19) $NaHCO_3 \rightarrow Na^+ + HCO_3^-$

$Na_2CO_3 \rightarrow 2Na^+ + CO_3^{2-}$ } Buffer b/c weak acid: HCO_3^- and its conj. base: CO_3^{2-}

Rxns: $\underset{\text{strong acid}}{H^+} + CO_3^{2-} \rightarrow HCO_3^-$

$OH^- + HCO_3^- \rightarrow H_2O + CO_3^{2-}$ } Both H^+ & OH^- have something to react with, so they don't accumulate (which means pH doesn't change).

$\uparrow$ strong base

---

21) 0.100 M $HC_3H_5O_2$ $K_a = 1.3 \times 10^{-5}$

a) weak acid: $HC_3H_5O_2 \rightleftharpoons H^+ + C_3H_5O_2^-$

I	0.100M	~0	0
C	-x	+x	+x
E	0.100-x	x	x

$K_a = 1.3 \times 10^{-5} = \dfrac{[H^+][C_3H_5O_2^-]}{[HC_3H_5O_2]} = \dfrac{x^2}{0.100-x} \approx \dfrac{x^2}{0.100}$

$x = 1.1 \times 10^{-3} M$ assump. is good.

$[H^+] = x = 1.1 \times 10^{-3} M$ $-\log[H^+] = pH$ $\boxed{pH = 2.96}$

Use this b/c OH^- in rxn, not H^+!

b) $\cancel{Na}\{C_3H_5O_2$: Salt!

$\cancel{SB}$ $\overset{\checkmark}{WA}$

$C_3H_5O_2^- + H_2O \rightleftharpoons HC_3H_5O_2 + OH^-$
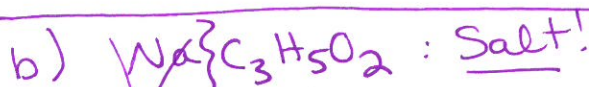
$K_b = \dfrac{K_w}{K_a} = \dfrac{1.0 \times 10^{-14}}{1.3 \times 10^{-5}}$

I	0.100M	0	0
C	-x	+x	+x
E	0.100M-x	x	x

$K_b = 7.7 \times 10^{-10} = \dfrac{x^2}{0.100-x} \approx \dfrac{x^2}{0.100}$

$x = 8.8 \times 10^{-6} M$ Assump. is good. $[OH^-] = x = 8.8 \times 10^{-6} M$

$pOH = 5.06 \rightarrow \boxed{pH = 8.94}$

c) pure H_2O: $[H+] = [OH-] = 1.0 \times 10^{-7} M$ $\boxed{pH = 7.00}$

---

d) *This is a buffer solution!

$HC_3H_5O_2 \rightleftharpoons H^+ + C_3H_5O_2^-$

I	0.100 M	~0	0.100 M
C	$-x$	$+x$	$+x$
E	$0.100-x$	x	
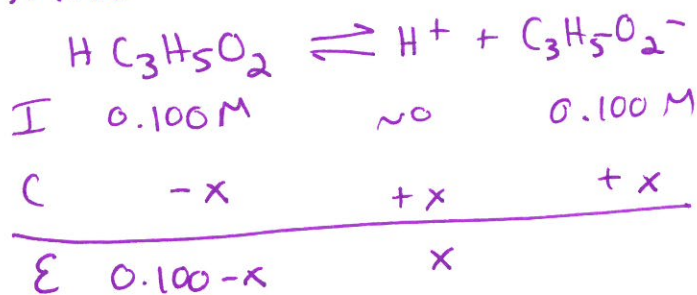
$K_a = 1.3 \times 10^{-5} \approx \dfrac{(0.100) x}{(0.100)}$

Assump. is good.

$x = [H+] = 1.3 \times 10^{-5} M$

$\boxed{pH = 4.89}$

OR Use HH equation:

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)$$

$$pH = -\log(1.3 \times 10^{-5}) + \log\left(\frac{0.100 \, m}{0.100 M}\right)$$

$\overset{C_3H_5O_2^-}{\nwarrow}$

$\underset{HC_3H_5O_2}{\swarrow}$

$\boxed{pH = 4.89}$

---

23)   a) 0.100 M $HC_3H_5O_2$ % diss $= \dfrac{[H+]}{[HC_3H_5O_2]_I} \times 100 = \dfrac{1.1 \times 10^{-3} M}{0.100 M} \times 100$

$\boxed{= 1.1\%}$

d) 0.100 M $HC_3H_5O_2$ +

0.100 M $NaC_3H_5O_2$

% diss $= \dfrac{1.3 \times 10^{-5}}{0.100} \times 100 = $
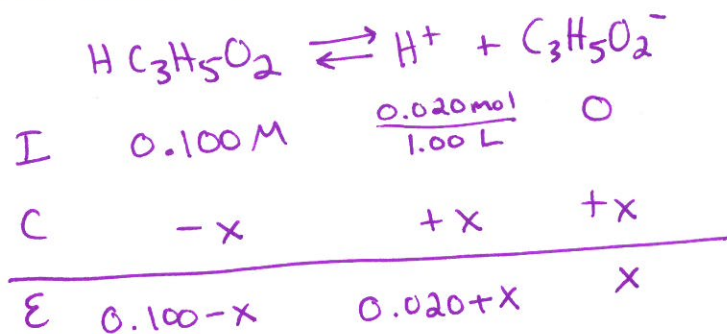
$\boxed{1.3 \times 10^{-2}\%}$

The percent dissociation decreases when $C_3H_5O_2^-$ is present. This is due to the common ion effect.

25) a & b only

a) H^+, Cl^-, $HC_3H_5O_2$

↳ Will react 1st... but nothing for it to react w/.

So start w/ the weak acid.

$$HC_3H_5O_2 \rightleftarrows H^+ + C_3H_5O_2^-$$

	$HC_3H_5O_2$	H^+	$C_3H_5O_2^-$
I	0.100 M	$\frac{0.020 mol}{1.00 L}$	0
C	$-x$	$+x$	$+x$
E	$0.100-x$	$0.020+x$	x

$$Ka = \frac{(0.020 + x)(x)}{(0.100 - x)} = 1.3 \times 10^{-5}$$

$$x = 6.5 \times 10^{-5}$$

assump. is good.

$$[H+] = 0.020 + (6.5 \times 10^{-5})$$
$$-\log [H+] = \boxed{pH = 1.70}$$

---

b) H^+, Cl^-, Na^+, $C_3H_5O_2^-$

H^+ will react w/ $C_3H_5O_2^-$ until one is used up.

$$H^+ + C_3H_5O_2^- \rightarrow HC_3H_5O_2$$

	H^+	$C_3H_5O_2^-$	$HC_3H_5O_2$
I	$\frac{0.020 mol}{1.00 L}$	0.100 M	0
C	-0.020	-0.020	$+0.020$
E	0	0.080 M	0.020
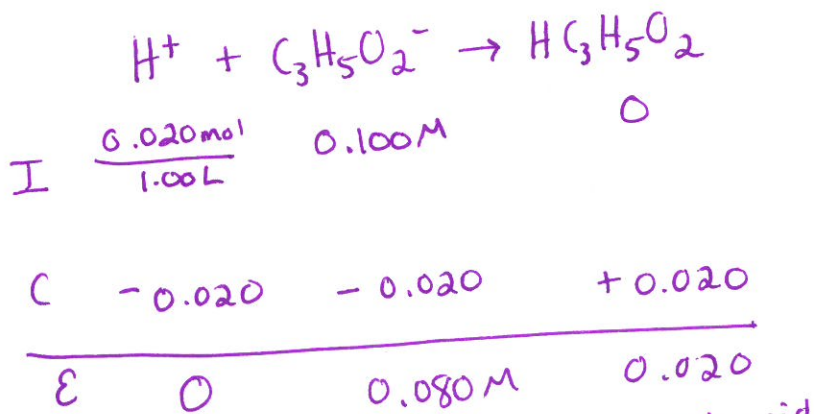
0.080 M → conj. base
0.020 → weak acid

So Buffer! use HH eqn.

