Week 8 KEY

1. When 0.45 M HCN is added to a 0.50 M NaCN solution, what is the pH of the solution after equilibrium is established?

$$HCN + H_2O \rightleftharpoons CN^- + H_3O^+$$

	HCN	H_2O	CN^-	H_3O^+
I	0.45		0.5	0
C	$-x$		$+x$	$+x$
E	$.45-x$		$.5+x$	x

major species:
HCN
CN^-
H_2O
Na^+

$$K_a = [CN^-][H_3O^+]/[HCN]$$

$$6.2\times10^{-10} = x(.5+x)/(.45-x)$$

assume negligible

$$x = [H_3O^+] = 5.58\times10^{-10}$$

5% test: $\frac{5.58\times10^{-10}}{0.45}\times 100$ ✓✓✓ passes

pH = 9.25

2. When 1.00 mole of NaF is added to a 1 liter 0.5 M HF solution, what is the pH of the solution after equilibrium is established? Assume no change in volume.

$$F^- + H_2O \rightleftharpoons HF + OH^-$$

	F^-	H_2O	HF	OH^-
I	1.0		0.5	0
C	$-x$		$+x$	$+x$
E	$1-x$		$.5+x$	x

major species:
Na^+
F^-
HF
H_2O

* when you have a buffer (aka acid/base AND conjugate), you can always write the K_a OR K_b expression

$$K_b = [HF][OH^-]/[F^-]$$

$$1.39\times10^{-11} = x(.5+x)/(1-x)$$

assume x is negligible

$$x = [OH^-] = 2.78\times10^{-11}$$

$$pOH = 10.56$$

∴ pH = 3.44

3. How many mL of 2.0 M KOH is necessary to neutralize 300 mL of 0.85 M HCl?

$$0.3\,L\left(\frac{0.85\text{ mol }HCl}{L}\right)\left(\frac{1\text{ mol }KOH}{1\text{ mol }HCl}\right)\left(\frac{L}{2\text{ mol }KOH}\right) = 0.128\,L$$

$= 128\text{ mL}$

4. What is the pH at the halfway point of titrating 200 mL of 2.0 M acetic acid with 0.4 M NaOH? How many mL of NaOH are necessary to reach the equivalence point and what is the pH?

@ halfway point pH = pKa $\therefore$ pH = 4.74

equivalence point: moles acid = moles base

moles acid = 0.4 mol $HC_2H_3O_2$

* need to add 1.0 L (1000 mL) NaOH

	$HC_2H_3O_2$ +	OH^- →	$C_2H_3O_2^-$
B	0.400	0.40	0
R	− 0.4	− 0.4	+ 0.4
A	0	0	0.4 V = 1.2 L
C	—	—	0.333

	$C_2H_3O_2^-$ +	H_2O ⇌	$HC_2H_3O_2$ +	OH^-
I	0.333		0	0
C	− x		+ x	+ x
E	.333 − x		x	x

$$K_b = \frac{[HC_2H_3O_2][OH^-]}{[C_2H_3O_2^-]}$$

$5.56\times10^{-10} = x^2/(.333 - x)$

$x = [OH^-] = 1.36\times10^{-5}$

pOH = 4.86

$\therefore$ pH = 9.14

assume negligible

$\frac{1.36\times10^{-5}}{0.333}\times 100$ ✓✓✓ passes

Conceptual questions:

5. A solution of an acid and a salt of its conjugate base (e.g. HCl & NaCl) will be less acidic/more acidic than a solution of the acid alone.

less acidic, eg. shifts towards undissociated HCN

6. Around what pH would a mixture of $NaHSO_4$ and $CaSO_4$ best buffer?

around the pKa of HSO_4^-, $pH \approx 2$

from Ka_2 of H_2SO_4

7. What are the two different ways to make a buffer?

1. directly add an acid (or base) and the salt of the conjugate base (or acid). – e.g. HCN + NaCN
2. you can titrate your weak acid (or base) with a strong base (or acid), until you have a sufficient amount of the conjugate in soln.

