CHEMISTRY 204
Hour Exam II
March 14, 2019
Dr. D. DeCoste

Name **KEY**

Signature ______________________

T.A. ______________________

Section ______________________

This exam contains 23 questions on 10 numbered pages. Check now to make sure you have a complete exam. You have two hours to complete the exam. Determine the **best** answer to the first 20 questions and enter these on the special answer sheet. Also, circle your responses in this exam booklet. **Show all of your work and provide complete answers to questions 21, 22 and 23.**

1-20	(60 pts.)	______
21	(20 pts.)	______
22	(20 pts)	______
23	(20 pts.)	______
Total	(120 pts)	______

Useful Information:

- Unless otherwise noted, all solutions referred to on this exam are aqueous solutions at 25°C.
- On this exam, H_3O^+ and H^+ are used interchangeably.

$K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$ at 25°C.

For $ax^2 + bx + c = 0$, $x = \dfrac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

$pH = -\log[H^+]$

$$K_a = \frac{[H^+]^2 - K_w}{[HA]_o - \dfrac{[H^+]^2 - K_w}{[H^+]}}$$

21. We discussed in class that the best approach to solving acid-base problems is to think about major species, dominant equilibrium, etc. instead of labeling problems by type and forcing a memorized solution to each. Let's put this idea to practice. Consider mixing the following aqueous solutions together in one beaker:

- H_2A ($K_{a1} = 1.5 \times 10^{-4}$, $K_{a2} = 2.5 \times 10^{-7}$)
- KOH
- HCN ($K_a = 6.2 \times 10^{-10}$)

a. What are the initial **major species**? **Explain** your answer. **[5 points]**

MS: $H_2A(aq)$, $K^+(aq)$, $OH^-(aq)$, $HCN(aq)$, $H_2O(l)$

$H_2A(aq)$ and $HCN(aq)$ are weak acids, $KOH(aq)$ is soluble, and the solution is aqueous.

b. **List all possible reactions** that can occur between the major species and determine the values of the equilibrium constant, *K*, for all of these reactions. **Show all work. [12 points]**

$H_2A(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HA^-(aq)$ $K = K_{a1} = 1.5 \times 10^{-4}$.

$H_2A(aq) + OH^-(aq) \rightleftharpoons H_2O(l) + HA^-(aq)$ $K = K_{a1}/K_w = 1.5 \times 10^{10}$.

$$K = \frac{[HA^-]}{[H_2A][OH^-]} = \frac{[HA^-][H_3O^+]}{[H_2A]} \times \frac{1}{[H_3O^+][OH^-]}$$

$HCN(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CN^-(aq)$ $K = K_a = 6.2 \times 10^{-10}$.

$HCN(aq) + OH^-(aq) \rightleftharpoons H_2O(l) + CN^-(aq)$ $K = K_a/K_w = 6.2 \times 10^{4}$.

$$K = \frac{[CN^-]}{[HCN][OH^-]} = \frac{[CN^-][H_3O^+]}{[HCN]} \times \frac{1}{[H_3O^+][OH^-]}$$

$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$ $K = K_w = 1.0 \times 10^{-14}$.

21. (con't)

c. What is the **dominant reaction** that will take place given your answers to part b? **Why?** Could we consider the dominant reaction to go essentially to completion, or must we treat it as an equilibrium reaction? **Explain**. **[3 points]**

- $H_2A(aq) + OH^{-}(aq) \rightleftharpoons H_2O(l) + HA^{-}(aq)$
- Dominant because the *K* value is the largest.
- We can consider it to essentially to completion since the value of K is so large (much greater than 1)

22. Now let's start mixing! In this problem, you will be given different volumes of the aqueous solutions you were given in Problem 21 and asked to determine the pH of each of the mixtures at equilibrium. In both of the cases:

- **label major species** as/if they change
- **determine *K* values** for all reactions between new major species for which you did not determine *K* in Problem 21.
- **determine the pH** of the solution at equilibrium.