~~$Kb = \frac{[\ ][\ ]}{[\ ][\ ]}$~~

~~$Kb = \frac{[\ ][\ ]}{[\ ][\ ]}$~~

~~$Kb = 7.7 \times 10^{-10}$~~

$$pH = pKa + \log \left(\frac{[A^-]}{[HA]} \right)$$

$$pH = -\log (1.3 \times 10^{-5}) + \log \left(\frac{0.080 M}{0.020 M} \right)$$

$$\boxed{pH = 5.49}$$

31) Major Species: HNO_2, NO_2^-, Na^+. Na^+ will do nothing.

$$HNO_2 \rightleftharpoons NO_2^- + H^+$$

I	1.00 M	1.00 M	~0
C	−x	+x	+x
E	1.00−x	1.00+x	x
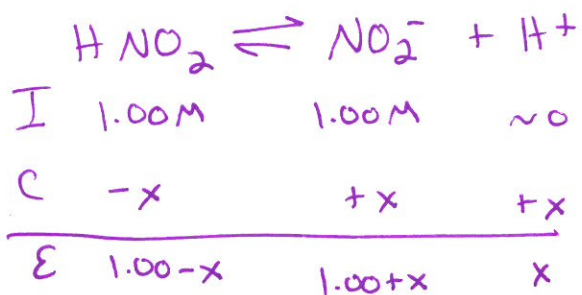
$$K_a = 4.0 \times 10^{-4} = \frac{(1.00+x)(x)}{(1.00-x)}$$

$x = 4.0 \times 10^{-4}$ assump. is good.

$x = [H^+] = 4.0 \times 10^{-4} M$ $pH = -\log(4.0 \times 10^{-4}) = \boxed{3.40}$
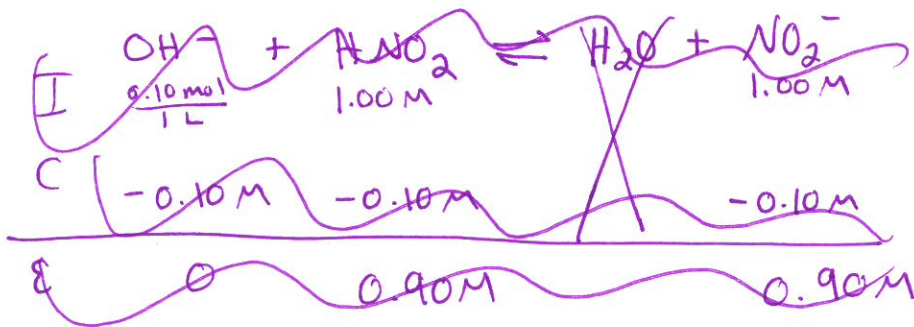
OR   HH eqn. b/c weak acid w/ its conj. base.

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right) = -\log(4.0 \times 10^{-4}) + \log\left(\frac{1.00M}{1.00M}\right)$$

$\boxed{pH = 3.40}$

zero

33) (a) 0.10 moles NaOH to 1.00 L of 1.00M HNO_2 & 1.00 M $NaNO_2$

Na^+, OH^-, HNO_2, NO_2^-

start w/ this & use up

$$OH^- + HNO_2 \rightleftharpoons H_2O + NO_2^-$$

I	$\frac{0.10 \text{ mol}}{1 L}$	1.00 M		1.00 M
C	−0.10 M	−0.10 M		−0.10 M
E	0	0.90 M		0.90 M

Now: Buffer! So use HH

$$pH = -\log(4.0 \times 10^{-4}) + \log\left(\frac{0.90M}{0.90M}\right)$$

$$pH = 3.40$$

35)
a) Use HH

$$pH = pKa + log\left(\frac{[A^-]}{[HA]}\right) = -log(1.8 \times 10^{-5}) + log\left(\frac{0.25}{0.10}\right)$$

$$pH = 5.14$$

---

37) $21.5g \; HC_7H_5O_2$, $37.7g \; Na(C_7H_5O_2)$ in 200 mL

SB ✗? WA ↗ ✓

$$\frac{21.5g \; HC_7H_5O_2}{} \left| \frac{1 \, mol}{122g} \right. = \frac{0.176 \, mol}{0.2 L} = 0.88 M \; HC_7H_5O_2$$

$$\frac{37.7g \; C_7H_5O_2^-}{} \left| \frac{1 \, mol}{121g} \right. = \frac{0.312 \, mol}{0.2 L} = 1.56 M \; C_7H_5O_2^-$$

Buffer! So HH or ICE

$$pH = -log(6.4 \times 10^{-5}) + log\left(\frac{1.56}{0.88}\right)$$

$$pH = 4.44$$

---

39) a) $[H^+]$ added $= \frac{0.010 \, mol}{0.25 L} = 0.040 M$

The added H^+ reacts completely w/ NH_3.

$$NH_3 + H^+ \rightleftharpoons NH_4^+$$

	Before		
Before	0.050	0.040	0.15 M
Δ	-0.040	-0.040	+0.040
after	0.010	0	0.190

Now Buffer!

$$pH = -log(5.6 \times 10^{-10}) + log\left(\frac{0.010}{0.19}\right)$$

$$pH = 7.97$$

43) a only

$$C_5H_5NH^+ \rightleftharpoons H^+ + C_5H_5N \qquad K_a = \frac{k_w}{k_b} = \frac{1.0 \times 10^{-14}}{1.7 \times 10^{-9}}$$
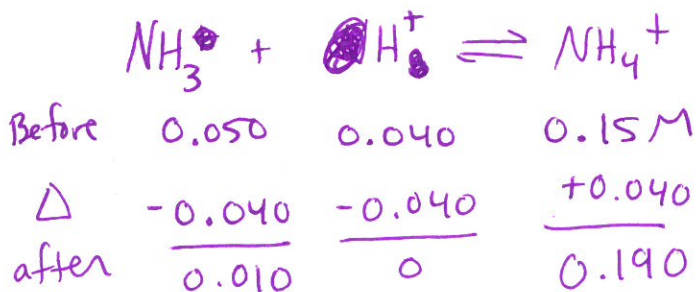
$$K_a = 5.9 \times 10^{-6}$$

a) $pH = pk_a + \log\left(\frac{[A^-]}{[HA]}\right)$

$$pk_a = -\log k_a = 5.23$$

$$4.50 = 5.23 + \log\left(\frac{[C_5H_5N]}{[C_5H_5NH^+]}\right)$$

$$\log\left(\frac{[C_5H_5N]}{[C_5H_5NH^+]}\right) = -0.73$$

$$\text{ratio} = 10^{-0.73} = \boxed{0.19}$$

---

45) $pH = pk_a + \log\left(\frac{[A^-]}{[HA]}\right)$

$$7.40 = -\log(4.3 \times 10^{-7}) + \log\left(\frac{X}{(0.0012)}\right)$$

$$1.03 = \log\left(\frac{X}{0.0012}\right)$$

$$10^{1.03} = \frac{X}{0.0012} \qquad X = \boxed{0.013 \, M \, HCO_3^-}$$

55)

