Slide 1	Solution Equilibria Of Buffers, Ions and Solubility Products I sing!!!!	
Slide 2	K IS K IS K IS K IS K If you truly grasp the nature of equilibrium reactions and can set up and solve ICE charts – there is nothing new here. Different type of reaction, same mechanics.	
Slide 3	Common Ion Effect We've already seen a version of the common Ion Effect pop up in our discussions of very weak acids (or bases) and in polyprotic acids. This has also implicitly arisen as an issue when discussing LeChatelier's Principle.	

Slide 4			
	An Old Friend – A Familiar Problem		
	What is the pH of a 0.100 M HOAc solution?		
	What's the 1 st thing we need?		
	4		
Slide 5			
	A Balanced Equation		
	HOAc + H ₂ O ↔ OAc ⁻ + H ₃ O ⁺		
	And next we need???		
	s		
			
Slide 6			
Silde 0	An ICE Chart & a K	 	
	HOAc + H2O ↔ OAc- + H3O+		
	K _a = <u>[OAc-][H₃O+]</u> = 1.8x10 ⁻⁵ [HOAc]		
	[HOAc]		
	6		

An ICE Chart

HOAc + $H_2O \leftrightarrow OAc^- + H_3O^+$ I 0.100 M - 0 0
C -x -x +x +x
E 0.100-x - x x

Now, back to the K!!

Slide 8

An ICE Chart & a K

 $\begin{aligned} & HOAc + \ H_2O \leftrightarrow OAc^- + \ H_3O^+ \\ & K_a = \underbrace{[x][x]}_{[0.100-x]} = 1.8 \times 10^{-5} \end{aligned}$

How do we solve it?

Slide 9

An ICE Chart & a K

 $HOAc + H_2O \leftrightarrow OAc^- + H_3O^+$

 $K_a = [x][x] = 1.8x10^{-5}$ [0.100-x]

How do we solve it?

Always try our simplifying assumption

		_
		_
		_
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,		 _
,		 _
,		 _
	 	 _
		 _
		_

Slide 10 | HOAC + H₂O \rightarrow OAC + H₂O² | K₃ = [AIDA] = 1.8x10³ | X<<0.100 | K₅ = [AIDA] = 1.8x10⁴ | X = 1.8x10⁴ | X = 1.3x10³ | M | | Slide 11 | PH = - log [H₃O⁺] | PH = - log (1.34x10⁻³ M) | PH = 2.87

Slide 12

New Problem

What is the pH of a solution that is 0.100 M HOAc AND 0.100 M NaOAc?

What's the first thing you need?

Slide 13	HOAc AND 0.100 M NaOAc?]	
	A. HOAc + NaOAc ↔		
	B. $HOAc + H_2O \leftrightarrow$ C. $NaOAc + H_2O \leftrightarrow$		
	D. $H_2O + H_2O \leftrightarrow$		
	E. OAC + HOAc ↔		
	13	_	
CI: L 44		1	
Slide 14	A Released Equation		
	A Balanced Equation But what's going on here?		
	Is this a familiar reaction or something completely new?		
	24		
		=,	
Slide 15			
	Critical Judgment		
	HOAc + H ₂ O ↔ OAc ⁻ + H ₃ O ⁺		
	How would you know this?		
	HOAc and NaOAc have only a couple		
	possible products if they were to react		
	15		
		4	

	1	
lid		

Critical Judgment

 $HOAc + H_2O \leftrightarrow OAc^- + H_3O^+$

HOAc is an "ionic-ish" compound. NaOAc is an ionic compound

 $\begin{aligned} & \text{HOAc} \rightarrow \text{H}^{\scriptscriptstyle{+}} + \text{OAc}^{\scriptscriptstyle{-}} \\ & \text{NaOAc} \rightarrow \text{Na}^{\scriptscriptstyle{+}} + \text{OAc}^{\scriptscriptstyle{-}} \end{aligned}$

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Slide 17

Critical Judgment

 $HOAc \rightarrow H^+ + OAc^ NaOAc \rightarrow Na^+ + OAc^-$

If new compounds were to form, it would need to be from the interaction of the cations with the anions and vice-versa

The only possible products are:

HOAc and NaOAc

They cannot react with each other!

17

Slide 18

Critical Judgment

It is also possible that an acid/base neutralization reaction could happen since HOAc is an acid and OAc is a base:

 $\mathsf{HOAc}\,+\,\mathsf{OAc}^{\scriptscriptstyle{-}}\to\mathsf{HOAc}\,+\,\mathsf{OAc}^{\scriptscriptstyle{-}}$

The only possible products are:

HOAc and OAc- - which is what you started with!

They cannot react with each other!

			-
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		 	_
		 	_

So – is there no reaction…

Well, there is actually one other thing in the beaker:



19

Slide 20

So – is there no reaction...

Well, there is actually one other thing in the beaker:

H₂O H₂O HOAc H₂O OAc HOAC OAC HOAC OAC

20

Slide 21

It's our old friend!

 $HOAc + H_2O \leftrightarrow OAc^- + H_3O^+$

Or...

