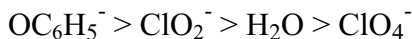


CHEM131 HOMEWORK #11 KEY

7-22. If you look at the previous question, 7-21 which was not assigned, you will see that 21 asks you to order a series of acids and 22 asks you to order the conjugate bases of the same acids. It is important to remember that the conjugate base of a strong acid is a very weak base, and *vice versa*. So the order of decreasing basicity is



7-31. a. HCl is a strong acid so $[\text{H}^+] = 0.10$, $\text{pH} = 1.00$

b. HClO_4 is a strong acid so $[\text{H}^+] = 5.0$, $\text{pH} = -0.70$. Note the minus sign; negative pH arise whenever $[\text{H}^+] > 1$

c. This one is a wringer. HI is strong acid so the dissociation of the HI contributes 1.0×10^{-11} M to the H^+ concentration, Considering just this source of $[\text{H}^+]$ gives $\text{pH} = 11$ which does not make any sense for an ACIDIC solution. But this really is not an acidic solution because the dominant source of $[\text{H}^+]$ is from water and the 10^{-11} $[\text{H}^+]$ is a negligible "impurity". The pH is 7.00

7-33. a. H^+ , Cl^- , and H_2O ; $\text{pH} = -\log(0.250) = 0.602$

b. H^+ , Br^- , H_2O , $\text{pH} = 0.602$ (essentially same as a.)

c. HClO_4 is also a strong acid so same deal and $\text{pH} = 0.602$

d. Same again!

e. Ah, the tedium is relieved. HNO_2 is a weak acid, $K_a = 4.0 \times 10^{-4}$, so the major species present are HNO_3 and H_2O . So we set up the usual equilibrium solution, but now there will be a convenient approximation to avoid the dreaded quadratic equation.

	HNO_3	\rightleftharpoons	H^+	+	NO_2^-
initial	.250		0		0
change	-x		x		x
equil.	$0.250 - x$		x		x

$$K_a = x^2 / (0.250 - x) = 4.0 \times 10^{-4}; \quad \text{Now assume that } x \text{ is much less than } 0.250 \text{ so we can ignore the } x \text{ in the denominator}$$

$$x^2 \cong 0.250 \cdot 4.0 \cdot 10^{-4} = 1.0 \cdot 10^{-4}; \quad x \cong 0.01 = [\text{H}^+], \quad \text{pH} = 2.0.$$

You always have to check the validity of the initial assumption, and here it is good to 4%. (.01/.25) We will typically assume anything within 5% is OK.

- f. Acetic acid, CH_3COOH , is the stuff in vinegar and is a weak acid having $K_a = 1.8 \cdot 10^{-5}$. The problem sets up just as in part e. and now the assumption will be even better because we have an even weaker acid.

$$x^2 \cong 0.250 \cdot 1.8 \cdot 10^{-5}; \quad x = 2.1 \cdot 10^{-3}; \quad \text{pH} = 2.68.$$

- g. HCN is a very weak acid, $K_a = 6.2 \cdot 10^{-10}$, so HCN and H_2O are the major species present. Following the same procedures as above we have $x^2 = 0.250 \cdot 6.2 \cdot 10^{-10}$, and $x = 1.2 \cdot 10^{-5}$; $\text{pH} = 4.92$. In the case of really weak acids, it always important to check that water is not a significant source of H^+ ion. In this we are OK since $\text{pH} = 4.92$ is still quite far from $\text{pH} = 7$ for plain water. See section 7.9 in the text for more on this topic.

- 7-39. Abbreviating benzoic acid as HBz and the benzoate ion as Bz^- we construct the ICE table for the dissociation of a weak acid: $\text{HBz} \rightleftharpoons \text{H}^+ + \text{Bz}^-$. The initial concentration of HBz is $0.56 \text{ g} / (122.1 \text{ g/mol} \cdot 1.00 \text{ L}) = 4.6 \cdot 10^{-3} \text{ M}$.

