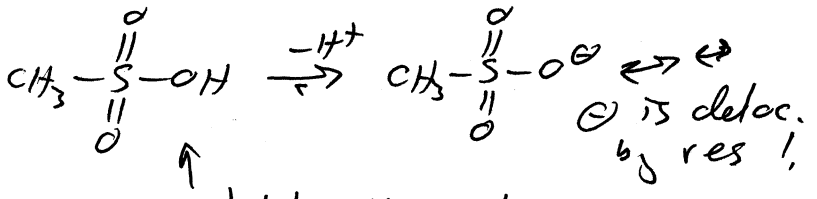
6

$7.9 \times 10^{-10} = (x)(0.50M + 2x)^2$ ← this must be small relative to 0.50 M

$x = [Sr^{2+}] = 3.2 \times 10^{-9}\ M$

7. (8 points) A 0.10 M solution of CH_3SO_3H in water has a pH of 1.0. Suggest a structure for CH_3SO_3H that is consistent with this observation.

⇒ completely ionized



just like H_2SO_4!

⊖ is deloc. by res!

structure may be similar to one of our strong acids

8. (12 points) 100 pounds of each substance below is dissolved in a small pond. Assume each pond initially consists of pure water (no algae, beer cans, or aquatic critters). Would each pond become acidic, become basic, or remain neutral?

3 (a) $(CH_3)_2CHCH_2CH_2\ddot{N}H_2$ Basic

3 (b) $(CH_3)_4NF$ $(CH_3)_4N^{\oplus}$ $F^{\ominus}$ ← weak base Basic

(no H on N so this is not a weak acid like NH_4^+)

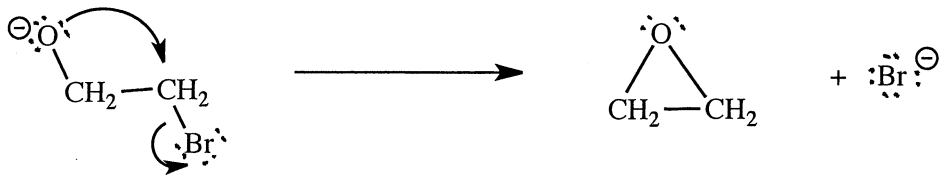
3 (d) KNO_3

K^+ NO_3^- ← super weak bases Neutral

3 (e) NH_4ClO_4

NH_4^+ ClO_4^- ← weak acid Acidic

9. (20 points) The reaction below is energetically favorable overall. To understand why and to estimate the energy change, we need to take several factors into account.



(a) First, let's consider the changes in bonding. Use the table of bond dissociation energies (*D*-values) on the following page to estimate the energy change that comes from bonding changes (in kJ/mol).

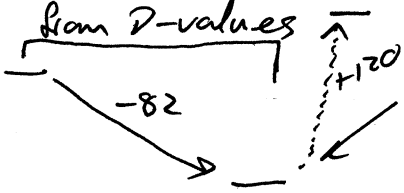
7

break C–Br +276
make C–O −358
−82 kJ/mol

of course we're ignoring the fact that there's a ⊖ & thus an e⁻ needs to be "moved" from O to Br ----

(b) Like in one of your homework problems, we also have to account for the fact that the product has a three-membered ring and therefore some "uncomfortably acute" bond angles. This raises its energy by about 120 kJ/mol. Combine this with your value from part a to adjust your estimate of the overall energy change in the reaction.

7



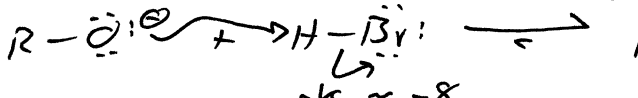
now this is destabilized by 120 kJ/mol, so our new estimate is −82 + 120 = +38 kJ/mol

(c) What other factor have we not accounted for? And how would this affect our estimate of the overall energy change?

6

The rxn trades an $R-\ddot{O}:^{\ominus}$, a relatively strong base, for a $:\ddot{B}r:^{\ominus}$, an extremely weak base. That provides additional "driving force" that makes the rxn favorable overall.

How much is this worth energetically? The corresponding a-b rxn –



$K_{eq} = 10^{24}$ ⇒ ~ −140 kJ/mol (we'll learn how to do this later)

20