 $OAc^- + H_2O \leftrightarrow HOAc + OH^-$

In either case it is the SAME reaction: \boldsymbol{K}_{a} or \boldsymbol{K}_{b}

It just happens that you have one of the reactants AND one of the products!

	,		

Slide 22	Returning to the Problem HOAc + $H_2O \leftrightarrow OAc^- + H_3O^+$ Next on the list of things we need is	- - -	
		-	
Slide 23	Returning to the Problem HOAC + H ₂ O ↔ OAC ⁻ + H ₃ O ⁺ Next on the list of things we need is The Equilibrium Constant Expression And maybe an ICE chart	- - -	
		- -	
Slide 24	The Equilibrium Constant Expression $HOAC + H_2O \leftrightarrow OAC^- + H_3O^+$ $K_8 = \underbrace{[OAC^-][H_3O^+]}_{[HOAC]} = 1.8 \times 10^{-5}$ The value is from the table in the book.	- - -	

e 2 5	ICE ICE DADY ICE ICE	
	$\frac{\text{ICE ICE, BABY, ICE ICE}}{\text{HOAc} + \text{H}_2\text{O} \leftrightarrow \text{OAc}^- + \text{H}_3\text{O}^+}$	
	I	
	С	
	E	
	What goes where?	
	25	
e 2 6		
e 26	In case you've forgotten the problem	
e 26	What is the pH of a solution that is 0.100 M	
e 26		
e 26	What is the pH of a solution that is 0.100 M	
e 26	What is the pH of a solution that is 0.100 M	
e 26	What is the pH of a solution that is 0.100 M HOAc AND 0.100 M NaOAc?	
e 26	What is the pH of a solution that is 0.100 M HOAc AND 0.100 M NaOAc? What's with the NaOAc?	
e 26	What is the pH of a solution that is 0.100 M HOAc AND 0.100 M NaOAc?	
e 26	What is the pH of a solution that is 0.100 M HOAc AND 0.100 M NaOAc? What's with the NaOAc?	
e 26	What is the pH of a solution that is 0.100 M HOAc AND 0.100 M NaOAc? What's with the NaOAc?	
e 26	What is the pH of a solution that is 0.100 M HOAc AND 0.100 M NaOAc? What's with the NaOAc?	
e 26	What is the pH of a solution that is 0.100 M HOAc AND 0.100 M NaOAc? What's with the NaOAc?	

In case you've forgotten the problem...

What is the pH of a solution that is 0.100 M HOAc AND 0.100 M NaOAc?

What's with the NaOAc?

It's just a source of OAc- in this reaction – Na is a spectator ion. We could just as easily have used KOAc, or even ${\rm Fe(OAc)_3}$

Slide 28		1		
	Why NaOAc?	_		
		_		
		_		
		_	 	
	28			
		_		
		_		
Slide 29		- 1		
Slide 29	Why NaOAc? You see Na salts used a lot.	_	 	
	Same 3 reasons as before: 1. Cheap.	_		
	2. Very soluble. 3. Mostly inert.	_		
	(K salts also work, things like Fe, Ca etc not so much.)	_	 	
ļ		<u> </u>	 	
Slide 30		- 1		
Slide 30	ICE ICE, BABY, ICE ICE HOAC + H₂O ↔ OAC + H₃O+	_		
	I 0.100 M - 0.100 M 0	_	 	
	C -x - +x +x E 0.100-x - 0.100+x x	_		
	Does it now start to feel like we're on familiar ground?			
	30			



The Equilibrium Constant Expression

 $HOAc + H_2O \leftrightarrow OAc^- + H_3O^+$

 $K_a = \frac{[OAc-][H_3O+]}{[HOAc]} = 1.8x10^{-5}$ $K_a = \frac{[0.100+x][x]}{[HOAc]} = 1.8x10^{-5}$

[0.100-x]
Can we make our assumption?

.

Slide 32

The Equilibrium Constant Expression

 $HOAc + H_2O \leftrightarrow OAc^- + H_3O^+$

 $K_a = [OAc-][H_3O+] = 1.8 \times 10^{-5}$ [HOAc]

 $K_a = [0.100 + x][x] = 1.8x10^{-5}$ [0.100 - x]

Can we make our assumption? Always worth a try! x << 0.100

32

Slide 33

The Equilibrium Constant Expression

 $K_a = \frac{[0.100][x]}{[0.100]} = 1.8x10^{-5}$

 $x = 1.8 \times 10^{-5}$

Looks like a pretty good assumption.

•				

ICE ICE, BABY, ICE ICE

 $HOAc + H_2O \leftrightarrow OAc^- + H_3O^+$

I 0.100 M - 0.100 M 0

C -1.8x10⁻⁵ - +1.8x10⁻⁵ +1.8x10⁻⁵

E 0.100 - 0.100 1.8x10⁻⁵

24

Slide 35

Calculating the pH

 $pH = - log[H_3O+]$

 $pH = -log (1.8x10^{-5})$

pH = 4.74

Slide 36

How does this compare to our HOAc without the NaOAc?

0.100 M HOAc

pH = 2.87

0.100 M HOAc & 0.100 M NaOAc

pH = 4.74

Does this make sense?

