

Assume $x \ll 0.20$ Then

$$\frac{x^2}{(0.20)} = 1.8 \times 10^{-5} ; \text{ so } x^2 = (0.20)(1.8 \times 10^{-5}) = 3.6 \times 10^{-6}$$

$$x = (3.6 \times 10^{-6})^{1/2} = 1.9 \times 10^{-3} \quad \text{pOH} = -\log_{10}(1.9 \times 10^{-3}) = 2.72$$

$$\text{pH} = 14.00 - 2.72 = 11.28$$

b) A solution that is 0.20 M in NH_3 and 0.30 in NH_4Cl .

NH_4Cl is a soluble ionic compound, so when added to water it undergoes the following reaction



Our solution initially contains 0.20 M NH_3 and 0.30 M NH_4^+ . This is a solution of a weak base and its conjugate acid, and so is a buffer solution.

The Henderson equation says $\text{pH} = \text{pK}_a + \log_{10}\{[\text{base}]/[\text{acid}]\}$

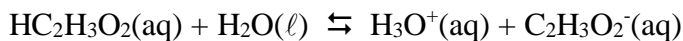
We have a value for K_b for NH_3 , and so K_a for NH_4^+ is

$$K_a = \frac{1.0 \times 10^{-14}}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

$$\text{pH} = \text{pK}_a + \log_{10}\{[\text{base}]/[\text{acid}]\} = -\log_{10}(5.6 \times 10^{-10}) + \log_{10}(0.20/0.30) = 9.08$$

3) Solve an equilibrium problem (using an ICE table) to calculate the pH of a solution that is 0.195 M in $\text{HC}_2\text{H}_3\text{O}_2$ and 0.125 M in $\text{KC}_2\text{H}_3\text{O}_2$. Note that $K_a = 1.8 \times 10^{-5}$ for $\text{HC}_2\text{H}_3\text{O}_2$.

Reaction is



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = 1.8 \times 10^{-5}$$

| | Initial | Change | Equilibrium |
|------------------------------------|---------|--------|-------------|
| $\text{HC}_2\text{H}_3\text{O}_2$ | 0.195 | - x | 0.195 - x |
| H_3O^+ | 0.0 | x | x |
| $\text{C}_2\text{H}_3\text{O}_2^-$ | 0.125 | x | 0.125 + x |

$$\frac{(x)(0.125 + x)}{(0.195 - x)} = 1.8 \times 10^{-5}$$

Assume $x \ll 0.125$. Then

$$\frac{x(0.125)}{(0.195)} = 1.8 \times 10^{-5} ; \text{ so } x = \frac{(0.195)(1.8 \times 10^{-5})}{(0.125)} = 2.81 \times 10^{-5}$$

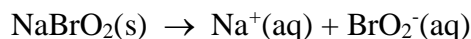
$$\text{pH} = -\log_{10}(2.81 \times 10^{-5}) = 4.55$$

Note that one could get the same result more quickly by using the Henderson equation

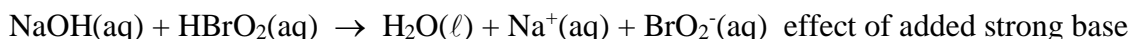
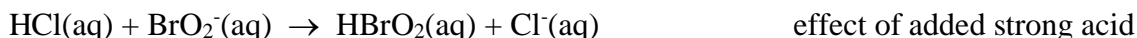
$$\text{pH} = \text{pK}_a + \log_{10}\{[\text{base}]/[\text{acid}]\} = -\log_{10}(1.8 \times 10^{-5}) + \log_{10}(0.125/0.195) = 4.54$$

4) A buffer contains significant amounts of bromous acid (HBrO_2) and sodium bromite (NaBrO_2). Write equations showing how this buffer neutralizes added acid and added base.

Bromous acid is a weak acid, and bromite ion is the conjugate base of bromous acid, and so is a weak base. It forms from the ionization of sodium bromite



Consider what happens when a strong acid (HCl) or a strong base (NaOH) is added to a solution containing the above substances.



