

Homework 4

16. Between the starting point of the titration and the equivalence point, we are dealing with a buffer solution. The Henderson-Hasselback equation can be used to determine pH:

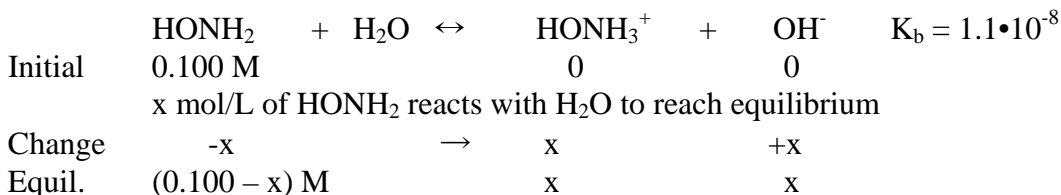
$$\text{pH} = \text{pK}_a + \log\left(\frac{[\text{Base}]}{[\text{Acid}]}\right)$$

At the halfway point to equivalence, enough OH^- has been added by the strong base to convert exactly one-half of the weak acid present initially into its conjugate base. Therefore, $[\text{conjugate base}] = [\text{weak acid}]$ so $\text{pH} = \text{pK}_a + \log 1 = \text{pK}_a$

The pK_a value can be determined at any point in a titration, from the initial point to the equivalence point. In Chapter 14, we calculated the K_a from a solution of only the weak acid. In the buffer region, we can calculate the ratio of base form to the acid form and use the Henderson-Hasselbach equation to determine the K_a value. The equivalence point data can be used to calculate the K_b value for the conjugate base which is related to K_a by the equation $K_a = K_w/K_b$.



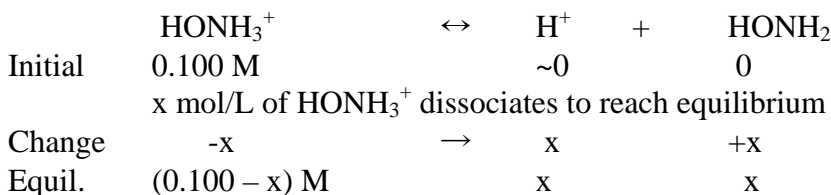
24. a. Weak base problem:



$$K_b = 1.1 \cdot 10^{-8} = x^2 / (0.100 - x) \approx x^2 / 0.100$$

$$x = [\text{OH}^-] = 3.3 \cdot 10^{-5} \text{ M}; \text{pOH} = 4.48,; \text{pH} = 9.52 \text{ Assumption good.}$$

- b. Weak acid problem (Cl^- has no acidic/basic properties)



$$K_a = K_w / K_b = 9.1 \cdot 10^{-7} = x^2 / (0.100 - x)$$

$$x = [\text{H}^+] = 3.0 \cdot 10^{-4} \text{ M}; \text{pH} = 3.52 \quad \text{Assumption good.}$$

- c. Pure H_2O , $\text{pH} = 7.00$

d. Buffer solution where $pK_a = -\log(9.1 \cdot 10^{-7}) = 6.04$. Using the Henderson-Hasselbach equation:

$$pH = pK_a + \log\left(\frac{[\text{Base}]}{[\text{Acid}]}\right) = 6.04 + \log\left(\frac{[\text{HONH}_2]}{[\text{HONH}_3^+]}\right) = 6.04 + \log(0.100/0.100) = 6.04$$

28. a. Added H^+ reacts completely with HONH_2 (the best base present) to form HONH_3^+ .

| | | | | | | |
|--------|-----------------|---|--------------|-------------------|-------------------|-------------------|
| | HONH_2 | + | H^+ | \leftrightarrow | HONH_3^+ | |
| Before | 0.100 M | | 0.020 M | | 0 | |
| Change | -0.020 | | -0.020 | | +0.020 | Reacts completely |
| After | 0.080 | | 0 | | 0.020 | |

After this reaction, a buffer solution exists, i.e., a weak acid (HONH_3^+) and its conjugate base (HONH_2) are present at the same time. Using the Henderson-Hasselbach equation to solve for the pH where $pK_a = -\log(K_w/K_b) = 6.04$:

$$pH = pK_a + \log\left(\frac{[\text{Base}]}{[\text{Acid}]}\right) = 6.04 + \log(0.080/0.020) = 6.04 + 0.60 = 6.64$$

b. We have a weak acid and a strong acid present at the same time. The H^+ contribution from the weak acid, HONH_3^+ , will be negligible. So, we have to consider only the H^+ from HCl. $[\text{H}^+] = 0.020 \text{ M}$; $pH = 1.70$.