How does this compare to our HOAc without the NaOAc?

0.100 M HOAc

pH = 2.87

0.100 M HOAc & 0.100 M NaOAc $\mathrm{pH} = 4.74$

Does this make sense? Of course! It's French!

37

Slide 38

Le Chatelier's Principle!

A system under "stress" responds to alleviate that stress.

By introducing a second source of OAc-, we force the K_{S} reaction of HOAc to shift to alleviate that stress.

It shifts back toward the reactants to try and use up some of the extra OAc- and keep K constant!

38

Slide 39

Le Chatelier's Principle!

All the "Common Ion Effect" is is LeChatelier's Principle where the "stress" is a "common ion"!

This problem is also an excellent example of something else...

Slide 40		
	Le Chatelier's Principle!	
	All the "Common Ion Effect" is is	
	LeChatelier's Principle where the "stress" is a "common ion"!	
	This problem is also an excellent example of	
	something else	
	It's a Buffer!	
	40	
I		1
Slide 41	What's a Buffer?	
	What's a Bufferr	
	41	
Slide 42		
	What's a Buffer?	
	A "buffer" is just an acid (or a base) and its conjugate base (or acid).	
	What's a buffer good for?	
	what's a buller good for:	
	42	

What's a Buffer?

A "buffer" is just an acid (or a base) and its conjugate base (or acid).

What's a buffer good for?

A buffer resists changes in its pH!

How?

43

Slide 44

What's a Buffer?

A "buffer" is just an acid (or a base) and its conjugate base (or acid).

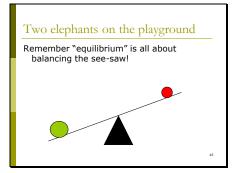
What's a buffer good for?

A buffer resists changes in its pH!

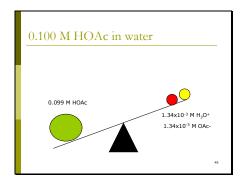
How?

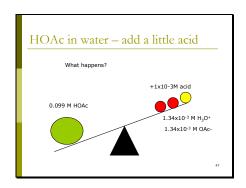
Le Chatelier's Principle, Common Ion Effect, 2 elephants on the playground...

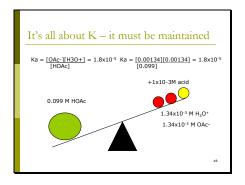
44



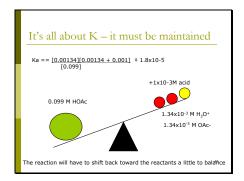
Slide 46

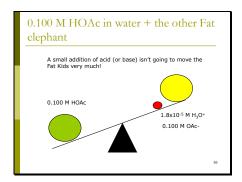


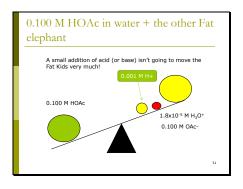




Slide 49







Buffers are NOTHING NEW

K is K is K is K

A buffer is just an acid (or base) with a conjugate base (or acid) thrown in.

It's just an ICE chart with different initial conditions.

52

Slide 53

Chemical Shorthand

Since the ICE chart for a buffer looks pretty much the same every time, doesn't it seem like there should be a way around having to set up and solve the ICE chart repeatedly?

Well, in fact, there is a chemical shorthand...

53

Slide 54

Henderson-Hasselbach

pH= pK_a + log [<u>base]</u> [acid]

This is actually just the ICE chart.

Recall the equilibrium expression we just used:

 $\mathsf{K}_\mathsf{a} = \underbrace{[\mathsf{O}\mathsf{A}\mathsf{c}\text{-}][\mathsf{H}_3\mathsf{O}\text{+}]}_{[\mathsf{H}\mathsf{O}\mathsf{A}\mathsf{c}]}$

Could I write it more generally for any acid?

		55
	de	

$Acid + H_2O \leftrightarrow Conj Base + H_3O^+$

 $K_a = [conj base][H_3O+]$ [acid]

Now, all I need to do is take the -log of both sides!!!

55

Slide 56

A little algebra

- $\log K_a = - \log [\underline{conj base}][\underline{H_3O+}]$ [acid]

Remember $\log A*B = \log A + \log B$

- log $K_a = - log [conj base] - log [H_3O+]$ [acid]

56

Slide 57

A little algebra

- log K_a = - log [base] - log [H₃O+] [acid]

What is "- $log [H_3O^+]''$? pH, of course! What is "- $log K_a''$? pK_a, of course!

 $pK_a = - log [base] + pH$ [acid]

Rearranging a little

 $\begin{aligned} pK_a &= -\log \underline{[base]} + pH \\ &\quad [acid] \\ pK_a &+ \log \underline{[base]} = pH \\ &\quad [acid] \end{aligned}$

Voila!!! The Henderson-Hasselbach equation!!!

You can also write it as: $pOH = pK_b + log [\underline{acid}]$ [base]

58

Slide 59

Returning to my original buffer...

If I mix 0.100 M HOAc and 0.100 M NaOAc, what's the pH?