The buffer converts HCl (a strong acid) into HBrO_2 (a weak acid), and converts NaOH (a strong base) into BrO_2^- (a weak base). By converting strong acid or base into weak acid or base the change in pH is minimized.

5) Use the Henderson-Hasselbalch equation to calculate the pH of a solution that is 0.135 M in HClO and 0.155 M in KClO . $\text{K}_a = 2.9 \times 10^{-8}$ for HClO .

The Henderson equation is

$$\text{pH} = \text{pK}_a + \log_{10}\{[\text{base}]/[\text{acid}]\}$$

$$\text{Also } \text{K}_a(\text{HClO}) = 2.9 \times 10^{-8} \quad [\text{HClO}] = 0.135 \text{ M} \quad [\text{ClO}^-] = 0.155 \text{ M}$$

$$\text{pH} = -\log_{10}(2.9 \times 10^{-8}) + \log_{10}\{(0.155)/(0.135)\} = 7.60$$

6) (17.18) Which of the following solutions can act as a buffer?

- a) KCN/HCN
b) Na₂SO₄/NaHSO₄
c) NH₃/NH₄NO₃
d) NaI/HI

a) This contains a weak acid (HCN) and its conjugate base (CN⁻), so a buffer.

b) This contains a weak acid (HSO₄⁻) and its conjugate base (SO₄²⁻), so a buffer.

c) This contains a weak base (NH₃) and its conjugate acid (NH₄⁺), so a buffer.

d) This contains a strong acid (HI) and its conjugate base (I⁻). The conjugate base of a strong acid has no acid/base properties, and so this is simply a solution of a strong acid, so not a buffer.

7) What mass of ammonium chloride (NH₄Cl) should you add to 2.55 L of a 0.155 M NH₃ solution to obtain a buffer with a pH of 9.55?

The Henderson equation is

$$\text{pH} = \text{pK}_a + \log_{10}\left\{\frac{[\text{base}]}{[\text{acid}]}\right\}$$

$K_b(\text{NH}_3) = 1.76 \times 10^{-5}$; so K_a for NH_4^+ can be found by

$$K_a K_b = 1.0 \times 10^{-14}, \text{ so } K_a(\text{C}_2\text{H}_5\text{NH}_3^+) = \frac{1.0 \times 10^{-14}}{1.76 \times 10^{-5}} = 5.68 \times 10^{-10}$$

$$9.55 = -\log_{10}(5.68 \times 10^{-10}) + \log_{10}\left\{\frac{[\text{base}]}{[\text{acid}]}\right\} = 9.25 + \log_{10}\left\{\frac{[\text{base}]}{[\text{acid}]}\right\}$$

So $\log_{10}\left\{\frac{[\text{base}]}{[\text{acid}]}\right\} = 9.55 - 9.25 = 0.30$ Take the inverse \log_{10} , to get

$$\frac{[\text{base}]}{[\text{acid}]} = 10^{0.30} = 2.00$$

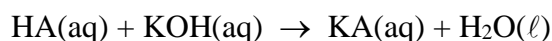
And so $[\text{acid}] = \frac{[\text{base}]}{2.00} = \frac{(0.155 \text{ M})}{2.00} = 0.0775 \text{ M}$

$M(\text{NH}_4\text{Cl}) = 53.49 \text{ g.mol}$

$$\text{So } g(\text{NH}_4\text{Cl}) = 2.55 \text{ L soln } \frac{0.0775 \text{ mol}}{1 \text{ L}} \frac{53.49 \text{ g}}{1 \text{ mol}} = 10.57 \text{ g NH}_4\text{Cl}$$

8) (17.27) A 0.2688 g sample of a monoprotic acid neutralizes 16.4 mL of a 0.08133 M solution of KOH. Find the molar mass of the acid.

The neutralization reaction is (with HA = weak monoprotic acid)



The moles of KOH is

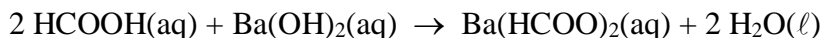
$$n(\text{KOH}) = (0.0164 \text{ L}) \frac{0.08133 \text{ mol}}{\text{L}} = 1.334 \times 10^{-3} \text{ mol}$$

Since 1 mole of HA reacts with 1 mole of KOH, this is the number of moles of HA.

