Practice problems6 from week 5:

Solutions:

1) We can start off by writing the $K_{sp}$ equilibrium equation for AgCl  (The precipitate that will eventually form is AgCl, right?).

let x = [Cl⁻] added. (we're using ICE as usual):

$$AgCl(s) <===> Ag^+ \quad + \quad Cl^- \qquad\qquad K_{sp} =[Ag^+][Cl^-] = 1.8x10^{-10}$$
$$1.50x10^{-6} \qquad x$$

At the first point of precipitation, we'll just have reached a saturated solution, beyond which precipitation will occur.  So we calculate x for a saturated solution, OK?

$$K_{sp} =[Ag^+][Cl^-] = 1.8x10^{-10} = (1.50x10^{-6})( x)$$
$$=> x = ( 1.8x10^{-10} )/(1.50x10^{-6}) = 1.2 \ x \ 10^{-4} \ M = [Cl^-] = [NaCl]$$

So how many grams of NaCl would that be?  (this is a typical Chem 101 unit conversion problem, where unk = given x conversion factors)

$$\#mg \ NaCl = (600.mL)x\frac{1L}{1000mL}x\frac{1.2x10^{-4} \, mol \ NaCl}{1 \ L}x\frac{58.5g \ NaCl}{mole \ NaCl}x\frac{1000 \ mg}{g} = 4.21 \ mg$$

2) a) $HNO_3$ is a strong acid.  For this, pH = -log[strong acid]

or, $[HNO_3] = 10^{-pH} = 10^{-1.70} = 0.0200 \ M$

b) This part suggests that a buffer may be forming.  We need to ascertain that we have both conjugate acid and base of procaine co existing in solution.  So we can "follow the moles":   $n^o_{procaine} = 100.0mL(.020M)=2.0 \ mmol. \ n^o_{HNO_3} = 50.0mL(.0200M)=1.0mmol$
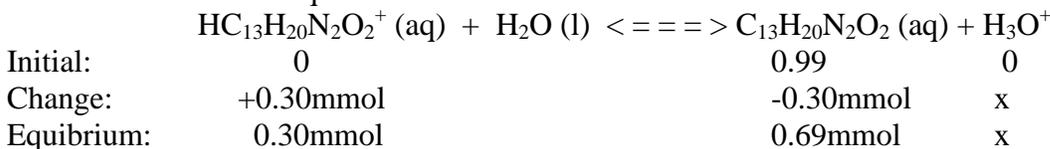
Aha!  If we add 1.0 mmol $HNO_3$  , it will convert half of the procaine to its conjugate acid,  and you know that a buffer with equal amounts of the weak acid and its conjugate base will have a pH = $pK_a$ ,  OK, so what is the $pK_a$=?

We're given $K_b$ so we can get $pK_b$ and subtract that from 14.00 OR, we can get $K_a$ and get $pK_a$ from that.  Let's do the former:  $pK_b = -log(7.1 \ x \ 10^{-6}) = 5.15$

and so, $pK_a = 14.00 – 5.15 = 8.85$

c) OK.  This problem is given just so you know what to do if it were a more general case than in b):

We'd  need to do ICE, following the moles is easier, since the buffer equation is dependent on the ratios of moles of base to moles of acid anyway (remember that the ratio of moles to moles is the same as molarity to molarity if we are talking about the same solution  - the volume is the same for both the base and the acid).  So we can "follow the moles":    It's more convenient to use the $K_a$ equilibrium since eventually that's what the buffer equation was derived from:

$$HC_{13}H_{20}N_2O_2^+ (aq) \ + \ H_2O \ (l) \ <===> C_{13}H_{20}N_2O_2 \ (aq) + H_3O^+$$

| | | | |
|---|---|---|---|
| Initial: | 0 | 0.99 | 0 |
| Change: | +0.30mmol | -0.30mmol | x |
| Equibrium: | 0.30mmol | 0.69mmol | x |

$n^o_{Proc} = 34.0mL(.029 \ M)= 0.99 \ mmol \ ; \ n^o_{HNO_3}= 15.0 \ mL(.020M)=0.30 \ mmol.$

So the resulting moles of base and acid forms of procaine are:

$$n_{Proc} = n^o_{HProc} - n^o_{HNO_3} = 0.99 \ mmol – 0.30 \ mmol = 0.69 \ mmol$$

$n_{HProc}$ = 30 mmol

so that the pH = $pK_a$ + log $\dfrac{69 \text{ mmol}}{30 \text{mmol}}$ = 8.85 + log (2.3)= 8.85+.36 = 9.21

Does this number make sense?  Yes because it is slightly more basic than 8.85. We still have more base than acid in the solution….