Let's revisit our solution but use Henderson-

59

Slide 60

ICE ICE, BABY, ICE ICE

•			
•			

ICE ICE, BABY, ICE ICE

$$\begin{split} pH &= pK_a + \log\left(\frac{[base]}{[acid]}\right) \\ pK_a &= -\log(1.8\times10^{-5}) = 4.74 \\ pH &= 4.74 + \log\left(\frac{[base]}{[acid]}\right) \end{split}$$

61

Slide 62

ICE ICE, BABY, ICE ICE

```
HOAC + H<sub>2</sub>O ↔ OAC + H<sub>3</sub>O +

I 0.100 M - 0.100 M 0

C -x - +x +x

E 0.100-x - 0.100+x x

pH = 4.74 + \log \left(\frac{[base]}{[acid]}\right)
pH = -\log(x) = 4.74 + \log \left(\frac{0.100 + x}{0.100 - x}\right)
Henderson-Hasselbach doesn't help me much!!!
```

Slide 63

The Equilibrium Constant Expression

Except, what if we make our assumption? $x \!<\! < \! 0.100$

$$pH = 4.74 + \log\left(\frac{0.100 + x}{0.100 - x}\right)$$

$$pH = 4.74 + \log\left(\frac{0.100}{0.100}\right) = 4.74$$

Henderson-Hasselbach is just the solution to your ICE chart if YOU MAKE THE ASSUMPTION!



ICE ICE, BABY, ICE ICE

 $HOAc + H_2O \leftrightarrow OAc^- + H_3O^+$

I INITIAL - INITIAL 0

C -SMALL - +SMALL +x

E INITIAL - INITIAL x

So, I get to use my INITIAL concentrations in H-H if I assume \boldsymbol{x} is small.

Slide 65

H-H makes buffers easy!

What is the pH of a solution made by mixing 500 mL of 3.0 M NH $_3$ and 500 mL of 3.0 M NH $_4$ Cl?

1st thing you need is...

 $NH_4CI = NH_4^+ + CI^-$

65

Slide 66

Balanced Equation!

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

Do I need to do an ICE chart?

Not with H-H!

H-H makes buffers easy!

What is the pH of a solution made by mixing 500 mL of 3.0 M NH₃ and 500 mL of 3.0 M NH₄Cl?

$$pOH = pK_b + \log(\frac{[acid]}{[base]})$$

$$pOH = [-\log(1.8 \times 10^{-5})] + \log(\frac{[1.5\ M\ NH_4^+]}{[1.5\ M\ NH_3]})$$

Why 1.5 M? Dilution!

$$\begin{array}{c} M_1 V_1 = M_2 V_2 \\ 500 \; mL \; (3.0 \; M \; NH_3) = 1000 \; mL \; (X \; M \; NH_3) \\ X = 1.5 \; M \; NH_3 \end{array}$$

(same for $\mathrm{NH_4^+}$)

Slide 68

H-H makes buffers easy!

What is the pH of a solution made by mixing 500 mL of 3.0 M $\rm NH_3$ and 500 mL of 3.0 M $\rm NH_4Cl?$

$$pOH = pK_b + \log(\frac{[acid]}{[base]})$$

$$pOH = [-\log(1.8 \times 10^{-5})] + \log(\frac{[1.5 M NH_4^+]}{[1.5 M NH_3]})$$

$$H = [-\log(1.8 \times 10^{-8})] + \log(\frac{1.5 M NH_3}{1})$$

$$pOH = 4.74 + \log(1) = 4.74 + 0 = 4.74$$

 $pH = 14 - pOH = 14 - 4.74 = 9.26$

Slide 69

Another little trick..

$$pH = pK_a + \log(\frac{[base]}{[acid]})$$

The [base] and [acid] are both MOLARITY.

What is M?

$$\frac{moles}{Liters}$$

But both the acid and the base are in the same beaker!



$$pH = pK_{\alpha} + \log(\frac{base}{[acid]})$$

$$mol base$$

$$pH = pK_{\alpha} + \log(\frac{base}{[acid]})$$

$$I. solution$$

$$mol base$$

$$pH = pK_{\alpha} + \log(\frac{base}{[acid]})$$

$$I. solution$$

$$mol base$$

$$pH = pK_{\alpha} + \log(\frac{base}{[acid]})$$

$$I. solution$$

$$I. soluti$$

Revisiting the previous problem:

What is the pH of a solution made by mixing 500 mL of 3.0 M $\rm NH_3$ and 500 mL of 3.0 M $\rm NH_4CI$?

$$\begin{split} pOH &= pK_b + \log \frac{\{acidl\}}{\{base\}} \\ pOH &= pK_b + \log \frac{moles\ acid}{moles\ base} \\ 0.500\ LNH_3 & \frac{3.0\ mol\ NH_3}{L} = 1.5\ moles\ NH_3 \\ 0.500\ LNH_4^* & \frac{3.0\ mol\ NH_4^*}{L} = 1.5\ moles\ NH_4^* \\ pOH &= \left[-\log(1.8\times10^{-5})\right] + \log\left(\frac{[1.5\ moles\ NH_4^*]}{[1.5\ moles\ NH_2]}\right) = 4.74 \end{split}$$

Even more helpful if I'm mixing 3 things...stay tuned.

