

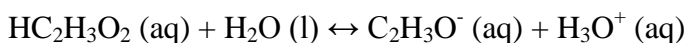
Chapter 16: 4, 6, 14, 22, 42, 52, 56, 60, 66

16.4 Solve an equilibrium problem (using an ICE table) to calculate the pH of each solution:

- A solution that is 0.175 M in $\text{HC}_2\text{H}_3\text{O}_2$ and 0.110 M in $\text{KC}_2\text{H}_3\text{O}_2$
- A solution that is 0.195 M in CH_3NH_2 and 0.105 M in $\text{CH}_3\text{NH}_3\text{Br}$

SOLUTION:

a.



	$\text{HC}_2\text{H}_3\text{O}_2 (\text{aq})$	$+ \text{H}_2\text{O} (\text{l})$	\leftrightarrow	$\text{C}_2\text{H}_3\text{O}^- (\text{aq})$	$+ \text{H}_3\text{O}^+ (\text{aq})$
I	0.175 M	-		0.110 M	0
C	-x	-		+x	+x
E	0.175-x	-		0.110+x	x

$$K_a = 1.8 \times 10^{-5} = \frac{(x)(0.110 + x)}{0.175 - x}$$

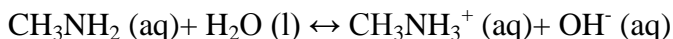
Always try the assumption. In this case $x \ll 0.110$

$$1.8 \times 10^{-5} = \frac{(x)(0.110 + x)}{0.175 - x} \cong \frac{(x)(0.11)}{(0.175)}$$

$x = 2.86 \times 10^{-5}$, good assumption

$$\text{pH} = -\log(2.86 \times 10^{-5}) = 4.54$$

b.



	$\text{CH}_3\text{NH}_2 (\text{aq})$	$+ \text{H}_2\text{O} (\text{l})$	\leftrightarrow	$\text{CH}_3\text{NH}_3^+ (\text{aq})$	$+ \text{OH}^- (\text{aq})$
I	0.195 M	-		0.105 M	0
C	-x	-		+x	+x
E	0.195-x	-		0.105+x	x

$$K_b = 4.4 \times 10^{-4} = \frac{(x)(0.105 + x)}{0.195 - x}$$

Always try the assumption. In this case $x \ll 0.105$

$$4.4 \times 10^{-4} = \frac{(x)(0.105 + x)}{0.195 - x} \cong \frac{(x)(0.105)}{(0.195)}$$

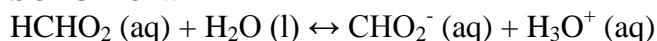
$x = 8.17 \times 10^{-4}$, good assumption

$$pOH = -\log(8.17 \times 10^{-4}) = 3.09$$

$$pH = 14 - pOH = 14 - 3.09 = 11.91$$

16.6 Calculate the percent ionization of a 0.13 M formic acid solution in pure water and also in a solution containing 0.11 M potassium formate. Explain the difference in percent ionization in the two solutions.

SOLUTION:



	HCHO ₂ (aq)	+ H ₂ O (l)	↔	CHO ₂ ⁻ (aq)	+ H ₃ O ⁺ (aq)
I	0.13 M	-		0	0
C	-x	-		+x	+x
E	0.13-x	-		x	x

$$K_a = 1.8 \times 10^{-4} = \frac{(x)(x)}{0.13 - x}$$

Always try the assumption. In this case $x \ll 0.13$

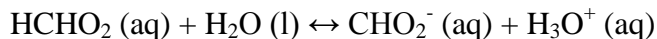
$$1.8 \times 10^{-4} = \frac{(x)(x)}{0.13 - x} \cong \frac{(x)(x)}{(0.13)}$$

$$x = 4.83 \times 10^{-3}$$

$$\frac{0.00483}{0.13} \times 100 = 3.7\%, \text{ good assumption}$$

	HCHO ₂ (aq)	+ H ₂ O (l)	↔	CHO ₂ ⁻ (aq)	+ H ₃ O ⁺ (aq)
I	0.13 M	-		0	0
C	-0.00483	-		+0.00483	+0.00483
E	0.125	-		0.00483	0.00483

$$\% \text{ ionization} = \frac{\text{moles ionized}}{\text{original moles}} \times 100 = \frac{.00483}{0.13} \times 100 = 3.7\%$$



