15. T dependence of K_w

Since Ks are equil. + equil. is Thermo and Thermo is temp. dependent ($\Delta G = \Delta H - T\Delta S$) then Ks are T dependent.

For example the autoprotolysis of water

$(H^+)(OH^-) = K_w = 10^{-14}$ at 25°!!

This is source of learning pH of $H_2O = 7$ at 25°!!

But at lower temp. H–Oζ_H dissociation is less likely so Kw is smaller so pH is larger (like pH = 8 at 0°C)

At high temp H–Oζ_H is more likely, so pH < 7 at 100°C

---

16. A/B strength from K values: easy.

Since A/B rxns are dissociation like

$HA \rightarrow H^+ + A^-$ then the greater the dissociation (the more H^+) the larger the K & stronger the acid

☑ the bigger the Ka the stronger the acid

but $K_aK_b = K_w$ so if Ka↑ Kb↓

☑ the stronger the acid the weaker the conj. base.

	Ka	Kb
acetic	10^{-5}	10^{-9}
formic	10^{-4}	10^{-10}

strongest acid / strongest base

17. Approximations of A/B equations.

Falling out of RICE, everything is a quadratic or higher.

But if we assume C is large and K's are separated then the following simple calculation results

$H^+ = C_a$ strong $\quad H^+ = (K_a C_a)^{1/2}$ weak $\quad H^+ = K \frac{C_a}{C_b}$ buffer $\quad H^+ = (K_1 K_2)^{1/2}$ amphiprotic

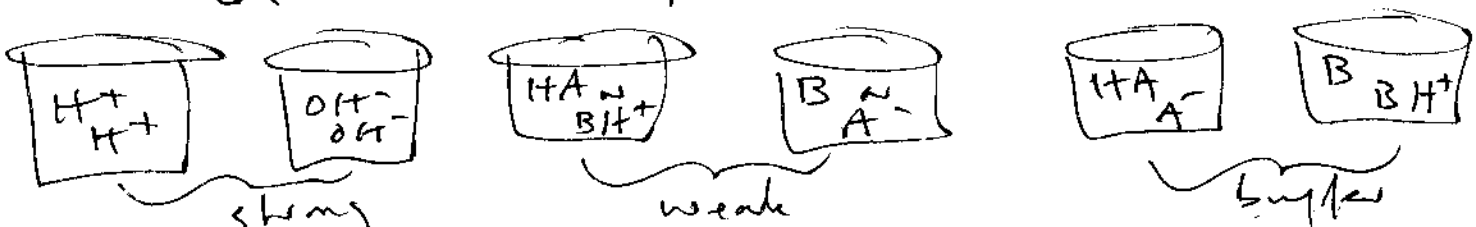
specifically for acids this means C is $> 10^{-2}$ or 10^{-3} M

and K_a value $10^{-4} < K_a < 10^{-10}$

↑ is too strong ↑ just right ↑ competes w/ K_w

18,19. There are 6 steps to A/B calculations. But if no neutralization, then actually just 4 steps.

1. get rid of spectators
2. identify if strong is H^+ or OH^-
3. identify is HA, A^-, B, BH^+
6. solve using (17) equations



20 Identify buffers (after neutralization)

A buffer is a weak acid + its conj. base.

ie. either HA, A^- or B, BH^+

PERFECT!!!

After 5 steps.

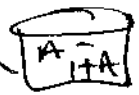
Example 0.1 M HCl + 0.1 M HA

1. .1 H^+ .1 HA
2. .1 H^+
3. .1 M HA
4. neutralize? no
5.  not a buffer

Example 0.1 M $HClO_4$ .2M NaA

1. .1 M H^+ .2 M A^-
2. .1 M H^+ 3. .2 M A^-
4. neutralize? yes
5. $H^+ + A^- \rightarrow HA$

H^+	A^-	HA
.1	.2	0
-.1	-.1	+.1
0	.1	.1

6.  yes, a buffer

21. Buffer neutralization calc.

This is a 6 step A/B problem. You will know it because there are 3 A or B to start.