Slide 72

Quick Comprehension test!

Slide 73			
	What is the pH of a solution that is 0.500 M HOAc and 0.250 M NaCl?		
	What is NaCl?		
	It's a salt!		
	Is this a buffer?		
	NO! The salt does NOT contain the conjugate base of HOAc.		
	conjugate base of HOAC.		
Slide 74		1	
Jilde 74	Consider the reaction:		
	It's all about the K_a (or K_b)		
	For HOAc:		
	$HOAc(aq) + H_2O(l) \leftrightarrow OAc^-(aq) + H_3O^+(aq)$		
	$NaCl(aq) \rightarrow Na^{+}(aq) + Cl^{-}(aq)$		
	There are no common ions		
	,		
Slide 75			
	Consider the reaction:		
	It's all about the K_a (or K_b)		
	For HOAc:		
	$HOAc(aq) + H_2O(l) \leftrightarrow OAc^-(aq) + H_3O^+(aq)$		
	Only an acetate salt will make it a buffer!		
	75		

Slide 76	What is the pH of a solution that is initially 0.100 M	
	NH ₃ and 0.050 M HCl?	
	$-K_b (NH_3) = 1.8 \times 10^{-5}$	
	K_a (HCI) = FB	
	What is NH ₃ ?	
	It's a base!	
	What is HCl?	
	It's an acid! (A strong acid, in fact!)	
	3111,	
	What do acids and bases do?	
	Neutralize each other!	
	76	
Slide 77	Now, we sort of have TWO	
Silue //		
	reactions (or maybe 4 ☺)	
	I have MULTIPLE acids and bases	
	I liave MOLITELE acids and bases	
	What are thou?	
	What are they?	
	NH ₃ is a base	
	HCl is an acid	
	And	
	H ₂ O is both an acid and a base!	
	77	
	"	
Slide 78		
	My TWO (or 4) reactions!	
	$NH_3 + HCl \rightarrow$	
	$NH_3 + H_2O \leftrightarrow$	
	11113 1 1120 11	
	$HCl + H_2O \rightarrow$	
	W O . W C	
	$H_2O + H_2O \rightarrow$	
	I can react any acid with any base!	
	2 22 react any acid men any base.	
	What do I do when I have multiple reactions?	
	. 78	

...

Slide	79
-------	----

I do each of them, one at a time, from biggest K to smallest K!

70

Slide 80

My TWO (or 4) reactions!

 $NH_3\ (aq) + HCl(aq) \rightarrow NH_4^+(aq) + Cl^-(aq)$ $NH_3(aq) + H_2O(l) \leftrightarrow NH_4^+(aq) + OH^-(aq)$ $HCl(aq) + H_2O(l) \rightarrow Cl^-(aq) + H_3O^+(aq)$ $H_2O(l) + H_2O(l) \rightarrow H_3O^+(aq) + OH^-(aq)$

Do I know the K's?

Slide 81

My TWO (or 4) reactions!

 $NH_3 (aq) + HCl(aq) \rightarrow NH_4^+(aq) + Cl^-(aq)$

 $\begin{array}{l} NH_3(aq) + H_2O(l) \leftrightarrow NH_4^+(aq) + OH^-(aq) \\ K_a = 1.8 \times 10^{-5} \\ HCl(aq) + H_2O(l) \rightarrow Cl^-(aq) + H_3O^+(aq) \\ K_a = HUGE, nearly infinite \\ H_2O(l) + H_2O(l) \rightarrow H_3O^+(aq) + OH^-(aq) \\ K_w = 1.0 \times 10^{-14} \end{array}$

What about the first reaction?

What about the first reaction?

 $NH_3(aq) + HCl(aq) \rightarrow NH_4^+(aq) + Cl^-(aq)$

It is NOT NOT NOT a Ka! How do I know? No water, no Ka! It's actually a combo of the other 3 reactions!

Slide 83

What about the first reaction?

 $NH_3(aq) + HCl(aq) \rightarrow NH_4^+(aq) + Cl^-(aq)$ If I add the first 2 and subtract the 3rd one, $\begin{array}{l} \text{I get...} \\ NH_3(aq) + H_2O(l) \leftrightarrow NH_4^+(aq) + OH^-(aq) \\ + BCl(aq) + H_2O(l) \rightarrow Cl^-(aq) + H_2O^+(aq) \\ NH_3(aq) + H_2O(l) + HCl(aq) + H_2O(l) \\ \rightarrow NH_4^+(aq) + OH^-(aq) + Cl^-(aq) + H_3O^+(aq) \\ + H_2O^+(aq) + OH^-(aq) \rightarrow H_2O(l) + H_2O(l) \\ NH_3(aq) + H_2O(l) + HCl(aq) + H_2O(l) + H_2O^+(aq) + OH^-(aq) \\ \rightarrow NH_3^+(aq) + OH^-(aq) + H_2O(l) + H_2O^+(aq) + H_2O(l) \\ + H_2O^+(l) \end{array}$

Slide 84

What about the first reaction?