Therefore $\text{MW} = \frac{0.2688 \text{ g}}{1.334 \times 10^{-3} \text{ mol}} = 201. \text{ g/mol}$

9) (17.30) In a titration experiment, 20.4 mL of a 0.833 M solution of HCOOH neutralizes 19.3 mL of a solution of Ba(OH)₂. What is the concentration of the Ba(OH)₂ solution?

The neutralization reaction is



The moles of Ba(OH)₂ is

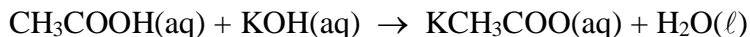
$$\begin{aligned} \text{moles Ba}(\text{OH})_2 &= 0.0204 \text{ L HCOOH} \frac{0.833 \text{ mol HCOOH}}{\text{L soln}} \frac{1 \text{ mol Ba}(\text{OH})_2}{2 \text{ mol HCOOH}} \\ &= 8.50 \times 10^{-3} \text{ mol Ba}(\text{OH})_2 \end{aligned}$$

$$[\text{Ba}(\text{OH})_2] = \frac{8.50 \times 10^{-3} \text{ mol Ba}(\text{OH})_2}{0.0193 \text{ L soln}} = 0.440 \text{ M Ba}(\text{OH})_2$$

10) For the following titrations indicate whether the pH at the equivalence point of the titration will be much larger than 7.0, approximately 7.0, or much smaller than 7.0.

a) Titration of CH₃COOH (a weak acid) with KOH (a strong soluble base).

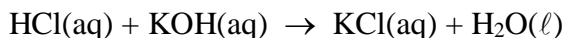
The neutralization reaction is



At the equivalence point all of the reactants will have been converted into KCH₃COO and water. K⁺ has no acid/base properties, while CH₃COO⁻ is the conjugate base of CH₃COOH, and so is a weak base. Therefore the pH will be much larger than 7.0.

b) Titration of HCl (a strong acid) with KOH (a strong soluble base).

The neutralization reaction is



At the equivalence point all of the reactants will have been converted into KCl and water. Neither K^+ nor Cl^- have any acid/base properties. Therefore the pH will be approximately 7.0.

11) Consider the titration of a 35.0 mL sample of 0.175 M HBr with a 0.200 M solution of KOH. Determine each quantity:

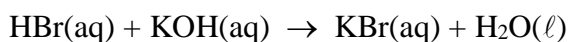
a) The initial pH

Since HBr is a strong acid

$$\text{initial } [H_3O^+] = \text{initial } [HBr] = 0.175 \text{ M, so } pH = -\log_{10}(0.175) = 0.76$$

b) The volume of added base required to reach the equivalence point

The neutralization reaction is



Since this is a 1:1 acid:base reaction, it follows that at the equivalence point moles acid = moles base

$$(35.0 \text{ ml}) (0.175 \text{ M}) = (x \text{ mL}) (0.200 \text{ M})$$

$$x = \frac{0.175 \text{ M}}{0.200 \text{ M}} (35.0 \text{ mL}) = 30.62 \text{ mL}$$

c) The pH after the addition of 10.0 mL of base

After 10.0 mL added base

$$\text{total volume} = 35.0 \text{ mL} + 10.0 \text{ mL} = 45.0 \text{ mL}$$

$$\text{initial moles acid} = (0.0350 \text{ L}) (0.175 \text{ M}) = 0.00612 \text{ mol acid}$$

$$\text{initial moles base} = (0.0100 \text{ L}) (0.200 \text{ M}) = 0.00200 \text{ mol base}$$

$$\text{moles excess acid} = 0.00612 \text{ mol} - 0.00200 \text{ mol} = 0.00412 \text{ mol}$$

$$\text{So the concentration of excess acid is } \frac{0.00412 \text{ mol}}{0.0450 \text{ L}} = 0.0916 \text{ M}$$

$$\text{Since the excess acid is a strong acid, } pH = -\log_{10}(0.0916) = 1.04$$

d) The pH at the equivalence point

At the equivalence point neutralization has occurred, and so what is present is a KBr solution, which has no acid-base properties. So the pH will be 7.0.