Example, 0.1M $HClO_4$ + .2M HA .3M NaA in equal amounts. what is pH?

1. .1 M H^+ .2M HA .3M A^-
2. .1M H^+ 3. .2M HA .3M A^-
4. neutralize? yes
5. $H^+ + A^- \rightleftharpoons HA$

.1	.3	.2
-.1	-.1	+.1
0	.2	.3

← now a buffer

6. $H^+ = Ka \frac{Ca}{Cb}$

I might ask you to recall or I might make you calculate.

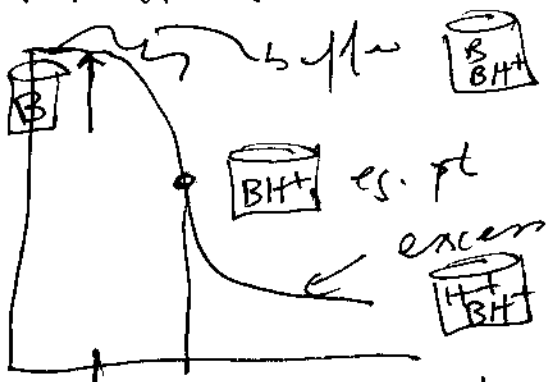
→ buffers have pH ~ pKa

but I will be making you calculate

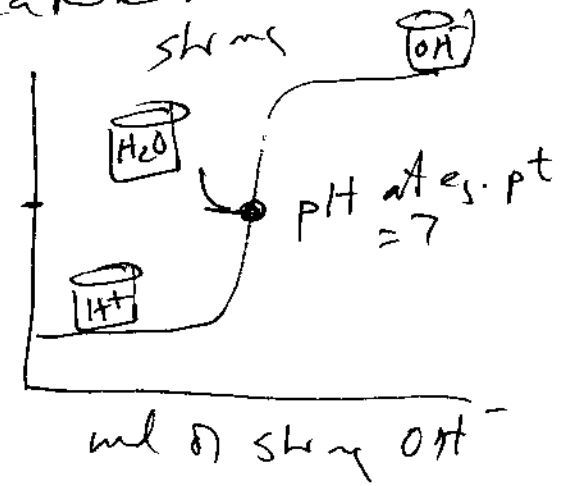
---

22. titration curve features

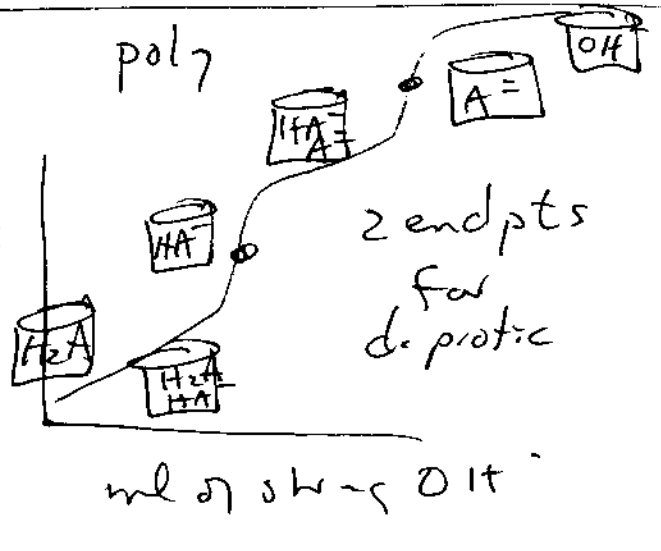
weak base buffer



strong



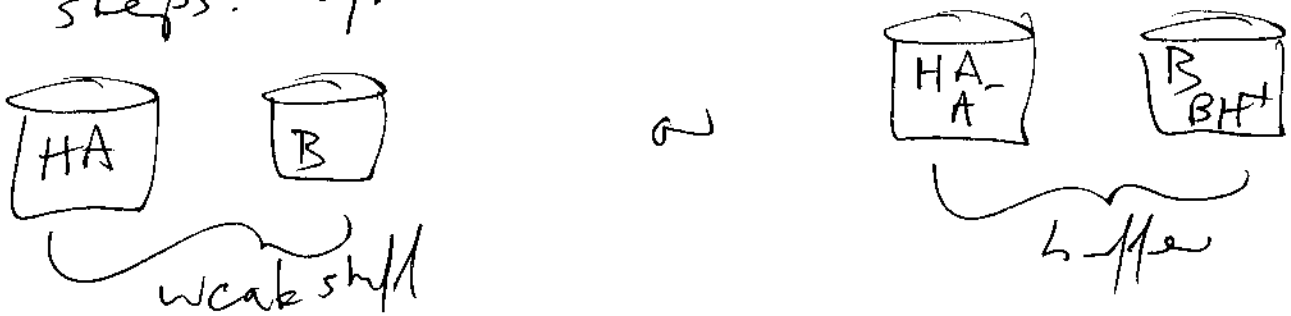
poly



Two things to say 1. $pK_a < 7$
2. ½ way to eq. pt $pH = pK_b$

23. Titration strong w/ strong.
understand that a titration is just an acid base problem. So do the 6 steps
In this case we only H^+, OH^-, after neutralization the answer is either $H^+ = Ca$ or $OH^- = Cb$ or pH 7

24-25. Titration of weak w/ strong.
This is just an acid base problem. So do the 6 steps. Your answer will be either



Remember to work in same terrains
- OH^- w/ Kb w/ pOH
- H^+ w/ Ka w/ pH using $[H^+][OH^-] = Kw$ or $KaKb = Kw$