 $NH_3(aq) + HCl(aq) \rightarrow NH_4^+(aq) + Cl^-(aq)$ So, I could get the K by compaining the K's from the other reactions! $K = \frac{K_a(HCl) \times K_b(NH_3)}{K_w} = \frac{FB \times 1.8 \times 10^{-5}}{1.0 \times 10^{-14}}$ $= FB \times 1.8 \times 10^9 = FB \times FB = SFB$

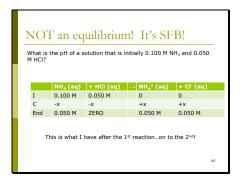
My TWO (or 4) reactions!

 $\begin{array}{c} NH_{3}\;(aq) + HCl(aq) \rightarrow NH_{4}^{+}(aq) + Cl^{-}(aq) \\ K_{neutral} = SFB \\ NH_{3}(aq) + H_{2}O(l) \leftrightarrow NH_{4}^{+}(aq) + OH^{-}(aq) \\ K_{a} = 1.8 \times 10^{-5} \\ HCl(aq) + H_{2}O(l) \rightarrow Cl^{-}(aq) + H_{3}O^{+}(aq) \\ K_{a} = FB \\ H_{2}O(l) + H_{2}O(l) \rightarrow H_{3}O^{+}(aq) + OH^{-}(aq) \\ K_{w} = 1.0 \times 10^{-14} \\ \end{array}$ So...the neutralization goes 1st.

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Slide 86

NOT an equilibrium! It's SFB! What is the pH of a solution that is initially 0.100 M NH₃ and 0.050 M HC!? NH₄ (aq) + HCl (aq) - NH₄* (aq) + CF (aq) I 0.100 M 0.050 M 0 0 C -x -x +x +x +x HCl is the limiting reactant...so...



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My TWO (or 4) reactions!

```
NH_3\ (aq) + HCl(aq) \rightarrow NH_4^+(aq) + Cl^-(aq)
        K_{neutral} = SFB

NH_3(aq) + H_2O(l) \leftrightarrow NH_4^+(aq) + OH^-(aq)

K_a = 1.8 \times 10^{-5}
        K_a = 1.6 \times 10^{-1}

HCl(aq) + H_2O(l) \rightarrow Cl^{-1}(aq) + H_3O^{+}(aq)

K_a = FB

H_2O(l) + H_2O(l) \rightarrow H_3O^{+}(aq) + OH^{-}(aq)

K_w = 1.0 \times 10^{-14}
The K_a of HCl would go second...BUT....!!!!
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I'm out of HCl!

 2^{nd} reaction always starts where the 1^{st} ends...so this is what's in the beaker...along with water.

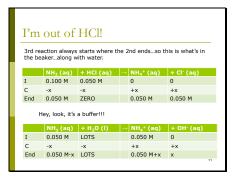
	NH ₃ (aq)	+ HCl (aq)	\rightarrow	NH ₄ + (aq)	+ Cl ⁻ (aq)		
I	0.100 M	0.050 M		0	0		
C	-x	-x		+x	+x		
End	0.050 M	ZERO		0.050 M	0.050 M		
So, on to the 3 rd							

Slide 90

My TWO (or 4) reactions!

 $NH_3\ (aq) + HCl(aq) \rightarrow NH_4^+(aq) + Cl^-(aq)$ $\begin{array}{l} {\rm NH_3\ (aq) + HCl(aq) \to NH_4^+(aq) + Cl^-(aq)} \\ {\rm K_{neutral} = SFB} \\ {\rm NH_3(aq) + H_2O(l) \to NH_4^+(aq) + OH^-(aq)} \\ {\rm K_a = 1.8 \times 10^{-5}} \\ {\rm HCl(aq) + H_2O(l) \to Cl^-(aq) + H_3O^+(aq)} \\ {\rm K_a = FB} \\ {\rm H_2O(l) + H_2O(l) \to H_3O^+(aq) + OH^-(aq)} \\ {\rm K_w = 1.0 \times 10^{-14}} \\ {\rm 2.K_a \ Of \ NH_2 \ would \ acc \ part} \end{array}$ The K_b of NH_3 would go next...

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Slide 92

Let's H-H!

$$\begin{split} pOH &= pK_b + \log\left(\frac{[acid]}{[base]}\right) = 4.74 + \log\left(\frac{0.5M}{0.5M}\right) \\ &= 4.74 \\ pH &= 14 - pOH = 14 - 4.74 = 9.26 \end{split}$$

Gee...it's almost tooo easy with H-H!

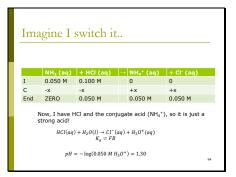
Slide 93

This is a general rule:

If you neutralize a weak base (or weak acid) with a strong acid (or strong base) you get a buffer...

 \dots unless there is more of the strong acid (or strong base) than weak base (or weak acid).

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,			



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That's why I said 2 (4) reactions

While there are technically 4 reactions that can happen, we usually only have 2 we need to worry about. And, at most, only 1 is an actual equilibrium.

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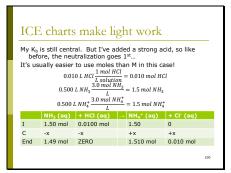
Slide 96

A new question

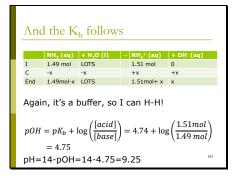
A solution is made by mixing 500 mL of 3.0 M $\rm NH_3$ and 500 mL of 3.0 M $\rm NH_4CI$. What is the pH of the solution after addition of 10 mL of 1.0 M HCl?

What kind of problem is this?

Slide 97 IT'S A BUFFER! So, H-H still rules! But what's with the HCI? HCl is an acid, so what's it going to do? Neutralize some base, that's what! Slide 98 HCl is the acid, what's the base? $NH_3!!!$ (It's not the only base, but it's the BEST base!) $NH_3 + HCI \rightarrow NH_4^+ + CI^-$ So every mole of acid eliminates a mole of $\mathrm{NH_3}$ and creates one of $\mathrm{NH_4^+}$ Slide 99 Again, it is really a choice of multiple acids/bases



Slide 101



Slide 102

ICE charts make light work —

DOUBLE ICE charts are 2x the fun!

Adding 10 mL of 1.0 M HCl is adding 0.01 moles acid!

1.0 mol HCl * 0.010 L HCl solution = 0.010 moles
L HCl sol
NH₃ + H,0 o NH₄* + OH
I 1.5 mol
C - 0.01 mol
I 1.49 mol
I 1.51 mol
C LE

You don't need to finish the chart, of course, because you've got HH!!

 $p0H = pK_b + \log\left(\frac{(acid)}{(base)}\right) = 4.74 + \log\left(\frac{1.51mol}{1.49\ mol}\right) = 4.75$ pH=14-pOH=14-4.75=9.25 You might recall that the pH of the buffer was 9.26 before addition of the HCl. A very small change.

Slide 104

A solution is made by mixing 500 mL of 3.0 M NH $_3$ and 500 mL of 3.0 M NH $_4$ Cl. What is the pH of the solution after addition of 10 mL of 1.0 M NaOH?

 $NaOH = Na^+ + OH^-$

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\begin{array}{c} OH^- + NH_4^{+} = NH_3 + H_2O \\ \hline NH_3 + H_2O \leftrightarrow NH_4^{+} + OH^- \\ I \quad 1.5 \text{ mol} \qquad \qquad 1.5 \text{ mol} \\ C \quad +0.01 \text{ mol} \qquad -0.01 \text{ mol} \\ I \quad 1.51 \text{ mol} \qquad 1.49 \text{ mol} \\ C \quad \\ LE \\ \hline pOH = pK_b + \log\left(\frac{1.49}{1.51}\right) = 4.73 \\ pH = 14 - pOH = 14 - 4.73 = 9.27 \\ \hline \text{Again, a small change from the 9.26} \\ \text{originally.} \end{array}
```