	HCHO ₂ (aq)	+ H ₂ O (l)	↔	CHO ₂ ⁻ (aq)	+ H ₃ O ⁺ (aq)
I	0.13 M	-		0.11	0
C	-x	-		+x	+x
E	0.13-x	-		0.11+x	x

$$K_a = 1.8 \times 10^{-4} = \frac{(x)(0.11 + x)}{0.13 - x}$$

Always try the assumption. In this case $x \ll 0.13$

$$1.8 \times 10^{-4} = \frac{(x)(0.11 + x)}{0.13 - x} \cong \frac{(x)(0.11)}{(0.13)}$$

$$x = 2.13 \times 10^{-4}$$

$$\frac{0.000213}{0.13} \times 100 = 0.16\%, \text{ good assumption}$$

	HCHO ₂ (aq)	+ H ₂ O (l)	↔	CHO ₂ ⁻ (aq)	+ H ₃ O ⁺ (aq)
I	0.13 M	-		0.11	0
C	-2.13 × 10 ⁻⁴	-		+2.13 × 10 ⁻⁴	+2.13 × 10 ⁻⁴
E	0.1298	-		0.1102	2.13 × 10 ⁻⁴

$$\% \text{ ionization} = \frac{\text{moles ionized}}{\text{original moles}} \times 100 = \frac{2.13 \times 10^{-4}}{0.13} \times 100 = 0.16\%$$

It's just LeChatelier's principle. If I put a bunch of product (formate ion) into the mix, I shift the equilibrium back towards the reactants which decreases the amount of acid that dissociates.

- 16.14 Use the Henderson-Hasselbalch equation to calculate the pH of a solution that is
- 0.155 M in propanoic acid and 0.110 M in potassium propanoate
 - 0.15 M in C₅H₅N and 0.10 M in C₅H₅NHCl
 - 15.0 g of HF and 25.0 g of NaF in 125 mL of solution

SOLUTION:

a. $pH = pK_a + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right)$

$$pH = [-\log(1.3 \times 10^{-5})] + \log\left(\frac{0.110 \text{ M}}{0.155 \text{ M}}\right)$$

$$pH = 4.886 + (-0.149) = 4.74$$

b. $pH = pK_a + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right)$

$$pH = [14 - (-\log(1.7 \times 10^{-9}))] + \log\left(\frac{0.15 \text{ M}}{0.10 \text{ M}}\right)$$

$$pH = 5.23 + (0.176) = 5.41$$

c. $pH = pK_a + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right)$

$$15.0 \text{ g HF} \frac{1 \text{ mol HF}}{20.01 \text{ g HF}} = 0.75 \text{ mol HF}$$

$$25.0 \text{ g NaF} \frac{1 \text{ mol NaF}}{42 \text{ g NaF}} = 0.595 \text{ mol NaF}$$

$$pH = [-\log(3.5 \times 10^{-4})] + \log\left(\frac{0.595 \text{ mol}}{0.75 \text{ mol}}\right)$$

$$pH = 3.46 + (-0.1) = 3.36$$

16.22 A 100.0 mL buffer solution is 0.175 M in HClO and 0.150 M in NaClO.

- What is the initial pH of this solution?
- What is the pH after addition of 150.0 mg of HBr?
- What is the pH after addition of 85.0 mg of NaOH?

$$\text{HClO } K_a = 2.9 \times 10^{-8}$$

SOLUTION:

It's a buffer, H-H will work.

$$pK_a = -\log(K_a) = -\log(2.9 \times 10^{-8}) = 7.54$$

$$pH = pK_a + \log \frac{[\text{ClO}^-]}{[\text{HClO}]} = 7.54 + \log\left(\frac{0.150}{0.175}\right) = 7.47$$

HBr is a strong acid, it dilutes an equivalent amount of the best base available: ClO⁻

Since I'm using H-H, I can do everything in moles.

$$0.150 \text{ M} \times 0.100 \text{ L} = 0.015 \text{ moles}$$

$$0.175 \text{ M} \times 0.100 \text{ L} = 0.0175 \text{ moles}$$

$$0.150 \text{ g HBr} \frac{1 \text{ mol}}{80.904 \text{ g}} = 0.001854 \text{ moles}$$

	HBr +	ClO ⁻	→	HClO	+ Br ⁻
I	0.001854 mol	0.0150 moles		0.0175 moles	0
Neutralized	-0.001854	-0.001854		+0.001854	+0.001854
Left	0	0.013146		0.019354	0.019354

$$pH = pK_a + \log \frac{[\text{ClO}^-]}{[\text{HClO}]} = 7.54 + \log\left(\frac{0.013146}{0.019354}\right) = 7.372$$

NaOH does the opposite: neutralize the equivalent amount of the best available acid HClO

$$0.085 \text{ g NaOH} \frac{1 \text{ mol NaOH}}{40 \text{ g}} =$$

	OH ⁻ +	HClO	→	ClO ⁻	+ H ₂ O

I	0.002125	0.01750 moles		0.015 moles	0
Neutralized	-0.002125	-0.002125		+0.002125	+0.002125
Left	0	0.015375		0.017125	0.002125

$$pH = pK_a + \log \frac{[ClO^-]}{[HClO]} = 7.54 + \log \left(\frac{0.017125}{0.015375} \right) = 7.587$$

16.42 A 20.0 mL sample of 0.125 M HNO₃ is titrated with 0.150 M NaOH. Calculate the pH for at least five different points throughout the titration curve and make a sketch of the curve. Indicate the volume at the equivalence point on your graph.