e) A suitable indicator for the titration (see Table 17.3)

We would like an indicator that changes color at pH ~ 7.0 (see Fig. 17.3 for an example of a titration curve for a strong acid titrated by a strong base). Suitable indicators would be methyl red (4.2-6.3), chlorophenol blue (4.8-6.4), bromothymol blue (6.0-7.6), cresol red (7.2-8.8), or phenolphthalein (8.3-10.0)

f) The pH after adding 5.0 mL of base beyond the equivalence point

$$\begin{aligned} \text{volume} &= \text{volume at equivalence} + \text{excess volume} \\ &= 35.0 \text{ mL} = 30.62 \text{ mL} + 5.0 \text{ mL} = 70.6 \text{ mL} \end{aligned}$$

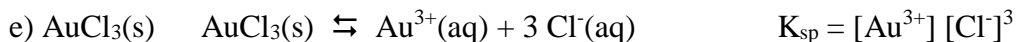
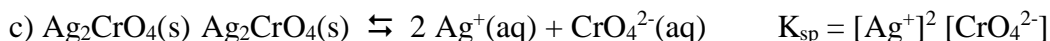
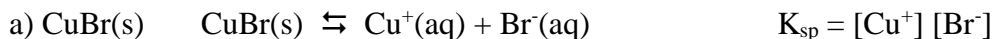
$$\text{mol excess base} = (0.005 \text{ L}) (0.200 \text{ M}) = 0.00100 \text{ mol}$$

$$\text{concentration of excess base} = \frac{0.00100 \text{ mol}}{0.0706 \text{ L}} = 0.0142 \text{ M}$$

$$\text{Since the base is strong, } \text{pOH} = -\log_{10}(\text{excess base}) = -\log_{10}(0.0142) = 1.84$$

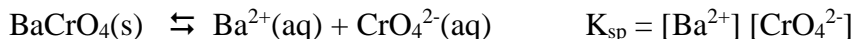
$$\text{And so } \text{pH} = 14.00 - \text{pOH} = 14.00 - 1.84 = 12.16$$

12) (17.45 a,c,e) Write balanced equations and solubility product expressions for each of the following compounds.



13) Use the given molar solubilities in pure water to calculate K_{sp} for each compound.

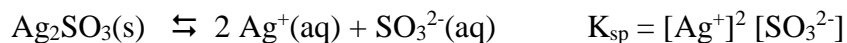
a) BaCrO₄; molar solubility = 1.08×10^{-5} M



$$[\text{Ba}^{2+}] = 1.08 \times 10^{-5} \text{ M} \quad [\text{CrO}_4^{2-}] = 1.08 \times 10^{-5} \text{ M}$$

$$K_{\text{sp}} = (1.08 \times 10^{-5})(1.08 \times 10^{-5}) = 1.17 \times 10^{-10}$$

b) Ag_2SO_3 ; molar solubility = $1.55 \times 10^{-5} \text{ M}$



$$[\text{Ag}^+] = 2 (1.55 \times 10^{-5} \text{ M}) = 3.10 \times 10^{-5} \text{ M} \quad [\text{SO}_3^{2-}] = 1.55 \times 10^{-5} \text{ M}$$

$$K_{\text{sp}} = (3.10 \times 10^{-5})^2 (1.55 \times 10^{-5}) = 1.49 \times 10^{-14}$$

c) $\text{Pd}(\text{SCN})_2$; molar solubility = $2.22 \times 10^{-8} \text{ M}$

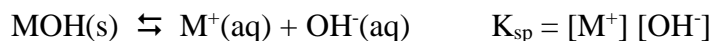


$$[\text{Pd}^{2+}] = 2.22 \times 10^{-8} \text{ M} \quad [\text{SCN}^-] = 2 (2.22 \times 10^{-8} \text{ M}) = 4.44 \times 10^{-8} \text{ M}$$

$$K_{\text{sp}} = (2.22 \times 10^{-8}) (4.44 \times 10^{-8})^2 = 4.38 \times 10^{-23}$$

14) (17.56) The pH of a saturated solution of a metal hydroxide with formula MOH is 9.68. Find K_{sp} for this compound.