↑ pH

(f) all points after stoichiometric point

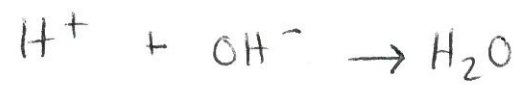(a) and (e)

(c)

(d)

(b)

— mL base →
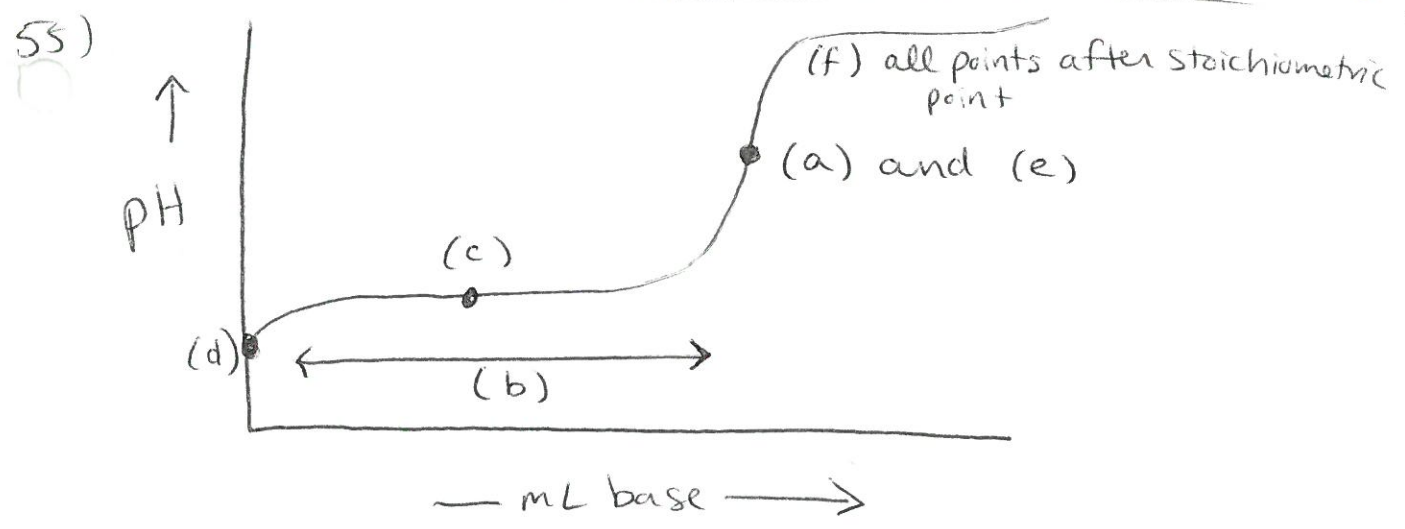
57) Strong acid: $HClO_4$ titrated w/ strong base: KOH. The added OH^- will react completely w/ H^+ to make H_2O.

a) Only strong acid present: $[H^+] = 0.200 \, M$, $\boxed{pH = 0.699}$

b) mmol OH^- added = $10.0 \, mL \times \dfrac{0.100 \, mmol \, OH^-}{mL} = 1.00 \, mmol \, OH^-$

mmol H^+ present = $40.0 \, mL \times \dfrac{0.200 \, mmol \, H^+}{mL} = 8.0 \, mmol \, H^+$

side note

$\left[\;(mmol \text{ are sometimes easier to work w/ than moles.})\;\right.$

$\dfrac{mol}{L} = \dfrac{mmol}{mL}$ $\left.\right]$

$$H^+ \;+\; OH^- \longrightarrow H_2O$$

Before   8.00 mmol   1.00 mmol
~~Absa~~ Δ −1.00 mmol −1.00 mmol
After ~~Change~~ ──────────────────
          7.00 mmol   0

The excess H^+ determines pH.

$[H^+]_{excess} = \dfrac{7.00 \, mmol \, H^+}{40.0 \, mL + 10.0 \, mL} = 0.140 \, M$

$\boxed{pH = 0.854}$

c. mmol OH^- added = $40.0 \, mL \times 0.100 \, M$
                    $= 4.00 \, mmol \, OH^-$

$$H^+ \;+\; OH^- \longrightarrow H_2O$$

Before   8.00 mmol   4.00 mmol
After   4.00 mmol   0

$[H^+]_{excess} = \dfrac{4.00 \, mmol}{(40.0 + 40.0) \, mL} = 0.05_0$

$\boxed{pH = 1.301}$

57) d) mmol OH⁻ ⇒ $80.0 \text{mL} \times 0.100 \text{M} = 8.00 \text{mmol OH}^-$.

This is the equivalence point b/c just enough base has been added to react w/ all acid present. For S.A., S.B. titration, $\boxed{pH = 7.00}$ @ equiv. pt. b/c only neutral species are present.

e) mmol OH⁻ ⇒ $100.0 \text{mL} \times 0.100 \text{M} = 10.0 \text{mmol OH}^-$

$$H^+ + OH^- \rightarrow H_2O$$
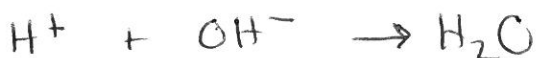
Before	8.00 mmol	10.0 mmol
After	0	2.0 mmol

Past the equiv. point, the pH is determined by excess OH⁻.

$$[OH^-]_{excess} = \frac{2.0 \text{mmol}}{(40.0 + 100.0) \text{mL}} = 0.014 \text{M} \; ; \; pOH = 1.85,$$

$$\boxed{pH = 12.15}$$

59) Weak acid ($HC_2H_3O_2$), strong base (KOH).

a) Only weak acid is present.
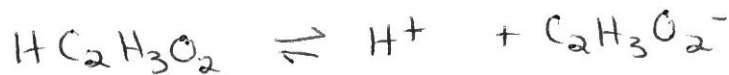
$$HC_2H_3O_2 \rightleftharpoons H^+ + C_2H_3O_2^-$$