3) For this buffer, you need to determine the correct ratio of base to acid then, by using the solution concentration, calculate the moles needed for each and then from that you can decide on the volume of glacial acetic acid and grams of sodium acetate to use to make your final solution.

From the buffer equation, you have:

pH = $pK_a$ + log $\dfrac{[A^-]}{[HA]}$ => $pK_a$= (-log1.78x10$^{-5}$) = 4.750

and, $\dfrac{[A^-]}{[HA]}$ = 10$^{pH\text{-}pKa}$ = 10$^{4.60-4.750}$ =10$^{-0.15}$ = 0.71

since we are given that [HA] = 0.125M, we can easily solve for [A⁻]:

$\dfrac{[A^-]}{[HA]}$ = $\dfrac{[A^-]}{.125M}$ =0.71, meaning that [A⁻] = (0.71)(0.125M)=0.088M

OK. Now, we use molarity x volume =moles, to get the moles of acetate needed:

#moles A⁻ = 0.088 M x 15.0L = 1.32 moles

#grams NaA = 1.32 mol A⁻ x $\dfrac{1 \text{ mol NaA}}{1 \text{ mol A}^-}$ x $\dfrac{82.0g}{1\text{mol NaA}}$ = 108  g NaA = 110 g NaA

How about the glacial HA?  Usually you don't weigh out liquids. Instead, you usually measure out the volume y ou need:

Again, we use molarity x volume =moles, to get the moles of glacial acetic acid needed:

#moles A⁻ = 0.125 M x 15.0L = 1.88 moles acetic acid, HA

# mL glacial HA = 1.88 mol HA x $\dfrac{60.0 \text{ g HA}}{\text{mol HA}}$ x $\dfrac{100.\text{g glacial HA}}{99.0\text{g HA}}$ x $\dfrac{1.00 \text{ mL}}{1.08 \text{ g}}$ =105 mL

OK. So how would you prepare it (at least in theory)?
Take 105 mL of glacial acetic acid , add to it 110 g sodium acetate, then make it up to volume, a total of 15.0 L.  Mix it like crazy as you add the water to make sure it's a homogeneous solution.

How does a biochemist really prepare such a solution?  Well in the first place, probably a biochemist would not need so much volume of buffer.  Secondly, even if she would need that much volume probably she would prepare a manageable amount each time because if you leave buffer hanging around guess what? Bacteria will grow on it!  And biochemists

are very conscious of living things like bacteria.  Finally, a biochemist would probably do it the "empirical way". Just calculate the total formal concentration and moles needed, then figure out how much NaA to use to achieve that formal concentration then add HCl to it while stirring the solution with a pH meter monitoring the actual pH, stopping only upon reaching the desired pH.
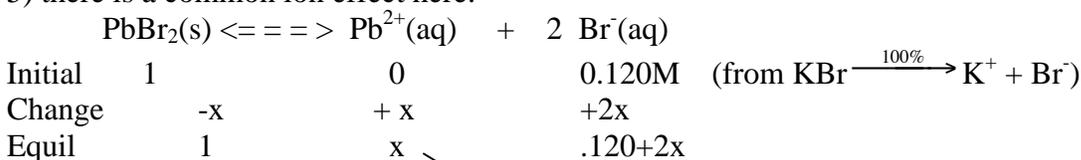
4) A) solution: $Mn(OH)_2(s) \Longleftrightarrow Mn^{2+}(aq) + 2\ OH^-(aq)$       $K_{sp} = [Mn^{2+}][OH^-]^2$
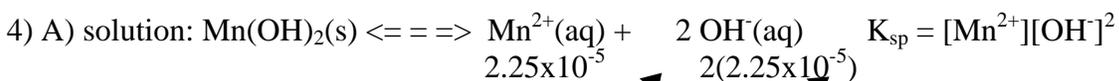
$2.25 \times 10^{-5}$       $2(2.25 \times 10^{-5})$