c. This is a strong acid in water. $[\text{H}^+] = 0.020 \text{ M}$; $pH = 1.70$

d. Major species: H_2O , Cl^- , HONH_2 , HONH_3^+ , H^+

H^+ will react completely with HONH_2 , the best base present.

| | | | | | | |
|--------|-----------------|---|--------------|-------------------|-------------------|-------------------|
| | HONH_2 | + | H^+ | \leftrightarrow | HONH_3^+ | |
| Before | 0.100 M | | 0.020 M | | 0.100 | |
| Change | -0.020 | | -0.020 | | +0.020 | Reacts completely |
| After | 0.080 | | 0 | | 0.120 | |

A buffer solution results after reaction. Using the Henderson-Hasselbach equation:

$$pH = pK_a + \log\left(\frac{[\text{Base}]}{[\text{Acid}]}\right) = 6.04 + \log(0.080/0.120) = 6.04 - 0.18 = 5.86$$

30. a. We have a weak base and a strong base present at the same time. The OH^- contribution from the weak base, HONH_2 , will be negligible. Consider only the added strong base as the primary source of OH^- .

$$[\text{OH}^-] = 0.020 \text{ M}; p\text{OH} = 1.70, pH = 12.30$$

b. Added strong base will react to completion with the best acid present, HONH_3^+ .

| | | | | | | | |
|--------|-------------------|---|---------------|-------------------|-----------------|---|----------------------|
| | HONH_3^+ | + | OH^- | \leftrightarrow | HONH_2 | + | H_2O |
| Before | 0.100 M | | 0.020 M | | 0 | | |
| Change | -0.020 | | -0.020 | | +0.020 | | Reacts completely |
| After | 0.080 | | 0 | | 0.020 | | |

A buffer solution results after reaction. Using the Henderson-Hasselbach equation:

$$\text{pH} = \text{pK}_a + \log([\text{Base}]/[\text{Acid}]) = 6.04 + \log(0.020/0.080) = 6.04 - 0.60 = 5.44$$

c. This is a strong base in water. $[\text{OH}^-] = 0.020 \text{ M}$; $\text{pOH} = 1.70$; $\text{pH} = 12.30$

d. Major species present: H_2O , Cl^- , Na^+ , HONH_2 , HONH_3^+ , OH^-

Again, the added strong base reacts completely with the best acid present, HONH_3^+ .

| | | | | | | | |
|--------|-------------------|---|---------------|-------------------|-----------------|---|----------------------|
| | HONH_3^+ | + | OH^- | \leftrightarrow | HONH_2 | + | H_2O |
| Before | 0.100 M | | 0.020 M | | 0.100 M | | |
| Change | -0.020 | | -0.020 | | +0.020 | | Reacts completely |
| After | 0.080 | | 0 | | 0.120 | | |

A buffer solution results after reaction. Using the Henderson-Hasselbach equation:

$$\text{pH} = \text{pK}_a + \log([\text{Base}]/[\text{Acid}]) = 6.04 + \log(0.120/0.080) = 6.04 + 0.18 = 6.22$$

40. a. pK_b for $\text{C}_6\text{H}_5\text{NH}_2 = -\log(3.8 \cdot 10^{-10}) = 9.42$; pK_a for $\text{C}_6\text{H}_5\text{NH}_3^+ = 14.00 - 9.42 = 4.58$

$$\text{pH} = \text{pK}_a + \log([\text{C}_6\text{H}_5\text{NH}_2]/[\text{C}_6\text{H}_5\text{NH}_3^+]), 4.20 = 4.58 + \log(0.50 \text{ M}/[\text{C}_6\text{H}_5\text{NH}_3^+])$$

$$-0.38 = \log(0.50 \text{ M}/[\text{C}_6\text{H}_5\text{NH}_3^+]), [\text{C}_6\text{H}_5\text{NH}_3^+] = [\text{C}_6\text{H}_5\text{NH}_3\text{Cl}] = 1.2 \text{ M}$$