I	0.200M	~0	0
C	-x	+x	+x
E	0.200-x	x	x

$$K_a = 1.8 \times 10^{-5} = \frac{x^2}{0.200-x} \approx \frac{x^2}{0.200}$$
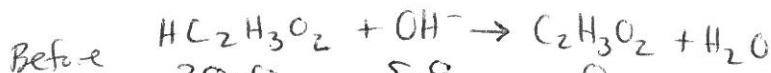
$$x = 1.9 \times 10^{-3} \text{M}$$

assumption is good.

$$x = [H^+] = 1.9 \times 10^{-3} \text{M}, \; \boxed{pH = 2.72}$$

b) Added OH⁻ will react completely w/ $HC_2H_3O_2$.

$$\text{mmol } HC_2H_3O_2 = 100.0 \text{mL} \times \frac{0.200 \text{mmol}}{\text{mL}} = 20.0 \text{mmol } HC_2H_3O_2$$

$$\text{mmol } OH^- = 50.0 \text{mL} \times \frac{0.100 \text{mmol}}{\text{mL}} = 5.00 \text{mmol } OH^-$$

$$HC_2H_3O_2 + OH^- \rightarrow C_2H_3O_2 + H_2O$$

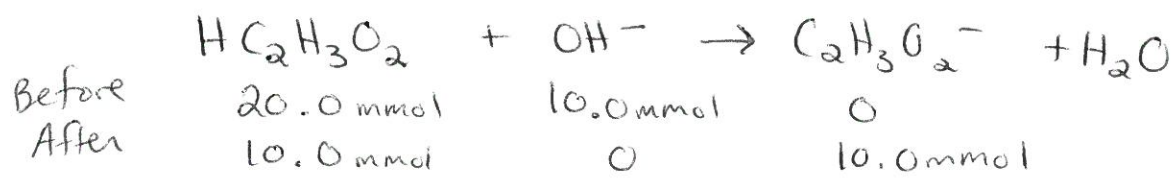|			
Before	20.0	5.0	0
After	-5.0	-5.0	+5.0
	15.0 mmol	0	5.0

→ After = Buffer! Use Henderson-Hasse

$$pH = pKa + \log \frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]} = -\log(1.8 \times 10^{-5}) + \log\left(\frac{5.00 \text{ mmol}/V_T}{15.0 \text{ mmol}/V_T}\right)$$

↑ total volume

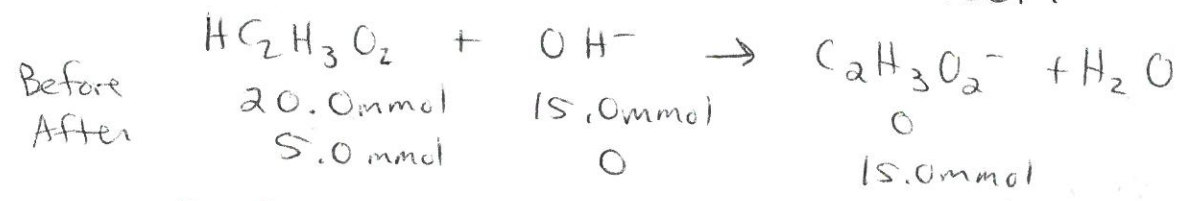$$pH = 4.74 + \log\left(\frac{5.00}{15.0}\right) = 4.74 + (-0.477)$$

$$\boxed{pH = 4.26}$$

c) mmol OH$^-$ added $= 100.0$ mL $\times 0.100$ mmol OH$^-$/mL $= 10.0$ mmol OH$^-$

$$HC_2H_3O_2 + OH^- \rightarrow C_2H_3O_2^- + H_2O$$

Before   20.0 mmol   10.0 mmol   0

After   10.0 mmol   0   10.0 mmol

Buffer soln! Since $[C_2H_3O_2^-] = [HC_2H_3O_2] = 10.0$ mmol/V_T,

pH = pKa. This is always true @ the ½ way point to equivalence for a weak acid/strong base titration, pH = pKa.

$$pH = -\log(1.8 \times 10^{-5}) = \boxed{\begin{array}{c} pH = \\ 4.74 \end{array}}$$

d) mmol OH$^-$ added $= 150.0$ mL $\times 0.100$ M

$$HC_2H_3O_2 + OH^- \rightarrow C_2H_3O_2^- + H_2O$$

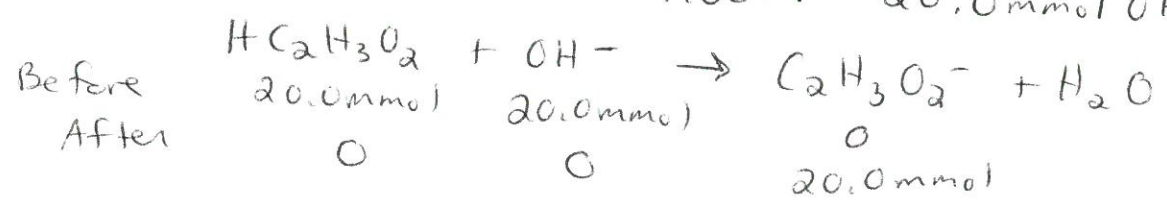Before   20.0 mmol   15.0 mmol   0

After   5.0 mmol   0   15.0 mmol

Buffer: $pH = pKa + \log \frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]} = 4.74 + \log\left(\frac{15.0 \text{ mmol}}{5.0 \text{ mmol}}\right)$

pH = 4.74 + 0.48 =

$$\boxed{pH = 5.22}$$

(Total volumes cancel)

e) mmol OH$^-$ $= 200.0$ mL $\times 0.100$ M $= 20.0$ mmol OH$^-$

$$HC_2H_3O_2 + OH^- \rightarrow C_2H_3O_2^- + H_2O$$

Before   20.0 mmol   20.0 mmol   0

After   0   0   20.0 mmol

This is the equivalence point. Enough OH$^-$ has been added to neutralize all the acid. The only thing left to affect pH is $C_2H_3O_2^-$. Weak base →

59) e) continued...

(59) $C_2H_3O_2^- + H_2O \rightleftharpoons HC_2H_3O_2 + OH^-$

$K_b = \dfrac{K_w}{K_a} = \dfrac{1 \times 10^{-14}}{1.8 \times 10^{-5}}$

I	20.0 mmol/300 mL		0	0
C	$-x$		$+x$	$+x$
E	@ $0.0667 - x$		x	x

$K_b = 5.6 \times 10^{-10}$

$K_b = 5.6 \times 10^{-10} = \dfrac{x^2}{0.0667 - x} \approx \dfrac{x^2}{0.0667}$, $x = [OH^-] = 6.1 \times 10^{-6}$ M

assumption is good. $pOH = 5.21$ $\boxed{pH = 8.79}$

---

f) mmol $OH^- \Rightarrow 250.0$ mL $\times 0.100$ M $= 25.0$ mmol OH^-

$HC_2H_3O_2 + OH^- \rightarrow C_2H_3O_2^- + H_2O$
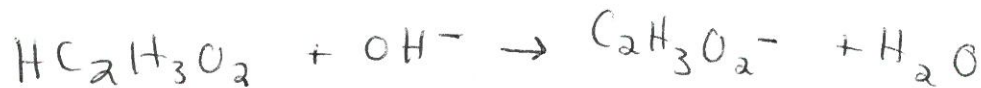
Before	20.0 mmol	25.0 mmol	0
After	0	5.0 mmol	20.0 mmol

We have 2 bases left: OH^- & $C_2H_3O_2^-$. Assume pH is mainly from strong base.