Full credit is reserved for coherent, systematic work that we can follow. Show all work,

a. 100.0 mL of 1.0*M* H_2A ($K_{a1} = 1.5 \times 10^{-4}$, $K_{a2} = 2.5 \times 10^{-7}$), 50.0 mL of 1.0*M* KOH, and 100.0 mL of 2.0*M* HCN ($K_a = 6.2 \times 10^{-10}$) **[10 points]**

MS: $H_2A(aq)$, $K^+(aq)$, $OH^-(aq)$, $HCN(aq)$, $H_2O(l)$

$H_2A(aq) + OH^-(aq) \rightleftharpoons H_2O(l) + HA^-(aq)$ $K = K_{a1}/K_w = 1.5 \times 10^{10}$.

	$H_2A(aq)$	$OH^-(aq)$	$H_2O(l)$	$HA^-(aq)$
B	0.10 mol	0.050 mol	--	0
A	0.05 mol	0	--	0.05 mol

MS: $H_2A(aq)$, $K^+(aq)$, $HA^-(aq)$, $HCN(aq)$, $H_2O(l)$

- $HA^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^{2-}(aq)$ $K = K_{a2} = 2.5 \times 10^{-7}$.
- $HA^-(aq) + H_2O(l) \rightleftharpoons H_2A(aq) + OH^-(aq)$ $K = K_b = K_w/K_{a1} = 6.67 \times 10^{-11}$.
- $HCN(aq) + HA^-(aq) \rightleftharpoons H_2A(aq) + CN^-(aq)$ $K = K_{a(HCN)}/K_{a1} = 4.1 \times 10^{-6}$.
- $HA^-(aq) + HA^-(aq) \rightleftharpoons H_2A(aq) + A^{2-}(aq)$ $K = K_{a2}/K_{a1} = 1.67 \times 10^{-3}$.

0.05mol/0.250L = 0.20M

$HA^-(aq) + HA^-(aq) \rightleftharpoons H_2A(aq) + A^{2-}(aq)$ $K = K_{a2}/K_{a1} = 1.67 \times 10^{-3}$.

	$HA^-(aq)$	$HA^-(aq)$	$H_2A(aq)$	$A^{2-}(aq)$
Initial	0.20M	0.20M	0.20M	0
Change	–2x	–2x	+x	+x
Equil	0.20–2x	0.20–2x	0.20+x	x

$\frac{[0.20+x][x]}{[0.20-2x][0.20-2x]} = 1.67 \times 10^{-3}$; solving we get x = 3.3×10^{-4} *M*.

Use K_{a1} or K_{a2} to solve for $[H^+]$:

$\frac{[H^+][0.20]}{[0.20]} = K_{a1} = 1.5 \times 10^{-4}$; solving we get $[H^+] = 1.5 \times 10^{-4}$ (K_{a1}); **pH = 3.82**

$\frac{[H^+][3.3 \times 10^{-4}]}{[0.20]} = K_{a2} = 2.5 \times 10^{-7}$; solving we get $[H^+] = 1.5 \times 10^{-4}$; **pH = 3.82**

[NOTE: pH = pK_{a1} for H_2A]

[HCN] = 0.8*M*; $\frac{[1.5 \times 10^{-4}+x][x]}{[0.80]} = 6.2 \times 10^{-10}$; x ~ 3.3×10^{-6} ; negligible contribution

22. b. 100.0 mL of 1.0*M* H_2A ($K_{a1} = 1.5 \text{ x } 10^{-4}$, $K_{a2} = 2.5 \text{ x } 10^{-7}$), 200.00 mL of 1.0*M* KOH, and 50.0 mL of 2.0*M* HCN ($K_a = 6.2 \text{ x } 10^{-10}$) **[10 points]**

MS: $H_2A(aq)$, $K^+(aq)$, $OH^-(aq)$, HCN(aq), $H_2O(l)$

$H_2A(aq) + OH^-(aq) \rightleftharpoons H_2O(l) + HA^-(aq)$ $K = K_{a1}/K_w = 1.5 \text{ x } 10^{10}$.