Initially, it is all just acid. Nitric acid is a strong acid.

$$pH = -\log(0.125 \text{ M}) = 0.90$$

The equivalence point is at:

$$0.125 \text{ M} (20.0 \text{ mL}) = 0.150 \text{ M} (x \text{ mL})$$

$$x = 16.67 \text{ mL}$$

Since it is a strong acid/strong base titration, the pH=7 at 16.67 mL

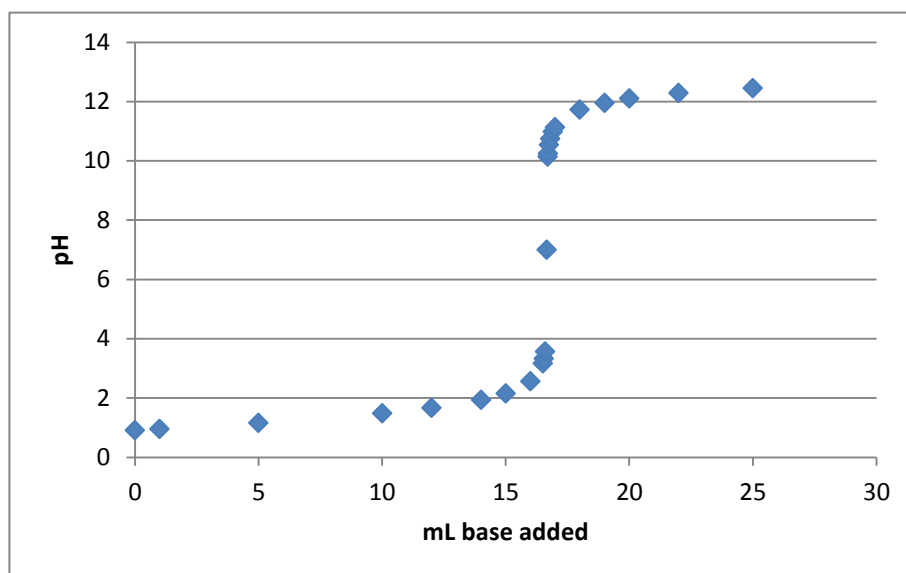
Between 0 mL and 16.67 mL added, it is just unneutralized strong acid, so I just subtract the moles of base added from the original moles of acid.

Between 16.67 mL and infinity, it is just excess base, so I subtract the original moles of acid from the moles of base added.

Hey look, Excel did all the work for me!

mL Base added	[base] original	mmol base added	mL acid original	[acid] original	mmol acid original	mol acid left	Total volume	[acid] remaining	pH
0	0.15	0	20	0.125	2.5	2.5	20	0.125	0.90309
1	0.15	0.15	20	0.125	2.5	2.35	21	0.1119048	0.951151
5	0.15	0.75	20	0.125	2.5	1.75	25	0.07	1.154902
10	0.15	1.5	20	0.125	2.5	1	30	0.0333333	1.477121
12	0.15	1.8	20	0.125	2.5	0.7	32	0.021875	1.660052
14	0.15	2.1	20	0.125	2.5	0.4	34	0.0117647	1.929419
15	0.15	2.25	20	0.125	2.5	0.25	35	0.0071429	2.146128
16	0.15	2.4	20	0.125	2.5	0.1	36	0.0027778	2.556303
16.5	0.15	2.475	20	0.125	2.5	0.025	36.5	0.0006849	3.164353
16.55	0.15	2.4825	20	0.125	2.5	0.0175	36.55	0.0004788	3.319849
16.6	0.15	2.49	20	0.125	2.5	0.01	36.6	0.0002732	3.563481

16.6666	0.15	2.49999	20	0.125	2.5	0	36.6666	0	7
						mmol excess base		[excess base]	
16.7	0.15	2.505	20	0.125	2.5	0.005	36.7	0.0001362	10.1343
16.71	0.15	2.5065	20	0.125	2.5	0.0065	36.71	0.0001771	10.24813
16.75	0.15	2.5125	20	0.125	2.5	0.0125	36.75	0.0003401	10.53165
16.8	0.15	2.52	20	0.125	2.5	0.02	36.8	0.0005435	10.73518
16.9	0.15	2.535	20	0.125	2.5	0.035	36.9	0.0009485	10.97704
17	0.15	2.55	20	0.125	2.5	0.05	37	0.0013514	11.13077
18	0.15	2.7	20	0.125	2.5	0.2	38	0.0052632	11.72125
19	0.15	2.85	20	0.125	2.5	0.35	39	0.0089744	11.953
20	0.15	3	20	0.125	2.5	0.5	40	0.0125	12.09691
22	0.15	3.3	20	0.125	2.5	0.8	42	0.0190476	12.27984
25	0.15	3.75	20	0.125	2.5	1.25	45	0.0277778	12.4437