8. Generally, how do buffers work? What makes a buffer "good"?

Buffers work by maintaining the pH of a solution at a (fairly) constant pH. The weak acid is able to react with H^+ and the weak base with OH^- to resist drastic pH change. Good buffers buffer around the pKa of the acid and have high enough conc. to buffer.

9. What are the major species in solution for the titration of acetic acid with NaOH?

   a. At the halfway point Na^+, H_2O, $HC_2H_3O_2$, $C_2H_3O_2^-$

   b. At the equivalence point Na^+, H_2O, $C_2H_3O_2^-$

   c. Beyond the equivalence Na^+, H_2O, $C_2H_3O_2^-$, OH^-

   d. For the situations in a,b, and c, which constitute a buffered solution?

   a only – both acetic acid and acetate present

10. For the following scenarios, would the final pH be equal to, greater than, or less than 7 at the equivalence point?

   a. Titrating acetic acid with NaOH **> 7**

   b. Titrating KOH with HCl = 7

   c. Titrating ammonium chloride with NaOH **> 7**

11. What are the characteristics of an appropriate indicator for a titration?

the pKa of the indicator should be near the pH of the soln. @ equivalence

12. In blood, the primary buffering system is composed of bicarbonate (HCO_3^-) in equilibrium with carbonic acid (H_2CO3). The healthy range of blood pH is 7.35-7.45. Is this within the optimal buffering range for this buffer? Why or why not?

Not really, the pKa of carbonic acid is 6.36, so this is a bit high of a range. But the body handles blood pH through ~~a lot~~ of other systems too.

Challenge Problems:

1. Tris(hydroxymethyl)aminomethane, commonly called TRIS or Trizma, is often used as a buffer in biochemical studies.
    a. What is the optimimal pH for TRIS buffers?
    b. Calculate the ratio [TRIS]/[TRISH+] at pH = 7.00 and pH = 9.00.
    c. A buffer is prepared by diluting 50.0 g TRIS base and 65.0 g TRIS Hydrochloride (TRISHCl) to a total volume of 2.0 L. What is the pH of this buffer? What is the pH after 2.00 mL of 12 M HCl is added to a 200 mL portion of the buffer?

a. around the pKa of the conjugate acid – $TRISH^+$; therefore around a pH of 8.1

b. $K_b = \frac{[TRISH^+][OH^-]}{[TRIS]} \Rightarrow \frac{[TRIS]}{[TRISH^+]} = \frac{[OH^-]}{K_b}$

@ pH = 7.00

$$\frac{[TRIS]}{[TRISH^+]} = \frac{1\times10^{-7}}{1.19\times10^{-6}} = 0.084$$

@ pH = 9.00

$$\frac{[TRIS]}{[TRISH^+]} = \frac{1\times10^{-5}}{1.19\times10^{-6}} = 8.4$$

c. $50.0\text{g TRIS}\left(\frac{\text{mol}}{121.14\text{g}}\right) \div 2.0\text{ L} = 0.206\text{ M TRIS}$

$65.0\text{g TRISHCl}\left(\frac{\text{mol}}{157.6\text{g}}\right) \div 2.0\text{ L} = 0.206\text{ M TRISHCl}$