- keep track of volumes in calculating Ca or Cb

26. solubility + K_{sp}.

in general, for dissociation, the bigger the K, the more soluble.

so $K = 10^{-2}$ is more soluble than $K = 10^{-50}$

but salts have several forms

$AB \rightarrow A^+ + B^-$ ~ $AB_2 \rightarrow A^{++} + 2B^-$ $AB_3 \rightarrow A^{+3} + 3B^-$

2 species take square root of K

3 species take cubed root

4 species take the fourth root

Example. $K_{sp} = 10^{-10}$ for AB + $K_{sp} = 10^{-12}$ for A_2B.

This is more soluble

---

27. in (26) we took estimates. Like square or cubed root

The actual solubility is $[\ ] = \sqrt{K_{sp}}$ for AB

$[\ ] = \sqrt[3]{\frac{K_{sp}}{4}}$ for AB_2 ~ A_2B

$[\ ] = \sqrt[4]{\frac{K_{sp}}{27}}$ for AB_3 ~ A_3B

For example.

What is Ca^{++} if $K_{sp} = 4 \times 10^{-12}$ for CaF_2 ** Hint ** $F^- = 2 \times 10^{-4}$ M because 2F

$[Ca^{++}] = \sqrt[3]{\frac{4 \times 10^{-12}}{4}} = 1 \times 10^{-4}$

28. A K_{sp} problem with 2 species present.

Example $AgCl$ in 0.1M $NaCl$ so $= [Ag^+]$

$\therefore K_{sp} = 1 \times 10^{-10}$ for $AgCl$

Le Chatelier says $AgCl \rightleftharpoons Ag^+ + Cl^-$ ← $\uparrow Cl^-$ Then $Ag^+ \downarrow$