$[Mn(OH)_2]_{dissolved} = \dfrac{0.401 \times 10^{-3}\,g}{200.\,mL}\left(\dfrac{1 mol}{88.9 g}\right)\left(\dfrac{1000 mL}{L}\right) = 2.25 \times 10^{-5}\,M = 0.0225\ M$

$pH = 14.0 - pOH = 14.00 - (-\log(2(2.25 \times 10^{-5}))) = 9.65$

B) $K_{sp} = (2.25 \times 10^{-5})(\,2(2.25 \times 10^{-5}))^2 = 4.56 \times 10^{-14}$
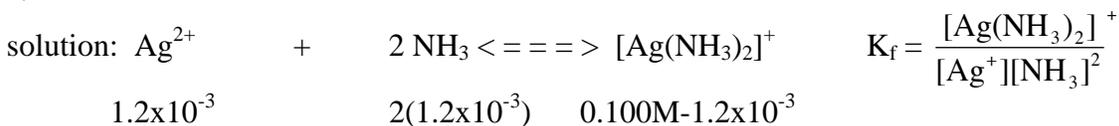
5) there is a common ion effect here.

$PbBr_2(s) \Longleftrightarrow Pb^{2+}(aq) + 2\ Br^-(aq)$

|          |    | $Pb^{2+}$ | $Br^-$ |
|----------|----|-----------|--------|
| Initial  | 1  | 0         | 0.120M  (from $KBr \xrightarrow{100\%} K^+ + Br^-$) |
| Change   | -x | + x       | +2x    |
| Equil    | 1  | x         | .120+2x |

(did you get the same thing?)
OK, now use the $K_{sp}$ equilibrium:  $K_{sp} = [Pb^{2+}][Br^-]^2 = (x)(2x+0.120)^2 = 6.3 \times 10^{-6}$
use 5% rule:  $x(.120^2) \approx 6.3 \times 10^{-6} \Rightarrow x = 4.4 \times 10^{-4}\ M$

(note: $\dfrac{4.4 \times 10^{-4} \times 100\%}{0.120} = 0.4\% < 5\%$ )  Can you imagine what a head ache this would

be to solve if we couldn't use the 5 % rule?  (if you want to try it, good luck!)
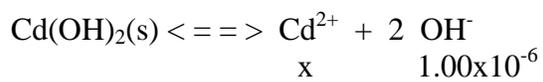
6)

solution:  $Ag^{2+} + 2\ NH_3 \Longleftrightarrow [Ag(NH_3)_2]^+$       $K_f = \dfrac{[Ag(NH_3)_2]^+}{[Ag^+][NH_3]^2}$

$1.2 \times 10^{-3}$       $2(1.2 \times 10^{-3})$    $0.100M - 1.2 \times 10^{-3}$

so $K_f = \dfrac{0.100 - 1.2 \times 10^{-3}}{(1.2 \times 10^{-3})(2.4 \times 10^{-3})^2} \approx \dfrac{0.100}{6.9 \times 10^{-9}} = 1.5 \times 10^{7}$
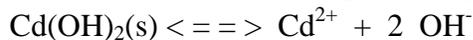
7) We can start with the $K_{sp}$ equilibrium. For that, we need the $[OH^-]$ something we can get indirectly from the pH:

$pOH = 14.0 - 8.00 = 6.00 : \ [OH^-] = 1.00 \times 10^{-6}$

$Cd(OH)_2(s) <==> Cd^{2+} + 2\ OH^-$
                    $x$          $1.00 \times 10^{-6}$

$x(1.00 \times 10^{-6})^2 = 1.2 \times 10^{-14}$ => $x = \dfrac{1.2 \times 10^{-14}}{(1.00 \times 10^{-6})^2} = 1.2 \times 10^{-2} = 0.012\ M$

b) Greater solubility:  Many ways to explain this, but a quick way would be to look at the chemical equilibrium and invoke the Le Chatelier's principle:

$Cd(OH)_2(s) <==> Cd^{2+} + 2\ OH^-$

In an acidic solution, [OH⁻] would be lower, and that would favor the product more, thus **increasing** the solubility. If pH is low enough, it would be 100% soluble.