Chapter 17: Additional Aspects of Aqueous Equilibria

Kahoot!

1. Adding Br- to a saturated aqueous solution of ___ decreases its solubility in water. $BaSO_4$, Li_2CO_3, PbS, AgBr
2. Which of the following mixtures could be used to prepare an effective buffer? HCl and KCl, HNO_3 and KNO_3, HCl and NH_4Cl, NH_3 and NH_4Cl
3. Which 1 L solution has the greatest buffer capacity? 0.1 M NH_3 and 0.1 M NH_4Cl, 0.05 M NH_3 and 0.05 M NH_4Cl, 0.1 M NH_3 and 0.01 M NH_4Cl, 0.5 M NH_3 and 0.5 M NH_4Cl
4. Select the best acid or base to pair with its conjugate salt to prepare a 8.5 pH buffer. acetic acid; $K_a = 1.8x10^{-5}$, ammonia; $K_b = 1.8x10^{-5}$, hydroxylamine; $K_b = 1.1x10^{-8}$, citric acid; $K_a = 7.5x10^{-4}$
5. Select the correct representation of the Henderson-Hasselbalch equation. $K_a = [H^+][A^-]$, $K_w = [H^+][OH^-] = 10^{-14}$, pH = pK_a + log [base]/[acid], pK_a = pH + log[base]/[acid]
6. Which indicator is preferable when titrating a weak base with a strong acid? Methyl red (color change pH = 5), bromothymol blue (pH = 7), phenolphthalein (pH = 9), None of the above
7. Which indicator is preferable when titrating a weak acid with a strong base? Methyl red (color change pH = 5), bromothymol blue (pH = 7), phenolphthalein (pH = 9), None of the above
8. For $BaCO_3$, $K_{sp} = 5.0 \times 10^{-9}$. What is $[Ba^{2+}]$? 7.1×10^{-5} M, 1.0×10^{-8} M, 2.5×10^{-9} M, 5.0×10^{-9} M
9. For BaF_2, $K_{sp} = 1.7 \times 10^{-6}$. What is $[Ba^{2+}]$? 1.7×10^{-6} M, 3.4×10^{-6} M, 7.6×10^{-3} M, 1.5×10^{-2} M
10. Which of the following reagents will reduce the solubility of BaF_2? NaCl, $Ba(C_2H_3O_2)_2$, KOH, NH_4Br
11. Which of the following reagents will increase the solubility of BaF_2? HCl, HF, KOH, NH_4Br

Whiteboard Examples

Example: Calculate the pH of a solution prepared by mixing equal volumes of 0.20 M CH_3NH_2 and 0.60 M CH_3NH_3Cl ($K_b = 3.7 \times 10^{-4}$). What is the pH of 0.20 M CH_3NH_2 without addition of CH_3NH_3Cl?

assuming we have 1 L of each

$$[CH_3NH_2]_0 = \frac{\frac{0.20\, moles\, CH_3NH_2}{L} \times 1L}{2.0\, L} = 0.10\, \underline{M}\, CH_3NH_2$$

$$[CH_3NH_3^+]_0 = \frac{\frac{0.60\, moles\, CH_3NH_3^+}{L} \times 1L}{2.0\, L} = 0.30\, \underline{M}\, CH_3NH_3^+$$

I	0.1	-	0.3	0
C	-x	-	+x	+x
E	0.1 - x	-	0.3 + x	+x

$$K_b = \frac{[CH_3NH_3^+][OH^-]}{[CH_3NH_2]} = \frac{(0.3+x)x}{0.1-x} = 3.7 \times 10^{-4}$$

$$x^2 + 0.3004x - 3.7 \times 10^{-5} = 0$$

$$x = 8.97 \times 10^{-5}\, \underline{M}\, OH^-$$

$$pH = 14 + \log(8.97 \times 10^{-5}) = 9.95$$

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pH of 0.20 M CH_3NH_2:

$$K_b = \frac{[CH_3NH_3^+][OH^-]}{[CH_3NH_2]} = \frac{x^2}{0.1-x} = 3.7\times10^{-4}$$

$$x^2 + 3.7\times10^{-4}x - 3.7\times10^{-5} = 0$$

$$x = 8.24\times10^{-3}\ \underline{M}\ OH^-$$

$$pH = 14 + \log(8.24\times10^{-3}) = 11.92$$

Buffer Example I: Calculate the pH and pOH of a 500.0mL solution containing 0.225M HPO_4^{2-} and 0.225M PO_4^{3-} at 25°C where the K_a(HPO_4^{2-}) = $4.2\text{x}10^{-13}$.