The solubility reaction for this compound is



The pOH of the solution is $\text{pOH} = 14.00 - \text{pH} = 14.00 - 9.68 = 4.32$. If we assume all of the hydroxide ion comes from the metal hydroxide, then

$$[\text{M}^+] = [\text{OH}^-] = 10^{-\text{pOH}} = 10^{-4.32} = 4.8 \times 10^{-5} \text{ M}$$

$$K_{\text{sp}} = [\text{M}^+] [\text{OH}^-] = (4.8 \times 10^{-5})^2 = 2.3 \times 10^{-9}$$

15) Calculate the molar solubility of copper II sulfide (CuS) in each liquid or solution. Note that $K_{\text{sp}}(\text{CuS}) = 1.27 \times 10^{-36}$.

Note that the reaction for the dissolution of $\text{CuS}(\text{s})$ is



a) pure water

| | Initial | Change | Equilibrium |
|------------------|---------|--------|-------------|
| Cu^{2+} | 0 | x | x |
| S^{2-} | 0 | x | x |

$$(x)(x) = x^2 = 1.27 \times 10^{-36} \quad ; \quad x = (1.27 \times 10^{-36})^{1/2} = 1.13 \times 10^{-18}$$

Molar solubility is $1.13 \times 10^{-18} \text{ M}$

b) 0.25 M CuCl_2 , which gives 0.25 M Cu^{2+}

| | Initial | Change | Equilibrium |
|------------------|---------|--------|-------------|
| Cu^{2+} | 0.25 | x | $0.25 + x$ |
| S^{2-} | 0 | x | x |

$(0.25 + x)(x) = 1.27 \times 10^{-36}$ Assume $x \ll 0.25$, then

$$(0.25)(x) = 1.27 \times 10^{-36} \quad x = (1.27 \times 10^{-36})/(0.25) = 5.08 \times 10^{-36}$$

Molar solubility is 5.08×10^{-36} M

c) 0.20 M K_2S , which gives 0.20 M S^{2-}

| | Initial | Change | Equilibrium |
|------------------|---------|--------|-------------|
| Cu^{2+} | 0 | x | x |
| S^{2-} | 0.20 | x | $0.20 + x$ |

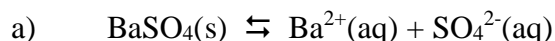
$(x)(0.20 + x) = 1.27 \times 10^{-36}$ Assume $x \ll 0.20$, then

$$(x)(0.20) = 1.27 \times 10^{-36} \quad x = (1.27 \times 10^{-36})/(0.20) = 6.35 \times 10^{-36}$$

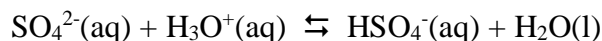
Molar solubility is 6.35×10^{-36} M

16) (17.78) Which of the following ionic compounds will be more soluble in acid solution than in water: a) BaSO_4 b) PbCl_2 c) $\text{Fe}(\text{OH})_3$ d) CaCO_3

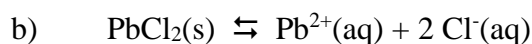
To answer this question we need to write the solubility reaction, and then see what effect, if any, increasing H_3O^+ concentration and decreasing OH^- concentration will have, based on Le Chatlier's principle.



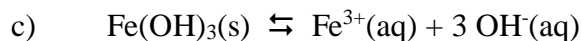
Since SO_4^{2-} will react with H_3O^+ by the process



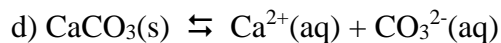
then in acid solution SO_4^{2-} will be removed by this process. Le Chatlier's principle predicts the system will respond by dissolving more BaSO_4 , so the solubility will increase.