	$H_2A(aq)$	$OH^-(aq)$	$H_2O(l)$	$HA^-(aq)$
B	0.10 mol	0.20 mol	--	0
A	0	0.10 mol	--	0.10 mol

MS: $OH^-(aq)$, $K^+(aq)$, $HA^-(aq)$, HCN(aq), $H_2O(l)$

$OH^-(aq) + HA^-(aq) \rightleftharpoons A^{2-}(aq) + H_2O(l)$ $K = K_{a2}/K_w = 2.5 \text{ x } 10^{7}$.

	$OH^-(aq)$	$HA^-(aq)$	$A^{2-}(aq)$	$H_2O(l)$
B	0.10 mol	0.10 mol	0	--
A	0	0	0.10 mol	

MS: $K^+(aq)$, $A^{2-}(aq)$, HCN(aq), $H_2O(l)$

[HCN] = 0.286*M*
$[A^{2-}]$ = 0.286*M*

$A^{2-}(aq) + H_2O(l) \rightleftharpoons HA^-(aq) + OH^-(aq)$ $K = K_w/K_{a2} = 4 \text{ x } 10^{-8}$.

$HCN(aq) + A^{2-}(aq) \rightleftharpoons CN^-(aq) + HA^-(aq)$ $K = K_{a(HCN)}/K_{a2} = 2.48 \text{ x } 10^{-3}$.

	HCN(aq)	$A^{2-}(aq)$	$CN^-(aq)$	$HA^-(aq)$
I	0.286	0.286	0	0
C	–x	–x	+x	+x
E	0.286–x	0.286–x	x	x

$\frac{[x][x]}{[0.286-x][0.286-x]} = 2.48 \text{ x } 10^{-3}$; solving we get x = 0.0136*M*.

Use K_a (HCN) or K_{a2} (H_2A) to solve for $[H^+]$:

$\frac{[H^+][0.0136]}{[0.2724]} = K_a = 6.2 \text{ x } 10^{-10}$; solving we get $[H^+] = 1.24 \text{ x } 10^{-8}$; **pH = 7.91**

$\frac{[H^+][0.2724]}{[0.0136]} = K_{a2} = 2.5 \text{ x } 10^{-7}$; solving we get $[H^+] = 1.24 \text{ x } 10^{-8}$; **pH = 7.91**

[Note: also pH = [pKa2 + pKa(HCN)]/2

23. Ionic solids (salts) are soluble in water, but their solubility varies. Some salts are more soluble in acidic solutions, and some are equally soluble in pure water and acidic aqueous solutions.

a. Consider the generic calcium salt: CaX_2. Given that $K_{sp} = 4.0 \times 10^{-11}$ for this salt, **determine the solubility of CaX_2** in pure water (ignore any potential basic properties of X^-). **Show all work. [3 points]**

$CaX_2(s) \rightleftharpoons Ca^{2+}(aq) + 2X^-(aq)$ $K_{sp} = 4.0 \times 10^{-11}$

I		0	0
C		+x	+2x
E		x	2x

$(x)(2x)^2 = 4x^3 = K_{sp} = 4.0 \times 10^{-11}$; $x = 2.15 \times 10^{-4}\ M$

Solubility in pure water = 2.15×10^{-4} *M*.

b. Knowing that HX is actually a weak acid, is the solubility of CaX_2 in pure water higher or lower than you determined in part a? Do not do any calculations here, but **explain your answer** conceptually, using chemical equations as appropriate. **[4 points]**

- The solubility will be higher in water than determined in part a.
- This is because if HX is a weak acid, X^- will act like a base in water.
  The reaction is: $X^-(aq) + H_2O(l) \rightleftharpoons HX(aq) + OH^-(aq)$.
- So as $X^-(aq)$ goes into solution, it reacts with water.
- As some $X^-(aq)$ is removed, it causes CaX_2 to dissolve more to make up for the loss.