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right) = -\log(4.2\times10^{-13}) + \log\left(\frac{0.225M}{0.225M}\right)$$

$$pH = 12.38$$

Buffer Example II: How would we prepare a pH = 4.44 buffer using CH_3CO_2H and CH_3CO_2Na?

$K_a = 1.8 \text{ x } 10^{-5}$

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right) \rightarrow \log\left(\frac{[CH_3CO_2^-]}{[CH_3CO_2H]}\right) = 4.44 + \log(1.8\times10^{-5}) = -0.305$$

$$\frac{[CH_3CO_2^-]}{[CH_3CO_2H]} = 10^{-0.305} = 0.496$$

Therefore, in order to make a 4.44 buffer solution we need 0.496 moles of CH_3CO_2Na for every mole of CH_3CO_2H

Comprehensive Example:Calculate the pH of each of the following solutions:

a. 0.100 M $HC_3H_5O_2$, $K_a = 1.3\times10^{-5}$

$$HC_3H_5O_2 \rightleftharpoons H^+ + C_3H_5O_2^- \rightarrow K_a = \frac{\left[H^+\right]\left[C_3H_5O_2^-\right]}{\left[HC_3H_5O_2\right]}$$

$$1.3\times10^{-5} = \frac{x^2}{0.100-x} \rightarrow x = 1.1\times10^{-3}M\ H^+ \quad pH = 2.96$$

b. 0.100 M $NaC_3H_5O_2$

$$NaC_3H_5O_2 \rightarrow Na^+ + C_3H_5O_2^-$$

$$C_3H_5O_2^- + H_2O \rightleftharpoons OH^- + HC_3H_5O_2 \rightarrow K_b = \frac{K_w}{K_a} = \frac{\left[OH^-\right]\left[HC_3H_5O_2\right]}{\left[C_3H_5O_2^-\right]}$$

$$7.7\times10^{-10} = \frac{x^2}{0.100-x} \approx \frac{x^2}{0.100} \rightarrow x = 8.8\times10^{-6}M\ OH^- \quad pH = 14 - pOH = 8.94$$

c. a mixture containing a. & b.

$$HC_3H_5O_2 \rightleftharpoons H^+ + C_3H_5O_2^- \rightarrow K_a = \frac{\left[H^+\right]\left[C_3H_5O_2^-\right]}{\left[HC_3H_5O_2\right]}$$

$$1.3\times10^{-5} = \frac{(0.100+x)x}{0.100-x} \rightarrow x = 1.3\times10^{-5}M\ H^+ \quad pH = 4.89$$

using Henderson-Hasselbach, $pH = pKa + \log\left(\left[A^-\right]/\left[HA\right]\right)$

$$pH = -\log 1.3\times10^{-5} + \log\left(\frac{0.100}{0.100}\right) = 4.89$$

d. a mixture containing c. and 0.020 mol of NaOH

when strong base is added to an acid containing solution it will neutralize the acid and so all of the OH^- will react completely with our propanoic acid

$$HC_3H_5O_2 + OH^- \rightleftharpoons H_2O + C_3H_5O_2^-$$

	$HC_3H_5O_2$	OH^-	$C_3H_5O_2^-$
B	0.100	0.020	0.100
C	-0.020	-0.020	+0.02
A	0.080	0	0.120

$$pH = -\log 1.3\times10^{-5} + \log\left(\frac{0.120}{0.080}\right) = 5.06$$

e. a mixture containing c. and 0.020 mol of HCl

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

	$C_3H_5O_2^-$	H^+	$HC_3H_5O_2$
B	0.100	0.020	0.100
C	-0.020	-0.020	+0.02
A	0.080	0	0.120

$$pH = -\log 1.3\times10^{-5} + \log\left(\frac{0.080}{0.120}\right) = 4.71$$

Titration Example I: What is [NH_3] if 22.35mL of 0.1145 M HCl were needed to titrate a 100.0mL sample?

$$NH_3 + HCl \rightleftharpoons NH_4^+ + Cl^-$$

$$[NH_3] = 0.02235L \times \frac{0.1145\ moles\ HCl}{L} \times \frac{1\ mole\ NH_3}{1\ mole\ HCl} \times \frac{1}{0.1000L} = 0.02259\underline{M}$$

Titration Example II – Strong with Strong: A 15.0 mL sample of 0.200 M NaOH is titrated with 0. 250 M of HCl. Calculate the pH of the mixture after 10.0, and 20.0 mL of acid have been added.

If you are not given a dissociation constant this should remind you that the acid/base is strong.