$TRIS + H_2O \rightleftharpoons TRISH^+ + OH^-$

	TRIS	H_2O	$TRISH^+$	OH^-
I	0.206		0.206	0
C	−x		+x	+x
E	.206−x		.206+x	x

$$K_b = \frac{[TRISH^+][OH^-]}{[TRIS]}$$

$$1.19\times10^{-6} = \frac{x(.206 + \cancel{x})}{(.206 - \cancel{x})}$$

passes 5% test

$x = [OH^-] = 1.19\times10^{-6}$

pH = 8.08

ADD HCl: $.002\text{ L}(12\text{ M}) = .024\text{ mol }H^+$

$TRIS + H^+ \longrightarrow TRISH^+$

	TRIS	H^+	$TRISH^+$
B	.0412	.024	0
R	−.024	−.024	+.024
A	.0172	0	.024
C	.085		0.119

V = .202 L

$$1.19\times10^{-6} = \frac{x(.119 + \cancel{x})}{(.085 - \cancel{x})}$$

passes 5% test

$x = 8.5\times10^{-7}$

pH = 7.93

2. To prepare a buffer solution with pH = 4.70, how many moles of NaN_3 should be added to a 1.0 L solution that is 0.40 M in HN_3? Assume no change in volume.

$$HN_3 + H_2O \rightleftharpoons N_3^- + H_3O^+$$

	HN_3	H_2O	N_3^-	H_3O^+
I	0.4		y	0
C	$-x$		$+x$	$+x$
E	$.4-x$		$y+x$	x

pH = 4.70

$\therefore [H_3O^+] = 1.995 \times 10^{-5} = x$

$K_a = [N_3^-][H_3O^+] / [HN_3]$

$$2.6 \times 10^{-5} = \frac{1.995 \times 10^{-5}\,(y + 1.995 \times 10^{-5})}{.4 - 1.995 \times 10^{-5}}$$

y = 0.52 moles NaN_3

3. You need 1.0 L of a buffer solution at a pH of 7.2 How would you prepare this buffer? (give the identity and appropriate amounts of buffers to use).

pKa of HOCl = 7.46, so it is the most appropriate choice for a pH = 7.2 buffer.

$$HOCl + H_2O \rightleftharpoons OCl^- + H_3O^+$$

	HOCl	H_2O	OCl^-	H_3O^+
I	2.0		y	0
C	$-x$		$+x$	$+x$
E	$2-x$		$y+x$	x

pH = 7.2

$\therefore x = [H_3O^+] = 6.3 \times 10^{-8}$

$$3.5 \times 10^{-8} = \frac{x(y+x)}{2-x}$$

$$3.5 \times 10^{-8} = \frac{6.3 \times 10^{-8}(y + 6.3 \times 10^{-8})}{2 - 6.3 \times 10^{-8}}$$

$y = [OCl^-]_0 = 1.11\text{ M}$

$\therefore$ to make this buffer I would add 2 moles HOCl and 1.11 moles NaOCl to a 1.0 L soln.

* you could also titrate HOCl with a strong base.

HA

4. Given a 200. mL solution of 1.2 M benzoic acid being titrated with 6.0 M NaOH, what would be the pH at the following points in the titration?