23. c. It turns out that the calcium salt with $K_{sp} = 4.0 \times 10^{-11}$ is CaF_2. Knowing that for HF $K_a = 7.2 \times 10^{-4}$, show that while the solubility of CaF_2 in pure water is different from what you determined in part a, it is not significantly different. You do not necessarily need to determine the solubility of CaF_2 in pure water, but you do need to **support your answer with numbers/calculations and an explanation**. **[5 points]**

- From part a (using Ksp) we see that $[F^-]$ in pure water = $2x = 4.3 \times 10^{-4}\ M$.
- Since F^- is the conjugate base of HF, $K_b = K_w/K_a = 1.4 \times 10^{-11}$.
- We have:

$$F^-(aq) + H_2O(l) \rightleftharpoons HF(aq) + OH^-(aq)$$

	$F^-(aq)$	$HF(aq)$	$OH^-(aq)$
I	$4.3 \times 10^{-4}\ M$	0	~0
C	$-x$	$+x$	$+x$
E	$4.3 \times 10^{-4} - x$	x	x

- Solve for x, we get $x = 7.8 \times 10^{-8}$.
- Too many assumptions, and we can use the equation in which water plays a role, but even in doing so, we will get x on the order of 10^{-7}. Thus, the change in $[F^-]$ is not significant enough to be measured.

d. **Determine the solubility** of CaF_2 in an aqueous solution buffered at a pH of 2.00. **Show all work**. **Is the solubility higher or lower** than you determined in part a? **Explain** conceptually why that answer makes sense. **[8 points]**

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq) \qquad K_{sp} = 4.0 \times 10^{-11}$$
$$HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq) \qquad K_a = 7.2 \times 10^{-4}$$

- If the amount of Ca^{2+} is "x", the total amount of "F" we have in solution is 2x
- The total [F] in solution = $[HF] + [F^-]$
- Since pH = 2.00, $[H^+] = 0.01$, so $7.2 \times 10^{-4} = \frac{[0.01][F^-]}{[HF]}$
- $[HF] = 13.89[F^-]$

$2x = 13.89[F^-] + [F^-] = 14.89[F^-]$; $[F^-] = 2x/14.89$

$(x)(2x/14.89)^2 = 4.0 \times 10^{-11}$; $x =$ $\mathbf{1.30 \times 10^{-3}}$***M***

- The solubility is **greater** [$1.30 \times 10^{-3} M > 2.15 \times 10^{-4}\ M$]
- This makes sense because F^- will react with H^+, taking F^- out of solution and driving the solubility equilibrium to the right.

[Alternative method on next page]

23d)

Alternative Method

$CaF_2\,(s) \rightleftharpoons Ca^{2+}\,(aq) + 2F^{-}\,(aq)$ $K_{sp} = 4.0 \times 10^{-11}$
$2F^{-}(aq) + 2H^{+}(aq) \rightleftharpoons 2HF(aq)$ $K = (1/7.2 \times 10^{-4})^2 = 1.93 \times 10^{6}$

Overall: $CaF_2\,(s) + 2H^{+}(aq) \rightleftharpoons Ca^{2+}\,(aq) + 2HF(aq)$ $K = 7.7 \times 10^{-5}$

Because pH is buffered at 2.00, $[H^+] = 0.01M$ at equilibrium.

$7.7 \times 10^{-5} = ;\ \frac{(x)(2x)^2}{(0.01)^2};\ x = 1.24 \times 10^{-3}M$

Solubility of solid is same as calcium ion concentration; solubility = **$1.24 \times 10^{-3}M$**

We get the correct relative value (and close to Method I – the assumption is not horrible): that is, the solubility is greater.

- The solubility is **greater** [$1.24 \times 10^{-3}M > 2.15 \times 10^{-4}\,M$]
- This makes sense because F^- will react with H^+, taking F^- out of solution and driving the solubility equilibrium to the right.

But in this case [HF] is close to $[F^-]$ and to $[H^+]$ so assumptions aren't valid. Note that we get in the second equation that $[HF] = 2[Ca^{2+}]$, which would mean $[F^-] = 0$.

We can calculate these:

$[Ca^{2+}] = 1.24 \times 10^{-3}M$
$[HF] = 2.48 \times 10^{-3}M$
$[F^-] = 1.79 \times 10^{-4}M$

Note than [HF] is not significantly larger than $[F^-]$