16.52 A 0.446 g sample of an unknown monoprotic acid was titrated with 0.150 M KOH and the resulting titration curve is shown below. Determine the molar mass and pK_a of the acid.

(see book for figure)

SOLUTION:

The equivalence point is at 35 mL so that is where the moles of base is equivalent to the moles of acid.

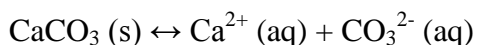
$$0.150 \text{ M KOH (0.035 L KOH)} = 0.00525 \text{ mol KOH added} = 0.00525 \text{ mol acid}$$

$$\frac{0.446 \text{ g acid}}{0.00525 \text{ mol acid}} = 84.95 \text{ g/mol}$$

The $pK_a = \text{pH}$ at $\frac{1}{2}$ equivalence. Half equivalence is 17.5 mL base added. The pH of the solution is 4 at 17.5 mL added, so the $pK_a = 4$.

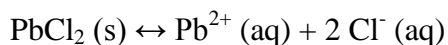
16.56 Write balanced equations and expressions for K_{sp} for the dissolution of each ionic compound:

a. CaCO_3



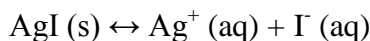
$$K_{sp} = [\text{Ca}^{2+}][\text{CO}_3^{2-}]$$

b. PbCl_2



$$K_{sp} = [\text{Pb}^{2+}][\text{Cl}^-]^2$$

c. AgI



$$K_{sp} = [\text{Ag}^+][\text{I}^-]$$

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

a. BaCrO_4 ; molar solubility = $1.08 \times 10^{-5} \text{ M}$

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

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

SOLUTION:

It all stems from the K_{sp}

$$\begin{aligned} \text{a. } K_{sp} &= [\text{Ba}^{2+}][\text{CrO}_4^{2-}] = (\text{S})(\text{S}) = \text{S}^2 \\ K_{sp} &= (1.08 \times 10^{-5})^2 = 1.17 \times 10^{-10} \end{aligned}$$

$$\text{b. } K_{sp} = [\text{Ag}^+]^2[\text{SO}_3^{2-}] = (2\text{S})^2(\text{S}) = (2 \times 1.55 \times 10^{-5})^2(1.55 \times 10^{-5}) = 1.49 \times 10^{-14}$$

$$\text{c. } K_{sp} = [\text{Pb}^{2+}][\text{SCN}^-]^2 = (\text{S})(2\text{S})^2 = (2.22 \times 10^{-8})(2 \times 2.22 \times 10^{-8})^2 = 4.38 \times 10^{-23}$$

16.66 Calculate the molar solubility of MX ($K_{sp} = 1.27 \times 10^{-36}$) in

a. pure water

It's an equilibrium problem, I'm guessing it has 3 parts:

	$\text{MX}(\text{s})$	\leftrightarrow	$\text{M}^{2+} (\text{aq})$	$+ \text{X}^{2-} (\text{aq})$
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I			0	0
C	-S		+S	+S
E			S	S

$$K_{sp} = 1.27 \times 10^{-36} = [M^{2+}][X^{2-}]$$

$$1.27 \times 10^{-36} = [S][S]$$

$$S = 1.13 \times 10^{-18}$$

b. 0.25 M MCl_2

	MX(s)	\leftrightarrow	M^{2+} (aq)	+ X^{2-} (aq)
I			0.25	0
C	-S		+S	+S
E			S+0.25	S

$$K_{sp} = 1.27 \times 10^{-36} = [M^{2+}][X^{2-}]$$

$$1.27 \times 10^{-36} = [S + 0.25][S] = S^2 + 0.25S$$

$$S = 5.08 \times 10^{-36}$$

c. 0.20 M Na_2X

	MX(s)	\leftrightarrow	M^{2+} (aq)	+ X^{2-} (aq)
I			0	0.20
C	-S		+S	+S
E			S	0.20+S

$$K_{sp} = 1.27 \times 10^{-36} = [M^{2+}][X^{2-}]$$

$$1.27 \times 10^{-36} = [S][0.20 + S] = S^2 + 0.20S$$

$$S = 6.35 \times 10^{-36}$$