b. $4.0 \text{ g NaOH} \cdot 1 \text{ mol NaOH}/40.00 \text{ g} \cdot 1 \text{ mol OH}^-/\text{mol NaOH} = 0.10 \text{ mol OH}^-$

$$[\text{OH}^-] = 0.10 \text{ mol}/1.0 \text{ L} = 0.10 \text{ M}$$

| | | | | | | | |
|--------|-------------------------------------|---|---------------|-------------------|-----------------------------------|---|----------------------|
| | $\text{C}_6\text{H}_5\text{NH}_3^+$ | + | OH^- | \leftrightarrow | $\text{C}_6\text{H}_5\text{NH}_2$ | + | H_2O |
| Before | 1.2 M | | 0.10 M | | 0.50 M | | |
| Change | -0.10 | | -0.10 | | +0.10 | | |
| After | 1.1 | | 0 | | 0.60 | | |

A buffer solution exists. $\text{pH} = 4.58 + \log(0.60/1.1) = 4.32$

48. a. No. A solution of a strong acid (HNO_3) and its conjugate base (NO_3^-) is not generally considered a buffered solution.

b. No. Two acids are present (HNO_3 and HF), so it is not a buffered solution.

c. H^+ reacts completely with F^- . Since equal volumes are mixed, the initial concentrations in the mixture are 0.10 M HNO_3 and 0.20 M NaF .

| | | | | | | |
|--------|--------------|---|--------------|-------------------|-------------|-------------------|
| | H^+ | + | F^- | \leftrightarrow | HF | |
| Before | 0.10 M | | 0.20 M | | 0 | |
| Change | -0.10 | | -0.10 | | +0.10 | Reacts completely |
| After | 0 | | 0.10 | | 0.10 | |

After H^+ reacts completely, a buffered solution results, i.e. a weak acid (HF) and its conjugate base (F^-) are both present in large quantities.

d. No. A strong acid (HNO_3) and a strong base (NaOH) do not form buffered solutions. They will neutralize each other to form H_2O .

54. This is a strong base, $\text{Ba}(\text{OH})_2$, titrated by a strong acid, HCl . The added strong acid will neutralize the OH^- from the strong base. As is always the case when a strong acid and/or strong base reacts, the reaction is assumed to go to completion.

a. Only a strong base is present, but it breaks up into two mol of OH^- ions for every mol of $\text{Ba}(\text{OH})_2$. $[\text{OH}^-] = 2 \times 0.100 \text{ M} = 0.200 \text{ M}$; $\text{pOH} = 0.699$; $\text{pH} = 13.301$

b. $\text{mmol OH}^- \text{ present} = 80.0 \text{ mL} \times 0.100 \text{ mmol Ba}(\text{OH})_2/\text{mL} \times 2 \text{ mmol OH}^-/\text{mmol Ba}(\text{OH})_2$
 $= 16.0 \text{ mmol OH}^-$

$\text{mmol H}^+ \text{ added} = 20.0 \text{ mL} \times 0.400 \text{ H}^+/\text{mL} = 8.00 \text{ mmol H}^+$

| | | | | | | |
|--------|---------------|---|--------------|---------------|----------------------|-------------------|
| | OH^- | + | H^+ | \rightarrow | H_2O | |
| Before | 16.0 mmol | | 8.00 mmol | | | |
| Change | -8.00 mmol | | -8.00 mmol | | | |
| After | 8.0 mmol | | 0 | | | Reacts completely |

$[\text{OH}^-]_{\text{excess}} = 8.0 \text{ mmol OH}^- / (80.0 \text{ mL} + 20.0 \text{ mL}) = 0.080 \text{ M}$; $\text{pOH} = 1.10$, $\text{pH} = 12.90$

c. $\text{mmol H}^+ \text{ added} = 30.0 \text{ mL} \times 0.400 \text{ M} = 12.0 \text{ mmol H}^+$

| | | | | | | |
|--------|---------------|---|--------------|---------------|----------------------|-------------------|
| | OH^- | + | H^+ | \rightarrow | H_2O | |
| Before | 16.0 mmol | | 12.00 mmol | | | |
| Change | -12.00 mmol | | -12.00 mmol | | | |
| After | 4.0 mmol | | 0 | | | Reacts completely |