Compare that to a non-buffer

Suppose I just had 1 L of 1.5 M $\rm NH_3$ that I add 10 mL of 1.0 M HCl – then what would the pH change be?

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Slide 107

Similar problem...

I have 500 mL of a solution that is 0.123 M $\rm NH_3$ and 0.325 M $\rm NH_4Cl.~I$ add 10.0 mL of 0.567 M HCl. What is the pH of the buffer after the addition of the HCl?

 $I^\prime m$ going to use moles to avoid dilution. Since it is a buffer, H-H doesn't require Molarities:

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Notice the volume goes with the M

$$0.500 L \frac{0.123 \text{ mol NH}_3}{L} = 0.0615 \text{ mol NH}_3$$

$$0.500 L \frac{0.325 \text{ mol NH}_4 Cl}{L} = 0.1625 \text{ mol NH}_4^+, 0.1625 \text{ mol Cl}^-$$

$$0.010 L \frac{0.567 \text{ mol HCl}}{L} = 0.00567 \text{ mol HCl}$$

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Slide 111

I could ICICLE.. NH₃ (aq) + H₂O (I) \rightarrow NH₄* (aq) + H₂O* (aq) I C I C LE The double ICE chart does confuse some people. This is especially true because there are really two different reactions represented in this ICE chart. So, if it confuses you...

You can treat it as 2 separate ICE charts: Neutralization followed by K_b | NH₃ (aq) + HCl (aq) | - NH₄* (aq) + Cl* (aq) | 0.1625 mol | 0.05583 | 0 | 0.16817 mol | 0.1

Slide 113

You can treat it as 2 separate ICE charts: Neutralization followed by K_b NH₄ (aq) + H₅O (I) - NH₄* (aq) + H₅O* (aq)

I 0.05583 mol - 0.16817 mol 0

C E

Of course, with H-H I only need the initial amounts... $pH = pK_a + \log\left(\frac{base}{acid}\right) = -\log\left(\frac{K_w}{K_b}\right) + \log\left(\frac{base}{acid}\right)$ $= 9.26 + \log\left(\frac{0.05583}{0.16817}\right) = 8.78$