For 10.0 mL of HCl & 15.0 mL of NaOH:

$$10.0\ mL \times \frac{1\ L}{1000\ mL} \times \frac{0.250\ mol\ H^+_{(aq)}}{1\ L} = 0.00250\ mol\ H^+_{(aq)}$$

$$15.0\ mL \times \frac{1\ L}{1000\ mL} \times \frac{0.200\ mol\ OH^-_{(aq)}}{1\ L} = 0.00300\ mol\ OH^-_{(aq)}$$

	$H^+_{(aq)}$ +	$OH^-_{(aq)}$ →	$H_2O_{(l)}$
B	0.00250	0.00300	-
C	-0.00250	-0.00250	-
A	0	0.00050	-

$$\left[OH^-\right] = \frac{0.0005\ moles}{0.025L} = 0.0200M$$

$$pH = 14 + \log(0.02) = 12.30$$

For 20.0 mL of HCl

$$20.0\ mL \times \frac{1\ L}{1000\ mL} \times \frac{0.250\ mol\ H^+_{(aq)}}{1\ L} = 0.00500\ mol\ H^+_{(aq)}$$

	$H^+_{(aq)}$ +	$OH^-_{(aq)}$ →	$H_2O_{(l)}$
B	0.00500	0.00300	-
C	-0.00300	-0.00300	-
A	0.00200	0	-

$$\left[H^+\right] = \frac{0.002\ moles}{0.035L} = 0.05714M$$
$$pH = -\log(0.05714) = 1.24$$

Titration Example III – Strong with Weak: A 25.0 mL sample of 0.100 M acetic acid ($HC_2H_3O_2$) is titrated with 0.125 M of NaOH. Calculate the pH of the mixture after 0.0,10.0, 20.0, and 30.0 mL of base have been added. (K_a = 1.8 x 10^{-5})

For 0.0 mL it is the same as a weak acid:

$$HC_3H_3O_2 \rightleftharpoons H^+ + C_3H_3O_2^- \rightarrow K_a = \frac{\left[H^+\right]\left[C_3H_3O_2^-\right]}{\left[HC_3H_3O_2\right]}$$
$$1.8\times10^{-5} = \frac{x^2}{0.100 - x}$$
assume x << 0.100
$$1.8\times10^{-5} \sim \frac{x^2}{0.100} \rightarrow x = 1.34\times10^{-3} M\ H^+$$
$$\text{verify assumption: } \frac{1.34\times10^{-3}}{0.100}\times100\% = 1.34\% < 5\%$$
$$pH = -\log\left(1.1\times10^{-3}\right) = \boxed{2.87}$$

For 10.0 mL:

Initially we have:
$$HC_2H_3O_{2(aq)} + NaOH_{(aq)} \rightarrow NaC_2H_3O_{2(aq)} + H_2O_{(l)}$$
Na^+ is a spectator ion so we are really looking at:
$$HC_2H_3O_{2(aq)} + OH^-_{(aq)} \rightarrow C_2H_3O^-_{2(aq)} + H_2O_{(l)}$$
This is in fact a neutralization reaction. For 10.0 mL of NaOH:
$$25.0\ mL \times \frac{1\ L}{1000\ mL} \times \frac{0.100\ mol\ HC_2H_3O_{2(aq)}}{1\ L} = 0.00250\ mol\ HC_2H_3O_{2(aq)}$$
$$10.0\ mL \times \frac{1\ L}{1000\ mL} \times \frac{0.125\ mol\ OH^-_{(aq)}}{1\ L} = 0.00125\ mol\ OH^-_{(aq)}$$

Now we set up a "BCA" table or before, change, after table

	$HC_2H_3O_{2(aq)}$	$+OH^-_{(aq)}$	$\rightarrow C_2H_3O^-_{2(aq)}$	$+H_2O_{(l)}$
B	0.00250	0.00125	0	-
C	-0.00125	-0.00125		-
A	0.00125	0	+0.00125	-

So, we have neutralized the acid with the given amount of base and are now ready to apply the Henderson-Hasselbalch equation:

$$pH = pK_a + \log\left(\frac{\left[A^-\right]}{\left[HA\right]}\right) = -\log\left(1.8\times10^{-5}\right) + \log\left(\frac{\frac{0.0125}{0.0350L}}{\frac{0.0125}{0.0350L}}\right) = 4.74$$

Time for 20.0 mL of NaOH:

$$20.0\ mL \times \frac{1\ L}{1000\ mL} \times \frac{0.125\ mol\ OH^-_{(aq)}}{1\ L} = 0.00250\ mol\ OH^-_{(aq)}$$

$$HC_2H_3O_{2(aq)} + OH^-_{(aq)} \rightarrow C_2H_3O^-_{2(aq)} + H_2O_{(l)}$$

B	0.00250	0.00250	0	-
C	-0.00250	-0.00250		-
A	0	0	+0.00250	-

All of the acid has reacted with all the base and so we are now at the equivalence point. However, since we had a weak acid and a strong base we should expect our pH to be higher than 7. To find the pH we need an "ICE" table.