$[\text{OH}^-]_{\text{excess}} = 4.0 \text{ mmol OH}^- / (80.0 \text{ mL} + 30.0 \text{ mL}) = 0.036 \text{ M}$; $\text{pOH} = 1.44$, $\text{pH} = 12.56$

d. $\text{mmol H}^+ \text{ added} = 40.0 \text{ mL} \times 0.400 \text{ M} = 16.0 \text{ mmol H}^+$. This is the equivalence point. Since the H^+ will exactly neutralize the OH^- from the strong base, all we have in solution is Ba^{2+} , Cl^- and H_2O . All are neutral species, so $\text{pH} = 7.00$.

e. $\text{mmol H}^+ \text{ added} = 80.0 \text{ mL} \times 0.400 \text{ M} = 32.0 \text{ mmol H}^+$

| | | | | | |
|--------|---------------|---|--------------|---------------|----------------------|
| | OH^- | + | H^+ | \rightarrow | H_2O |
| Before | 16.0 mmol | | 32.00 mmol | | |
| Change | -16.00 mmol | | -16.00 mmol | | |
| After | 0 | | 16 mmol | | |

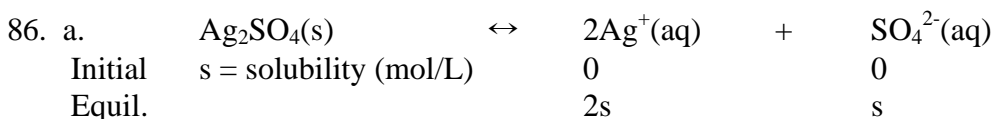
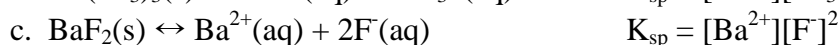
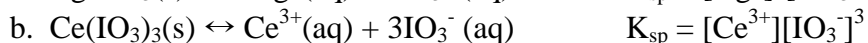
$$[\text{H}^+]_{\text{excess}} = 16.0 \text{ mmol H}^+ / (80.0 \text{ mL} + 80.0 \text{ mL}) = 0.100 \text{ M}; \text{pH} = 1.00$$

72. a. yellow

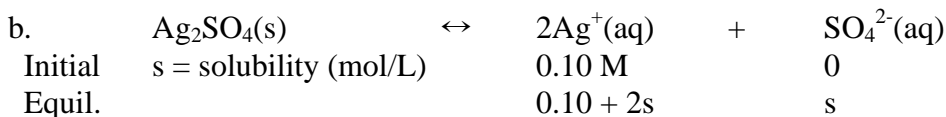
b. green (Both yellow and blue forms are present)

c. yellow

d. blue

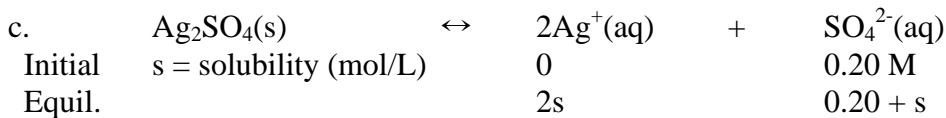


$$K_{\text{sp}} = 1.2 \cdot 10^{-5} = [\text{Ag}^+]^2[\text{SO}_4^{2-}] = (2s)^2s = 4s^3, s = 1.4 \cdot 10^{-2} \text{ mol/L}$$



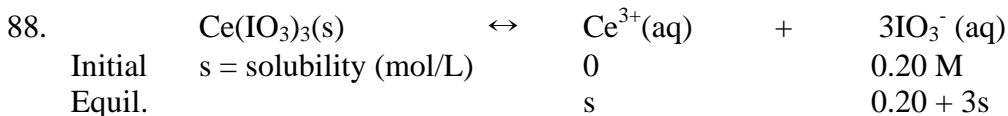
$$K_{\text{sp}} = 1.2 \cdot 10^{-5} = [\text{Ag}^+]^2[\text{SO}_4^{2-}] = (0.10 + 2s)^2s \approx (0.10)^2(s), s = 1.2 \cdot 10^{-3} \text{ mol/L},$$

Assumption good.



$$K_{\text{sp}} = 1.2 \cdot 10^{-5} = [\text{Ag}^+]^2[\text{SO}_4^{2-}] = (2s)^2(0.20 + s) \approx 4s^2(0.20), s = 3.9 \cdot 10^{-3} \text{ mol/L}.$$