	$\cancel{0}$	.1
	$+x$	$+x$
	x	$.1+x$

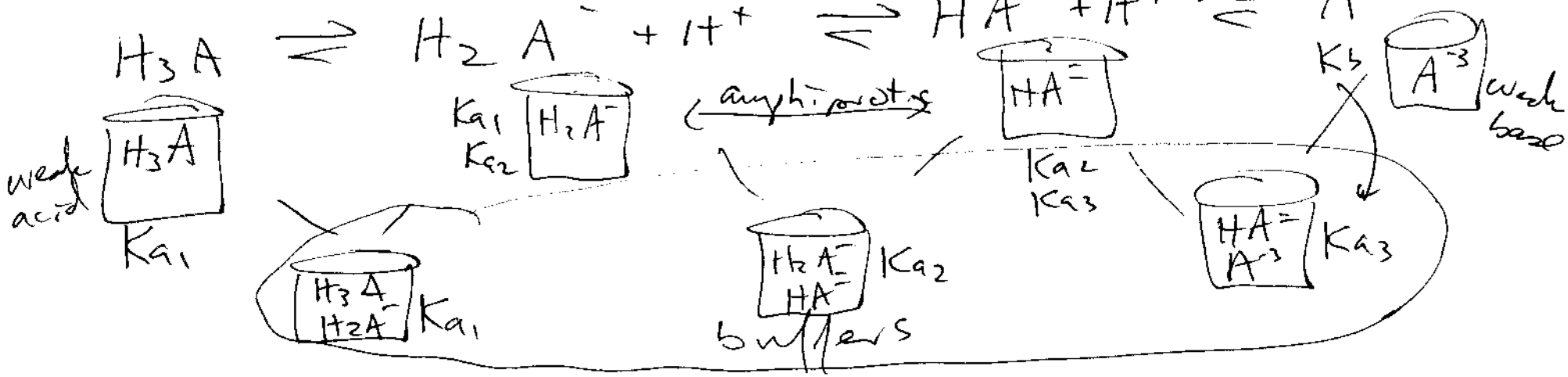
$K_{sp} = (x)(.1+x) = 10^{-10} \approx x(.1)$ so $x = 10^{-9}M$

↑ small

---

29. I will give you a diprotic or triprotic acid. Know what species are present and the equilibria that explain them.

$H_3A \rightleftharpoons H_2A^- + H^+ \rightleftharpoons HA^= + H^+ \rightleftharpoons A^{-3}$



30. neutralization reaction. I will give you some material, you neutralize it and tell me what is left?

There are 5 neutralization rxns

$$H^+ + B \rightleftharpoons BH^+$$
$$H^+ + A^- \rightleftharpoons HA$$
$$H^+ + OH^- \rightleftharpoons H_2O$$
$$HA + OH^- \rightleftharpoons A^-$$
$$BH^+ + OH^- \rightleftharpoons B$$

each has something strong on the left and a buffer pair $BH^+ + B$ or $HA + A^-$

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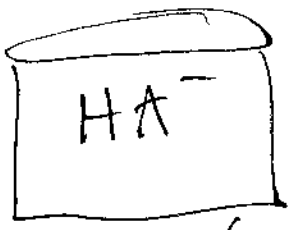
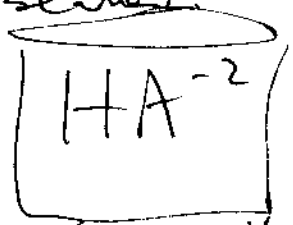
31. amphiprotic calculation This is for a diprotic or triprotic acid w/ following in a beaker



or

or



so do the 6 steps to get

SO simplified calculation is

$H^+ = (K_1K_2)^{1/2}$ for diprotic

$H^+ = (K_1K_2)^{1/2}$

$H^+ = (K_2K_3)^{1/2}$ for triprotic

Example Li_2HPO_4 is amphiprotic

32. Equilibrium calculation for polyprotic. You will do a calculation for one of the beakers in (29).

So do the 6 steps and then solve either.

1. weak acid or base
2. amphiprotic
3. buffer

---

33. mass + charge balance.

Be able to set up an equation used in solution of complex A/B equilibria.

charge balance

all the + over here = all the − over here

mass balance

all the atom you dump in = all the stuff it becomes

Example What is charge balance for $NaHCO_3$ in H_2O

The compds are $H_2O, H^+, OH^-, Na^+, HCO_3^-, CO_3^=, H_2CO_3$

so

$$H^+ + Na^+ = OH^- + HCO_3^- + 2CO_3^=$$

2 in front

What is mass balance of $CO_3^=$ in $NaHCO_3$

$$[NaHCO_3] = CO_3^= + HCO_3^- + H_2CO_3$$