Buffer capacity	
+/- 1 pH unit (Rule of thumb) pH=4.00 buffer	
pH stays between 3 and 5, it is still considered "buffered"	
	114

Calculating buffer capacity

I mix 250 mL of 0.5 M HOAc and 500 mL of 0.5 M NaOAc. What is the pH of the buffer? What is the buffer capacity? $(K_a=1.8\times10^{-5})$

$$pH = pK_a + \log(\frac{[base]}{[acid]})$$
 0.25 L * 0.5 M = 0.125 moles HOAc 0.500 L * 0.5 M = 0.25 moles OAc
$$pH = 4.74 + \log(\frac{[0.25moles]}{[0.125 moles]})$$

$$pH = 5.04$$

Slide 116

HOAc + H₂O = OAc⁻ + H₃O⁺

$$pH = pK_a + \log(\frac{[OAc -]}{[HOAc]})$$

If the pH=5.04, it is "balanced" until pH =4.04 or pH = 6.04

Let's do pH=4.04 1st.

Add HCl (acid lowers pH) HCl+OAc- = HOAc + Cl-

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$$\begin{array}{c} \text{HOAc} & + \text{H}_2\text{O} \leftrightarrow \text{OAc} + \text{H}_3\text{O} \\ \text{I} & 0.125 \text{ mol} & - & 0.250 \text{ mol} & 0 \\ \text{C} & + \text{acid} & - \text{acid} \\ \text{I} & 0.125 + \text{acid} & 0.250 \text{-acid} \\ pH = pK_a + \log\left(\frac{[base]}{[acid]}\right) = 4.74 + \log\left(\frac{0.250 - x}{0.125 + x}\right) \\ & 4.04 = 4.74 + \log\left(\frac{0.250 - x}{0.125 + x}\right) \\ & -0.70 = \log\left(\frac{0.250 - x}{0.125 + x}\right) \\ & 10^{-0.70} = 0.1995 = \left(\frac{0.250 - x}{0.125 + x}\right) \end{array}$$

$$0.1995 = \frac{0.250 - x}{0.125 + x}$$

0.025 + 0.1995 = 0.250-x 1.1995x = 0.2475X = 0.206 moles Acid

So, if I add 0.206 moles of acid to my buffer, it is "unbuffered".

Buffer capacity = moles acid/L solution

Buffer capacity = 0.206 moles/0.75 L = 0.275M acid

Slide 119

How much base, I can add?

$$6.04 = 4.74 + \log\left(\frac{0.250 + x}{0.125 - x}\right)$$

$$1.30 = \log\left(\frac{0.250 + x}{0.125 - x}\right)$$

$$10^{1.30} = \frac{0.250 + x}{0.125 - x}$$

$$19.95 = \frac{0.250 + x}{0.125 - x}$$

$$2.49 - 19.95x = 0.25 + x$$

2.24=20.95x X=0.1 moles

Slide 120

Buffer capacity

Buffer capacity =
$$\frac{0.1 \, mol \, base \, absorbed}{0.75 \, L}$$
 =0.133 M

Slide 121] _	
	What is the pH of 0.123 M HCIO?		
	macio dio pri oi diazzo i i noio	_	
		_	
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l	n	J	
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		_	
		_	
Slide 122		_	
	What is the pH of a solution that is 0.123 M HCIO and 0.123 M HOAc?		
	HCIO and 0.123 M HOAc?	_	
		_	
	122	-	
ļ] _	
		-	-
		_	
		•	
Slide 123		_	
	What is the pH of a solution that is 0.100 M $\mathrm{NH_3}$ and 0.250 M $\mathrm{NH_4Cl?}$	_	
	1113 and 0.250 11 1114 c.		
		_	-
	123	_	
'		-	
		_	

Slide 124		
	What is the pH of a solution that is 0.100 M	
	$\mathrm{NH_{3}}$ and 0.250 M NaOAc?	
	124	
		1
Slide 125		
	Though 0 100 M NH, and 0 500 M HCL. I	
	I have 0.100 M NH $_3$ and 0.500 M HCl. I want to make 1 L of a buffer that is pH 10.00. How do I do it?	
	10.00. How do I do it?	
	125	
•		
Slide 126		
	Ka and Kb table	
	$\begin{array}{lll} & \text{H}_3\text{C}_6\text{H}_5\text{O}_7 & \text{K}_{a1} = 7.4\text{x}10^{-4} \text{ K}_{a2} {=} 1.7\text{x}10^{-5} \text{ K}_{a3} {=} 4.0\text{x}10^{-7} \\ & \text{H}\text{C}_3\text{H}_5\text{O}_3 & \text{K}_{a1} = 1.4\text{x}10^{-4} \\ & \text{H}_2\text{C}_2\text{O}_4 & \text{K}_{a1} = 6.0\text{x}10^{-2} \text{ K}_{a2} {=} 6.1\text{x}10^{-5} \end{array}$	
	$R_{2} = 0.0 \times 10^{-8}$ HCIO $R_{a1} = 0.0 \times 10^{-8}$	
	HONH ₂ K _b =1.1x10 ⁻⁸	
	C ₅ H ₅ N K _b =1.7×10 ⁻⁹	
	126	
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