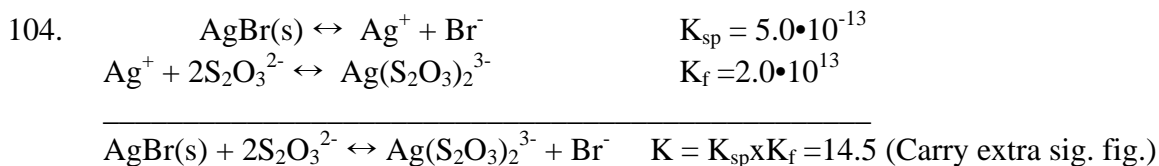
Assumption good.



$$K_{sp} = [\text{Ce}^{3+}][\text{IO}_3^-]^3 = s(0.20 + 3s)^3$$

From the problem, $s = 4.4 \cdot 10^{-8}$ mol/L; Solving for K_{sp} :

$$K_{sp} = (4.4 \cdot 10^{-8}) \times [0.20 + 3(4.4 \cdot 10^{-8})]^3 = 3.5 \cdot 10^{-10}$$



| | | | | | | | |
|---------|--|---|------------------------------|-------------------|--|---|---------------|
| | $\text{AgBr}(s)$ | + | $2\text{S}_2\text{O}_3^{2-}$ | \leftrightarrow | $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$ | + | Br^- |
| Initial | | | 0.500 M | | 0 | | 0 |
| | S mol/L AgBr(s) dissolved to reach equilibrium | | | | | | |
| Change | -s | | -2s | | +s | | +s |
| Equil. | | | 0.500 - 2s | | s | | s |

$$K = s^2 / (0.500 - 2s)^2 = 14.5; \text{ Taking the square root of both sides:}$$

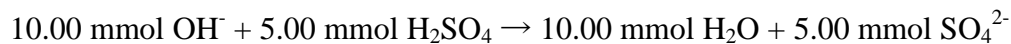
$$s / (0.500 - 2s) = 3.81, s = 1.91 - 7.92 s, s = 0.222 \text{ mol/L}$$

$$1.00 \text{ L} \times 0.222 \text{ mol AgBr/L} \times 187.8 \text{ g AgBr/mol AgBr} = 41.7 \text{ g AgBr} = 42 \text{ g AgBr}$$

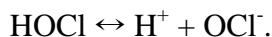
126. $50.0 \text{ mL} \times 0.100 \text{ M} = 5.00 \text{ mmol H}_2\text{SO}_4$; $20.0 \text{ mL} \times 0.100 \text{ M} = 3.00 \text{ mmol HOCl}$
 $25.0 \text{ mL} \times 0.200 \text{ M} = 5.00 \text{ mmol NaOH}$; $10.0 \text{ mL} \times 0.150 \text{ M} = 1.50 \text{ mmol KOH}$
 $25.0 \text{ mL} \times 0.100 \text{ M} = 2.50 \text{ mmol Ba}(\text{OH})_2 = 5.00 \text{ mmol OH}^-$

We have added 11.50 mmol OH^- total.

Let the OH^- reacts with the best acid present. This is H_2SO_4 , which is a diprotic acid. For H_2SO_4 , $K_{a1} \gg 1$ and $K_{a2} = 1.2 \cdot 10^{-2}$. The reaction is:



OH^- still remains, and it reacts with the next best acid, HOCl ($K_a = 3.5 \cdot 10^{-8}$). The remaining 1.50 mmol OH^- will convert 1.50 mmol HOCl into 1.50 mmol OCl^- , resulting in a solution containing 1.50 mmol OCl^- and $(3.00 - 1.50 =)$ 1.50 mmol HOCl . Major species present at this point are: HOCl , OCl^- , SO_4^{2-} , H_2O plus cations that don't affect the pH. SO_4^{2-} is an extremely weak base ($K_b = 8.3 \cdot 10^{-13}$). Major equilibrium affecting the pH is therefore:



Since $[\text{HOCl}] = [\text{OCl}^-]$, then:

$$[\text{H}^+] = K_a = 3.5 \cdot 10^{-8} \text{ M}, \text{ pH} = 7.46 \text{ Assumptions good.}$$