a. 15.0 mL NaOH added

MAJOR SPECIES: H_2O, Na, HA, A^-

$HA + OH^- \rightarrow A^-$

	HA	OH^-	A^-
B	.24	.09	0
R	−.09	−.09	+0.09
A	.15	—	.09
C	0.70	—	0.42

÷ 215 mL

$HA + H_2O \rightleftharpoons A^- + H_3O^+$

	HA	H_2O	A^-	H_3O^+
I	.7		.42	0
C	−x		+x	+x
E	.7−x		.42+x	x

$$6.3\times10^{-5} = \frac{x(.42+\cancel{x})}{.7-\cancel{x}}$$

passes 5% test

$x = [H_3O^+] = .000105$

$\therefore pH = 3.98$

b. The equivalence point

.24 moles HA = .24 mol NaOH
= 40.0 mL NaOH added

$HA + OH^- \rightarrow A^-$

	HA	OH^-	A^-
B	.24	.24	0
R	−.24	−.24	+.24
A	—	—	.24
C	—	—	1.0

÷ 240 mL

$A^- + H_2O \rightleftharpoons HA + OH^-$

	A^-	H_2O	HA	OH^-
I	1.0		0	0
C	−x		+x	+x
E	1.0		x	x

passes 5% test

$$K_b = 1.59\times10^{-10} = x^2/1.0\cancel{-x}$$

$x = [OH^-] = 1.26\times10^{-5}$ $\therefore pH = 9.1$

c. 5.00 mL beyond the equivalence point = 45.00 mL NaOH added

$HA + OH^- \rightarrow A^-$

	HA	OH^-	A^-
B	.24	.27	0
R	−.24	−.24	+.24
A	—	.03	.24
C	—	0.12	0.98

÷ 245 mL

EXCESS STRONG BASE DOMINATES

$pOH = -\log[OH^-]$
$= -\log(.12)$
$= 0.92$

$\therefore pH = 13.08$

HA

5. You have a 250 mL buffered solution that is 0.5 M in benzoic acid and 0.6 M in sodium benzoate. What is the pH if you add 25.0 mL of 1.0 M HCl? What is the pH if you add 25.0 mL of 1.0 M NaOH?

I. add 25.0 mL 1.0M HCl, reacts with benzoate (A^-)

	H^+	+ A^- →	HA
B	.025	.15	.125
R	-.025	-.025	+.025
A	—	.125	0.15
C	—	0.45	0.545

÷ 275mL

	HA + H_2O ⇌		A^- +	H_3O^+
I	.545		.45	0
C	−x		+x	+x
E	.545-x		.45+x	x

$$K_a = [A^-][H_3O^+]/[HA]$$

$$6.3\times10^{-5} = x(.45+x)/.545-x$$

$$x = [H_3O^+] = 7.63\times10^{-5}$$

$$\therefore pH = 4.12$$

II. add 25.0 mL 1.0 M NaOH, reacts with benzoic acid (HA)

	OH^-	+ HA →	A^-
B	.025	.125	.15
R	-.025	-.025	+.025
A	—	0.1	.175
C	—	0.36	0.64

÷ 275mL

	HA + H_2O ⇌		A^- +	H_3O^+
I	0.36		0.64	0
C	−x		+x	+x
E	.36-x		.64+x	x

$$K_a = [A^-][H_3O^+]/[HA]$$

$$6.3\times10^{-5} = x(.64+x)/.36-x$$

$$x = [H_3O^+] = 3.55\times10^{-5}$$

$$\therefore pH = 4.45$$

6. If you start with 40.0 mL of 2.00 M $HClO_4$, calculate $[H^+]$ after the addition of 60.0 mL of 0.60 M KOH. Is this before or after the equivalence point?

H^+ OH^-

strong - strong titration

$$H^+ + OH^- \rightarrow H_2O$$

	H^+	OH^-	H_2O
B	.08	.036	
R	-.036	-.036	
A	.044	—	
C	.44	—	$\div$ 100mL

$pH = -\log[H^+]$

$\therefore pH = 0.36$

this is before the equivalence point

7. You have a 1.0 L buffered solution of 2.0 M ammonia (NH_3) and 1.5 M ammonium chloride. How many [redacted] moles HCl would you have to add to shift the pH to 8.0?

* added HCl will react with NH_3 in soln.

$$H^+ + NH_3 \rightarrow NH_4^+$$

	H^+	NH_3	NH_4^+
B	y	2.0	1.5
R	-y	-y	+y
A	—	2 - y	1.5+y $\div$ 1L
C	—		

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

	NH_3	H_2O	NH_4^+	OH^-
I	2-y		1.5+y	0
C	-x		+x	+x
E	2-y-x		1.5+y+x	x

$pH = 8.0 \therefore [OH^-] = 1\times10^{-6}$

$K_b = [NH_4^+][OH^-] / [NH_3]$

$1.8\times10^{-5} = \dfrac{x(1.5+y+x)}{(2-y-x)}$ assume negligible

$1.8\times10^{-5} = 1\times10^{-6}\left(\dfrac{1.5+y}{2-y}\right)$

$18 = 1.5 + y / 2 - y$

$36 - 18y = 1.5 + y$

$y = 1.82$ moles HCl