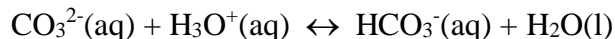
Increasing H_3O^+ concentration has no effect on this process, so no change.



In acid solution OH^- concentration will decrease. Le Chatlier's principle predicts the system will respond by dissolving more Fe(OH)_3 to oppose this decrease. So solubility will increase.



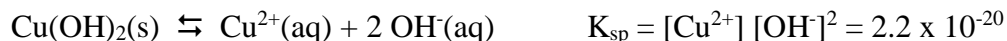
Since CO_3^{2-} will react with H_3O^+ by the process



then in acid solution CO_3^{2-} will be removed by this process. Le Chatlier's principle predicts the system will respond by dissolving more CaCO_3 , so the solubility will increase.

17) Calculate the molar solubility of copper II hydroxide (Cu(OH)_2 , $K_{sp} = 2.2 \times 10^{-20}$) in a solution buffered at each of the following values for pH.

- a) pH = 4.0 b) pH = 7.0 c) pH = 9.0



$$\text{So } [\text{Cu}^{2+}] = \frac{2.2 \times 10^{-20}}{[\text{OH}^-]^2}$$

a) pH = 4.00 ; pOH = 14.00 - 4.00 = 10.00 ; $[\text{OH}^-] = 10^{-10.00} = 1.00 \times 10^{-10}$

$$[\text{Cu}^{2+}] = \text{molar solubility} = \frac{2.2 \times 10^{-20}}{(1.0 \times 10^{-10})^2} = 2.2 \text{ M}$$

b) pH = 7.00 ; pOH = 14.00 - 7.00 = 7.00 ; $[\text{OH}^-] = 10^{-7.00} = 1.00 \times 10^{-7}$

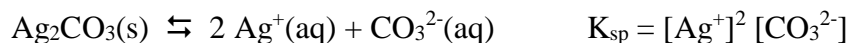
$$[\text{Cu}^{2+}] = \text{molar solubility} = \frac{2.2 \times 10^{-20}}{(1.0 \times 10^{-7})^2} = 2.2 \times 10^{-6} \text{ M}$$

c) pH = 9.00 ; pOH = 14.00 - 9.00 = 5.00 ; $[\text{OH}^-] = 10^{-5.00} = 1.00 \times 10^{-5}$

$$[\text{Cu}^{2+}] = \text{molar solubility} = \frac{2.2 \times 10^{-20}}{(1.0 \times 10^{-5})^2} = 2.2 \times 10^{-10} \text{ M}$$

18) (17.99) Calculate the solubility (in g/L) of Ag_2CO_3 . $K_{sp} = 8.1 \times 10^{-12}$.

The reaction is



| | Initial | Change | Equilibrium |
|-------------------------------|---------|--------|-------------|
| Ag ⁺ | 0.0 | 2x | 2x |
| CO ₃ ²⁻ | 0.0 | x | x |

$$(2x)^2 (x) = 4x^3 = 8.1 \times 10^{-12}$$

$$x = [(8.1 \times 10^{-12})/4]^{1/3} = 1.27 \times 10^{-4}$$

So the molar solubility of Ag₂CO₃ is 1.27 x 10⁻⁴ mol/L.

Since MW(Ag₂CO₃) = 275.8 g/mol

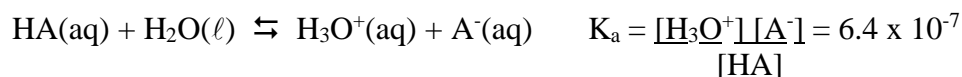
then the solubility in g/L is (1.27 x 10⁻⁴ mol/L) (275.8 g/mol) = 0.0350 g/L

19) (17.106) Cacodylic acid ((CH₃)₂AsO₂H) has an ionization constant K_a = 6.4 x 10⁻⁷ at T = 25. °C.

a) Find the pH of 50.0 mL of a 0.100 M solution of cacodylic acid.

We will represent cacodylic acid as HA, and let A⁻ = (CH₃)₂AsO₂⁻ be the conjugate base of cacodylic acid.