Initial	$4.6 \cdot 10^{-3}$	0	0
change	-X	X	X
equilibrium	$4.6 \cdot 10^{-3} - X$	X	X

$K_a = 6.4 \cdot 10^{-5} = x^2 / (4.6 \cdot 10^{-3} - x)$ Unfortunately, if you drop the x in the denominator and solve for x, you find that $x = 5.4 \cdot 10^{-4}$ which is 12% of $4.6 \cdot 10^{-3}$ ☹! Bummer. (Watch out for this on the tests) The quad. eq. solution gives $x = 5.1 \cdot 10^{-4} = [\text{H}^+] = [\text{Bz}^-]$, $[\text{HBz}] = 4.6 \cdot 10^{-3} - x = 4.1 \cdot 10^{-3}$.

- 7-43. a. Here we have the dissociation of a weak acid with additional $[\text{H}^+]$ present from a strong acid. The presence of the strong acid means less of the weak acid will dissociate. Write down standard ICE relations.

	HOCl	\rightleftharpoons	H^+	+	OCl^-
Initial	0.10		0.10		0
Change	-x		+x		+x
Equil.	$0.10 - x$		$0.10 + x$		x

$K_a = (0.10 + x)x/(0.10 - x) = 3.5 \cdot 10^{-8}$; assume $x \ll 0.10$ and drop the x in each set of parentheses

$x \approx 3.5 \cdot 10^{-8}$ and the assumption is very good. This does NOT mean that $x = [H^+]$ and $pH = 7.5$. Remember the 0.10 M strong acid. Clearly the HOCl dissociates a completely negligible amount and we can ignore x altogether. $[H^+] = 0.1$ and $pH = 1.00$

b. This example follows exactly the same pattern as part a. Here $x = 1.8 \cdot 10^{-4}$ and $[H^+] = 0.05 + 1.8 \cdot 10^{-4} \approx 0.05$ to within our 5% threshold, and $pH = 1.30$

7-59. The base with the larger K_b is the stronger. Remember that the conjugate base of a strong acid is a very poor base and that $K_a \cdot K_b = K_w = 10^{-14}$ for an acid and its conjugate base or a base and its conjugate acid.

a. $C_2H_5NH_2$ since NO_3^- is the conjugate base of a strong acid.

b. $C_2H_5NH_2$

c. You cannot get a stronger base than OH^- in aqueous solution.

d. $C_2H_5NH_2$.

7-72. Let's label pyrrolidine, C_4H_8NH , PY and write equilibrium equation that generates OH^- . Then use the given pH to calculate $[OH^-]$ to evaluate K_b .

	PY +	H ₂ O	⇌	PYH ⁺	+	OH ⁻
Initial	1.00*10 ⁻³			0		0
Change	-x			+x		+x
Equil.	1.00*10 ⁻³ - x			x		x

$K_b = x^2/[(1.00 \cdot 10^{-3} - x)]$; where $x = [OH^-]$. At this point, you might automatically drop the x in the parentheses. There are two reasons not to do this. First, you don't have to drop x to simplify the problem because we can calculate x from the given pH. Second, the approximation is also bad in this case. From $pH = 10.82$ and $pH + pOH = 14.00$ we have $pOH = 3.18$. $[OH^-] = 10^{-3.18} = 6.6 \cdot 10^{-4}$ (note $6.6 \cdot 10^{-4}$ is not small relative to 10^{-3}).

Put this value in $K_b = [OH^-]^2/(1.00 \cdot 10^{-3} - [OH^-])$ gives $K_b = 1.3 \cdot 10^{-3}$.

7-73. It is easy to put HCl at the head of the list and KOH at the end. A little thought puts KCl in the middle because it is a fully dissociated salt arising from a strong acid (HCl say) and a strong base (KOH say) in water and will not effect the pH. This leaves KCN and NH₄Cl. Dissolving KCN generates K⁺ and CN⁻. The K⁺ doesn't get involved in any acid/base equilibria, but CN⁻ + H₂O ⇌ HCN + OH⁻. So dissolving KCN in water generates OH⁻ ions and is a weak base. The same argument has NH₄⁺ slightly dissociating in water to give NH₃ and H⁺. NH₄Cl gives a weakly acidic solution.

HCl NH₄Cl KCl KCN KOH

It is useful to remember that the salt of a strong acid and a weak base gives an acidic solution while the salt of a weak acid and a strong base gives a basic solution.

Next H.W. Ch 7: 76, 89, 101, Ch 8: 17,19, 27