$$\left[C_2H_3O^-_{2(aq)}\right] = 0.00250\ moles / 0.045L = 0.0556\underline{M}$$

$$C_2H_3O^-_{2(aq)} + H_2O_{(l)} \rightarrow HC_2H_3O_{2(aq)} + OH^-_{(aq)}$$

I	0.0556	-	0	0
C	-x	-	+x	+x
E	0.0556-x	-	+x	+x

$$K_b = \frac{\left[HC_2H_3O_{2(aq)}\right]\left[OH^-_{(aq)}\right]}{\left[C_2H_3O^-_{2(aq)}\right]} = \frac{K_w}{K_a} = \frac{10^{-14}}{1.8\times10^{-5}} = 5.6\times10^{-10} = \frac{x^2}{0.0556-x}$$

$$assume\ x \ll 0.0556 \quad 5.6\times10^{-10} \sim \frac{x^2}{0.0556} \quad x = \left[OH^-_{(aq)}\right] = 5.6\times10^{-6}M$$

$$ck\ assumption: \ \frac{5.6\times10^{-6}}{0.0556}\times100\% = 0.01\% < 5\%$$

$$pH = 14 + \log(5.6\times10^{-6}) = 8.75$$

Finally, 30.0 mL

$$30.0\ mL \times \frac{1\ L}{1000\ mL} \times \frac{0.125\ mol\ OH^-_{(aq)}}{1\ L} = 0.00375\ mol\ OH^-_{(aq)}$$

Now, we have more strong base than acid so we can set up the BCA table and then determine hydroxide concentration and pH directly.

$$HC_2H_3O_{2(aq)} + OH^-_{(aq)} \rightarrow C_2H_3O^-_{2(aq)} + H_2O_{(l)}$$

B	0.00250	0.00375	0	-
C	-0.00250	-0.00250		-
A	0	0.00125	+0.00375	-

$$\left[OH^-\right] = \frac{0.00125\ moles}{0.055L} = 0.0227M$$

$$pH = 14 + \log(0.0227) = 12.36$$

Solubility Example: Determine the equilibrium concentrations (and solubilities) of $BaF_{2(s)}$, $K_{sp} = 1.7\text{x}10^{-6}$.

$$BaF_{2(s)} \rightleftharpoons Ba^{2+}_{(aq)} + 2F^-_{(aq)} \qquad 1.7\times10^{-6}$$

s 2s

$$K_{sp} = [S][2S]^2$$

$$1.7\times10^{-6} = 4S^3 \rightarrow S = 0.0075\underline{M}$$

$$[Ba^{2+}] = 0.0075\underline{M} \quad and \quad [F^-] = 2\times0.0075 = 0.015\underline{M}$$

$$Ba^{2+}: \frac{0.0075\,moles}{L}\times\frac{137.327\,g}{mol} = 1.03\frac{g}{L}$$

$$F^-: \frac{0.015\,moles}{L}\times\frac{18.998\,g}{mol} = 0.285\frac{g}{L}$$

Common-Ion Solubility Example: Calculate the solubility of calcite ($CaCO_3$) in 0.00100 M of Na_2CO_3 and in just plain water ($K_{sp} = 4.5\text{x}10^{-9}$ at 25°C).

$$CaCO_{3(s)} \rightleftharpoons Ca^{2+}_{(aq)} + CO^{2-}_{(aq)}$$

	$Ca^{2+}_{(aq)}$	$CO^{2-}_{(aq)}$
Initial	0	0.0010
Change	+s	+s
Eq	s	0.0010+s

$K_{sp} = [s][0.001 + s]$

assume 0.001 >> s

$K_{sp} = 4.5\times10^{-9} \sim 0.001s \rightarrow s = 4.5\times10^{-6}\,M$

$ck: \quad \frac{4.5\times10^{-6}}{0.001}\times100\% = 0.45\% < 5\%$

Therefore the solubility of $CaCO_3$ is $4.5x10^{-6}$M with $[Ca^{2+}]$ = $4.5x10^{-6}$M & $[CO_3^{2-}]$ = 0.0010 M

How does this compare with the solubility of just $CaCO_3$?

	$Ca^{2+}_{(aq)}$	$CO^{2-}_{(aq)}$
Initial	0	0.0010
Change	+s	+s
Eq	s	+s

$K_{sp} = [s][s]$

$4.5\times10^{-9} = s^2 \rightarrow s = 6.71\times10^{-5}\,M$

$\left[Ca^{2+}\right] = \left[CO_3^{2-}\right] = 6.71\times10^{-5}\,M$

$6.71\times10^{-5}\,M > 4.5\times10^{-6}\,M$ thereby demonstrating how common-ion represses solubility