$[OH^-]_{excess} = \dfrac{5.0 \text{ mmol}}{100.0 \text{ mL} + 250.0 \text{ mL}} = 0.014$ M $pOH = 1.85$

$\boxed{pH = 12.15}$

---

65) a) weak acid/strong base. At the $\frac{1}{2}$ way point to equivalence, [weak acid] = [conj. base], so $pH = pK_a$

$pH = -\log(6.4 \times 10^{-5}) = \boxed{4.19}$

~~mmol of HC_7H_5O present =~~

(65)

mmol $HC_7H_5O_2$ present $= 100 \, mL \times 0.10M = 10.0$ mmol $HC_7H_5O_2$
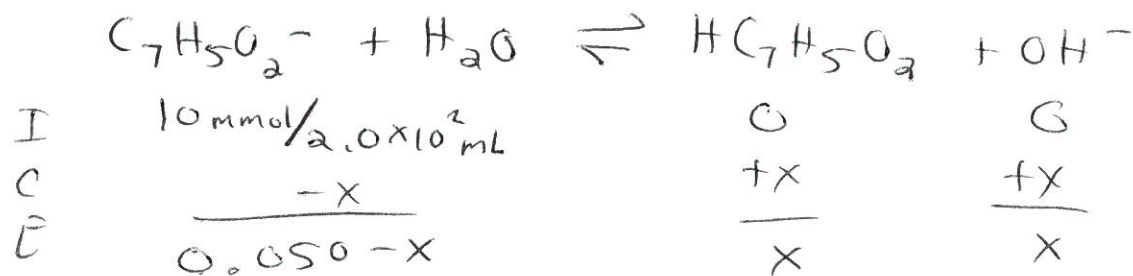
For the equiv. pt., 10.0 mmol of ~~mmol $HC_7H_5O_2$~~ OH^- must be added.

The vol. of OH^- added to reach the equiv. pt. is:

$$10.0 \, mmol \, OH^- \times \frac{1 \, mL}{0.10 \, mmol \, OH^-} = 1.0 \times 10^2 \, mL \, OH^-$$

@ the equiv. pt., $10.$ mmol of $HC_7H_5O_2$ is neutralized by $10.$ mmol of OH^- to produce $10.$ mmol of $C_7H_5O_2^-$. This is a weak base. The total vol. of soln. is

$$100.0 \, mL + (1.0 \times 10^2 \, mL) = 2.0 \times 10^2 \, mL.$$

$$C_7H_5O_2^- + H_2O \rightleftharpoons HC_7H_5O_2 + OH^-$$

	$C_7H_5O_2^-$	$HC_7H_5O_2$	OH^-
I	$10 \, mmol / 2.0 \times 10^2 \, mL$	0	0
C	$-x$	$+x$	$+x$
E	$0.050 - x$	x	x

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{6.4 \times 10^{-5}} = 1.6 \times 10^{-10} = \frac{x^2}{0.05 - x} \approx \frac{x^2}{0.05}$$

Assumption is good.

$x = [OH^-] = 2.8 \times 10^{-6} \, M$ $pOH = 5.55$

$$\boxed{pH = 8.45}$$

69)
(69)

$$HIN \rightleftharpoons In^- + H^+$$

$$K_a = \frac{[In^-][H^+]}{[HIn]} = 1.0 \times 10^{-9}$$

a) In a very acidic soln., the HIn form dominates, so the soln. would always be [yellow].

b) The color Δ occurs when the conc. of the more dominant form is $\sim 10 \times$ as great as the less dominant form of the indicator.

$$\frac{[HIn]}{[In^-]} = \frac{10}{1} ; \quad K_a = 1.0 \times 10^{-9} = \left(\frac{1}{10}\right)[H^+],$$

$$[H^+] = 1 \times 10^{-8} M \quad \boxed{pH = 8.0 \ @ \ color \ \Delta}$$

c) This is way past the equiv. point (100.0 mL OH added) so the soln. is very basic & the In^- form of indicator dominates. [Blue]

71) when choosing an indicator, we want the
(73) color Δ of the indicator to occur approximately
@ the pH of the equivalence point. Since the pH
generally changes very rapidly @ the equiv. pt.,
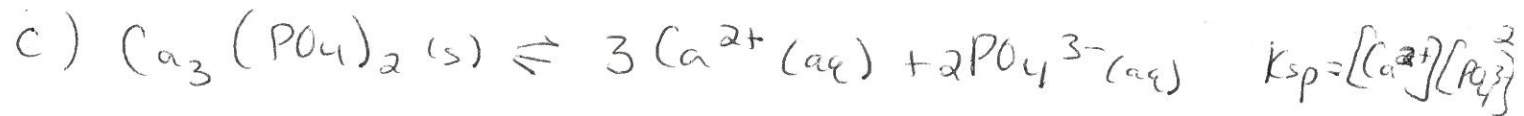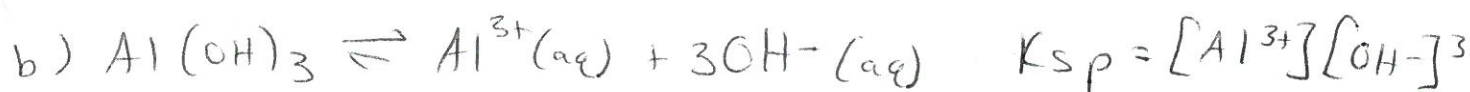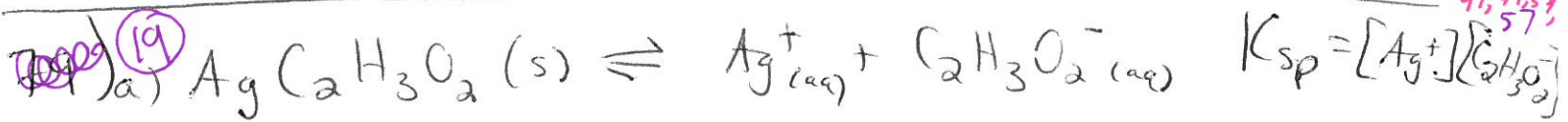we don't have to be exact. (Especially for SA/SB)

Some choices where color Δ occurs @ ~ the pH
of the equiv. point are:

Exercise	pH @ eq. pt.	Indicator
15.57	7.00	bromthymol blue or phenol red
15.59	8.79	o-cresol phthalein or phenolphthalein

---

73)

Exercise	pH @ eq. pt.	Indicator
15.61	8.28	phenolphthalein
15.63	8.28	bromcresol green

---

78) The pH will be less than ~ 0.5 since
crystal violet is yellow @ a pH < than 0.5.
The methyl orange result only tells us that
the pH is < about 3.5

---

79) a. yellow   b. green (Both yellow & blue forms are present)
c. yellow   d. blue