The equilibrium reaction is then



| | Initial | Change | Equilibrium |
|-------------------------------|---------|--------|-------------|
| H ₃ O ⁺ | 0 | x | x |
| A ⁻ | 0 | x | x |
| HA | 0.100 | - x | 0.100 - x |

$$\frac{(x)(x)}{(0.100 - x)} = 6.4 \times 10^{-7}$$

If we assume x << 0.100, then the above equation becomes

$$\frac{x^2}{(0.100)} = 6.4 \times 10^{-7} \quad x^2 = (0.100)(6.4 \times 10^{-7}) = 6.4 \times 10^{-8}$$

$$x = (6.4 \times 10^{-8})^{1/2} = 2.5 \times 10^{-4}$$

$$\text{pH} = -\log_{10}(2.5 \times 10^{-4}) = 3.60$$

b) Find the pH of 25.0 mL of a 0.150 M solution of $(\text{CH}_3)_2\text{AsO}_2\text{Na}$, the sodium salt of the conjugate base of cacodylic acid.

As before, let HA = cacodylic acid and A^- = the conjugate base of cacodylic acid. To find K_b for the conjugate base, we can use the expression

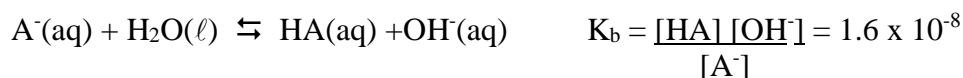
$$K_a K_b = 1.0 \times 10^{-14} \text{ (at } T = 25. \text{ }^\circ\text{C)}$$

$$K_b = \frac{1.0 \times 10^{-14}}{K_a} = \frac{1.0 \times 10^{-14}}{6.4 \times 10^{-7}} = 1.6 \times 10^{-8}$$

When the sodium salt of the conjugate base of cacodylic acid is added to water, it will completely dissociate (since sodium salts are expected to be soluble in water)



The equilibrium reaction is then ($\text{A}^- = (\text{CH}_3)_2\text{AsO}_2^-$)



| | Initial | Change | Equilibrium |
|---------------|---------|--------|-------------|
| HA | 0 | x | x |
| OH^- | 0 | x | x |
| A^- | 0.150 | - x | 0.150 - x |

$$\frac{(x)(x)}{(0.150 - x)} = 1.6 \times 10^{-8}$$

If we assume $x \ll 0.150$, the the above equation becomes

$$\frac{x^2}{(0.150)} = 1.6 \times 10^{-8} \quad x^2 = (0.150)(6.4 \times 10^{-8}) = 9.6 \times 10^{-9}$$

$$x = (9.6 \times 10^{-9})^{1/2} = 9.8 \times 10^{-5}$$

$$\text{pOH} = -\log_{10}(9.6 \times 10^{-5}) = 4.01$$

$$\text{pH} = 14.00 - 4.01 = 9.99$$

c) The solutions in a and b are mixed. Find the pH of the resulting solution.

When the solutions are mixed the total volume of solution will be $V = 50.0 \text{ mL} = 25.0 \text{ mL} + 25.0 \text{ mL}$. The initial concentrations of cacodylic acid (HA) and conjugate base (A^-) will therefore be

$$\text{Initial HA} = (0.100 \text{ M}) \frac{(50.0 \text{ mL})}{75.0 \text{ mL}} = 0.067 \text{ M}$$

$$\text{Initial A}^- = (0.150 \text{ M}) \frac{(25.0 \text{ mL})}{75.0 \text{ mL}} = 0.050 \text{ M}$$

We could do this problem as a normal equilibrium calculation, but since the solution contains a significant concentration of both a weak acid and its conjugate base, we can use the Henderson equation

$$\begin{aligned} \text{pH} &= \text{pK}_a + \log_{10} ([\text{base}]/[\text{acid}]) \\ &= -\log_{10}(6.4 \times 10^{-7}) + \log_{10}(0.050/0.067) \\ &= 6.19 - 0.18 = 6.01 \end{aligned}$$