(p.009) (19) a) $AgC_2H_3O_2 (s) \rightleftharpoons Ag^+_{(aq)} + C_2H_3O_2^-{}_{(aq)}$ $K_{sp} = [Ag^+][C_2H_3O_2^-]$

b) $Al(OH)_3 \rightleftharpoons Al^{3+}{}_{(aq)} + 3OH^-{}_{(aq)}$ $K_{sp} = [Al^{3+}][OH^-]^3$

c) $Ca_3(PO_4)_2 (s) \rightleftharpoons 3Ca^{2+}{}_{(aq)} + 2PO_4^{3-}{}_{(aq)}$ $K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2$
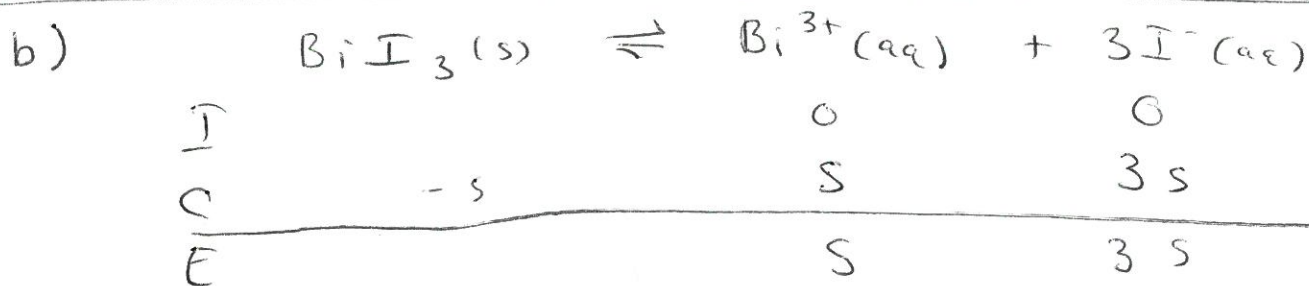
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21) a) S = solubility of the ionic solid in $^{mol}/_L$. This is defined as the max. amount of a salt that can dissolve. Since solids do not appear in the K_{sp} expression, we do not need to worry about their initial equil. amounts.

$$CaC_2O_4 (s) \rightleftharpoons Ca^{2+}{}_{(aq)} + C_2O_4^{2-}{}_{(aq)}$$

	CaC_2O_4	Ca^{2+}	$C_2O_4^{2-}$
I		0	0
C	−S	+S	+S
E		S	S
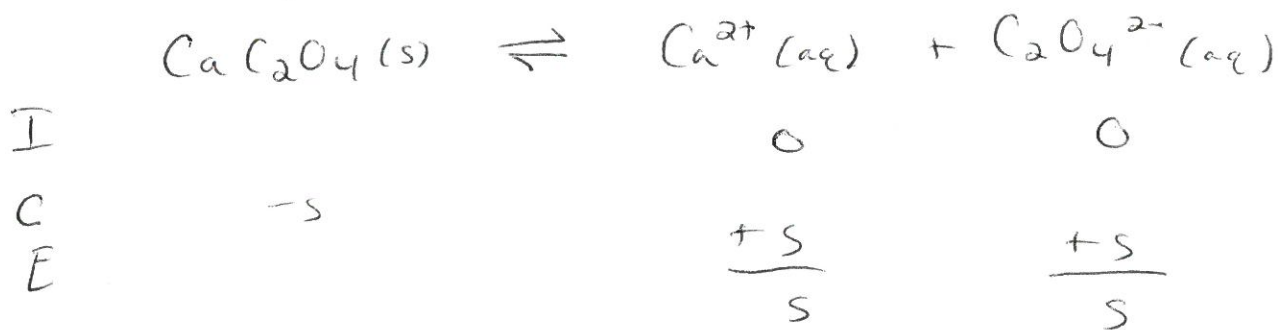
From the problem, $S = 4.8 \times 10^{-5}$ mol/L

$$K_{sp} = [Ca^{2+}][C_2O_4^{2-}] = (S)(S) = S^2$$

$$\boxed{K_{sp} = (4.8 \times 10^5)^2 = 2.3 \times 10^{-9}}$$

---

b)
$$BiI_3 (s) \rightleftharpoons Bi^{3+}{}_{(aq)} + 3I^-{}_{(aq)}$$

	BiI_3	Bi^{3+}	$3I^-$
I		0	0
C	−S	S	3S
E		S	3S

$$K_{sp} = [Bi^{3+}][I^-]^3 = (S)(3S)^3 = 27S^4,$$ $$K_{sp} = 27(1.32 \times 10^{-5})^4$$ $$\boxed{K_{sp} = 8.20 \times 10^{-19}}$$

$$PbBr_2 (s) \rightleftharpoons Pb^{2+} (aq) + 2Br^- (aq)$$
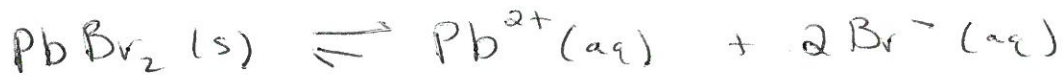
I		0	0
C		+s	+2s
E		s	2s

From the problem, $s = [Pb^{2+}] = 2.14 \times 10^{-2} M$

$$K_{sp} = [Pb^{2+}][Br^-]^2 = @ s(2s)^2 = 4s^3$$

$$K_{sp} = 4(2.14 \times 10^{-2})^3 \quad \boxed{K_{sp} = 3.92 \times 10^{-5}}$$

Let $s =$ solubility of $Co(OH)_3$ in mol/L. (from H_2O)

$$Co(OH)_3 (s) \rightleftharpoons Co^{3+} (aq) + 3OH^- (aq)$$

I		0	$1.0 \times 10^{-7} M$
C		+s	+3s
E		s	$(1.0 \times 10^{-7}) + 3s$

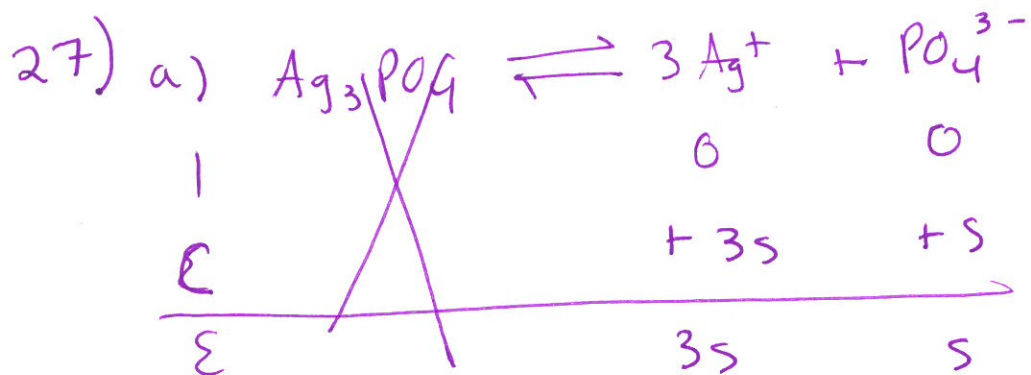$$K_{sp} = 2.5 \times 10^{-43} = [Co^{3+}][OH^-]^3 = (s)(1.0 \times 10^{-7} + 3s)^3$$
$$\approx s(1.0 \times 10^{-7})^3$$

$$\boxed{s = \frac{2.5 \times 10^{-43}}{1.0 \times 10^{-21}} = 2.5 \times 10^{-22} \, mol/L} \quad \text{Assumption is } \underline{good}$$

Since both solids dissolve to produce 3 ions in solution, we can just compare values of K_{sp} to determine relative molar solubility. The K_{sp} for CaF_2 is smaller ~~so~~ so $CaF_2 (s)$ is less soluble (in mol/L).
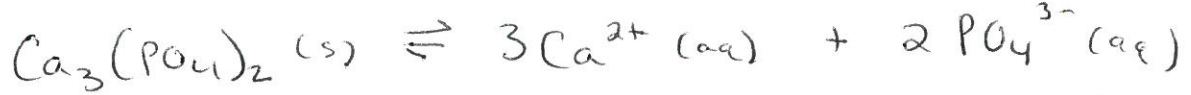
27) a) $Ag_3PO_4 \rightleftharpoons 3Ag^+ + PO_4^{3-}$

		$3Ag^+$	PO_4^{3-}
I		0	0
C		$+3s$	$+s$
E		$3s$	s

$$K_{sp} = [Ag^+]^3[PO_4^{3-}] = (3s)^3(s) = 27s^4 = K_{sp}$$

$$1.8 \times 10^{-18} = 27s^4$$

$$\boxed{s = 1.6 \times 10^{-5} \, \text{mol}/L}$$

41)

$$Ca_3(PO_4)_2 \,(s) \rightleftharpoons 3\,Ca^{2+}\,(aq) + 2\,PO_4^{3-}\,(aq)$$

I   0   0.20 M

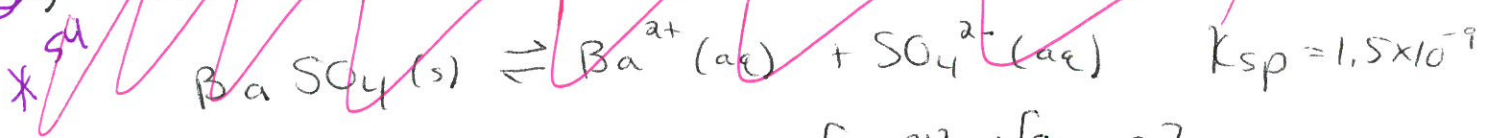C $+3s$ $+2s$

E $3s$ $0.20 + 2s$

$$K_{sp} = 1.3 \times 10^{-32} = [Ca^{2+}]^3 [PO_4^{3-}]^2 = (3s)^3 (0.20 + 2s)^2$$

Assuming $0.20 + 2s \approx 0.20$: $1.3 \times 10^{-32} = (3s)^3 (0.20)^2$

$$= 27 s^3 (0.040)$$

$\boxed{s = \text{molar solubility} = 2.3 \times 10^{-11} \,\text{mol/L}}$

(Assumption is g<u>oo</u>d.)

---

42) Potentially, $BaSO_4\,(s)$ could form if $Q > K_{sp}$.

$$BaSO_4\,(s) \rightleftharpoons Ba^{2+}\,(aq) + SO_4^{2-}\,(aq) \qquad K_{sp} = 1.5 \times 10^{-9}$$

To calc. Q, we need initial $[Ba^{2+}]$ & $[SO_4^{2-}]$.

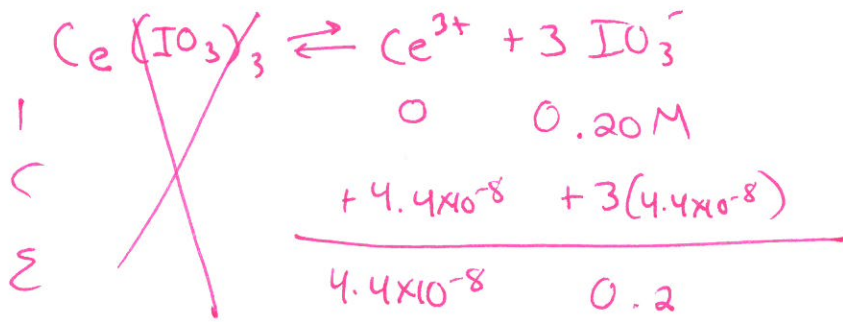$$[Ba^{2+}]_{Initial} = \frac{\text{mmol } Ba^{2+}}{\text{total mL soln.}} = \frac{75.0\,mL \times \frac{0.020\,mmol\ Ba^{2+}}{mL}}{75.0\,mL + 125\,mL} = 0.0075\,M$$

$$[SO_4^{2-}]_{Initial} = \frac{\text{mmol } SO_4^{2-}}{\text{total mL soln.}} = \frac{125\,mL \times \frac{0.040\,mmol\ SO_4^{2-}}{mL}}{200.\,mL} = 0.025\,M$$

$$Q = [Ba^{2+}]_I [SO_4^{2-}]_I = (0.0075\,M)(0.025\,M) = 1.9 \times 10^{-4}$$

$\boxed{Q > K_{sp} \text{, so } BaSO_4\,(s) \underline{\text{will}} \text{ form.}}$

$\underset{\uparrow}{}$
1.5×10^{-9}

43) Solubility $(x) = 4.4 \times 10^{-8} M$

$$Ce(IO_3)_3 \rightleftharpoons Ce^{3+} + 3\,IO_3^-$$

I		0	0.20 M
C		$+4.4\times10^{-8}$	$+3(4.4\times10^{-8})$
E		4.4×10^{-8}	0.2

$$K_{sp} = (4.4\times10^{-8})(0.2)^3 = \boxed{3.52\times10^{-10}}$$

---

45) 27) a) Ag_3PO_4 28) a) $Pb\cancel{X}_2$ (HI is a strong acid.)
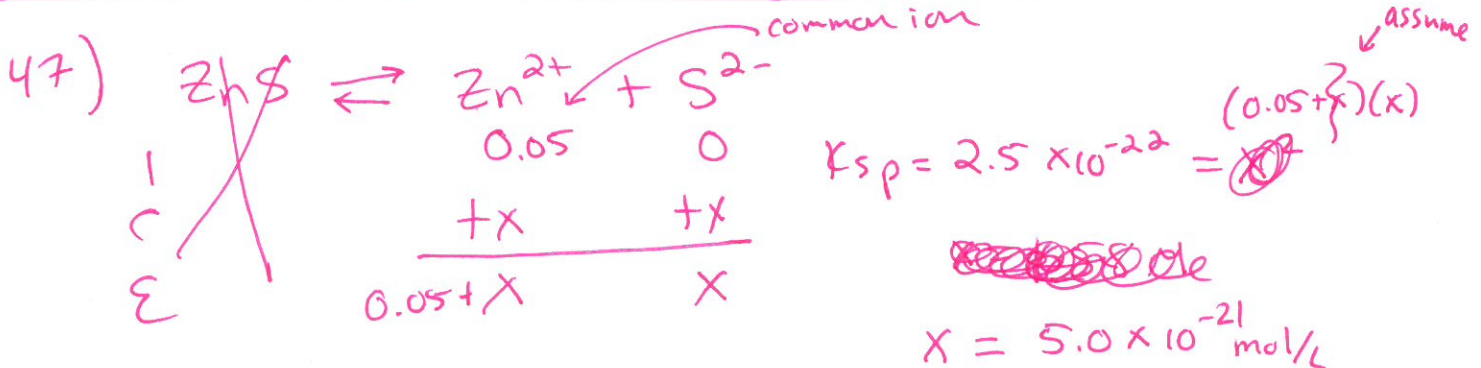
   b) $CaCO_3$ b) $CdCO_3$

   c) $\cancel{Hg_2Cl_2}$ c) $Sr_3(PO_4)_2$

   ↓

   H^+ would try to
   bond to Cl^-, which
   would form HCl. Strong
   acid, so breaks apart. So Cl^- wouldn't
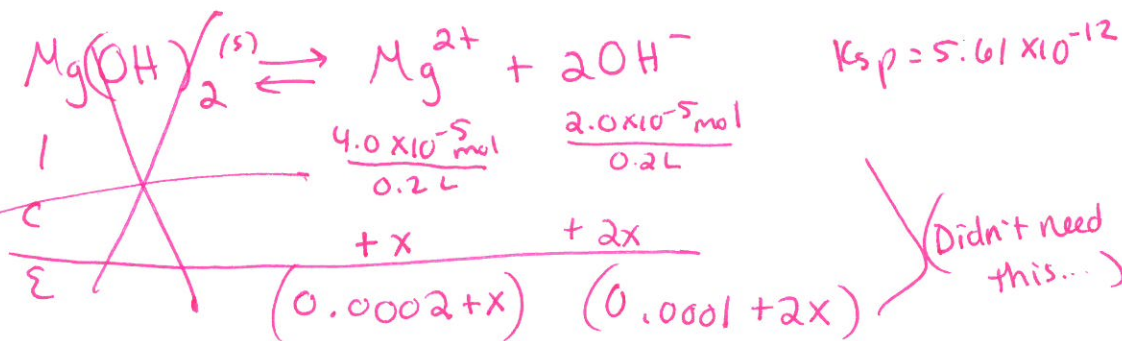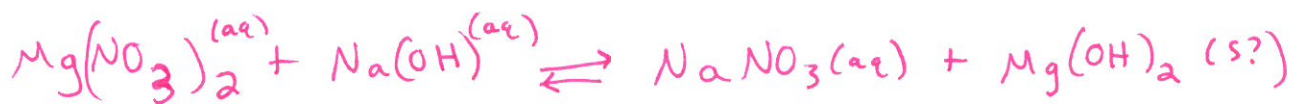   get used up.

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47) $$ZnS \rightleftharpoons \underset{\text{common ion}}{Zn^{2+}} + S^{2-}$$

I		0.05	0
C		$+x$	$+x$
E		$0.05+x$	x

$$K_{sp} = 2.5\times10^{-22} = \overset{\text{assume}}{(0.05+x)(x)}$$

$$X = 5.0\times10^{-21}\,mol/L$$

$$\frac{5.0\times10^{-21}\,mol\,\cancel{S^{2-}}}{\cancel{L}} \bigg| \frac{1\,mol\,ZnS}{1\,mol\,\cancel{S^{2-}}} \bigg| \frac{0.300\cancel{L}}{} \bigg| \frac{97.44g\,ZnS}{1\,mol\,ZnS} =$$

$$\boxed{1.5\times10^{-19}\,g\,ZnS}$$

49) $(0.100 L)(4.0 \times 10^{-4} \text{mol}/L) = 4.0 \times 10^{-5} \text{mol } Mg(NO_3)_2$

$(0.100 L)(2.0 \times 10^{-4} \text{mol}/L) = 2.0 \times 10^{-5} \text{mol } NaOH$

$$Mg(NO_3)_2^{(aq)} + Na(OH)^{(aq)} \rightleftharpoons NaNO_3(aq) + Mg(OH)_2 (s?)$$

$$Mg(OH)_2^{(s)} \rightleftharpoons Mg^{2+} + 2OH^- \qquad Ksp = 5.61 \times 10^{-12}$$

I

~~$\frac{4.0 \times 10^{-5} \text{mol}}{0.2 L}$~~ $\quad$ ~~$\frac{2.0 \times 10^{-5} \text{mol}}{0.2L}$~~

C

E $\quad$ $+x \quad\quad +2x$ $\quad$ (Didn't need this...)

$\overline{\quad (0.0002+x) \quad (0.0001+2x) \quad}$

~~Ksp = 5.61 × 10⁻¹² = (0.0002 + x)(0.0001 + 2x)²~~

$Q = (0.0002)(0.0001)^2$

$Q = 2.0 \times 10^{-12}$

$Q < K$ so shift right. No ppt.

---

51) $(.100 L)(1.0 \times 10^{-2} M) = (1.0 \times 10^{-3} M) \, Pb(NO_3)_2$

$(.100 L)(1.0 \times 10^{-3} M) = 1.0 \times 10^{-4} M \, NaF$

$$PbF_2 \rightleftharpoons Pb^{2+} + 2F^-$$

$Q = [Pb^{2+}][F^-]^2$

$\quad = (1.0 \times 10^{-3} M)(1.0 \times 10^{-4})^2$

$Q = 1.0 \times 10^{-11}$

$Q < K$ so shift right. No ppt. PbF_2 will not form.

57) $Ag_3PO_4(s) \rightleftharpoons 3 Ag^+(aq) + PO_4^{3-}(aq).$
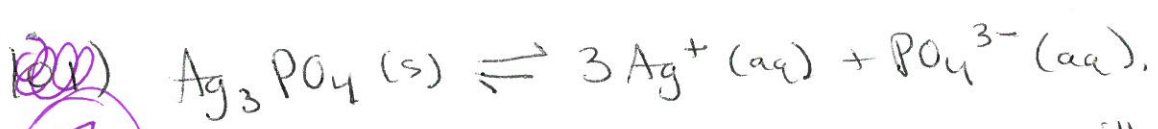
When $Q > K_{sp}$, ppt will occur. We will calc. the $[Ag^+]_0$ necessary for $Q = K_{sp}$. Any $[Ag^+]_0$ greater than this calc. # will cause ppt of $Ag_3PO_4(s)$.

In this problem, $[PO_4^{3-}]_0 = [Na_3PO_4]_0 = 1.0 \times 10^{-5} M.$

$K_{sp} = 1.8 \times 10^{-18}; \quad Q = 1.8 \times 10^{-18} = [Ag^+]_0^3 [PO_4^{3-}]_0 =$

$$[Ag^+]_0^3 (1.0 \times 10^{-5} M)$$

$$[Ag^+]_0 = \left(\frac{1.8 \times 10^{-18}}{1.0 \times 10^{-5}} \right)^{1/3}, \quad \boxed{[Ag^+]_0 = 5.6 \times 10^{-5} M}$$