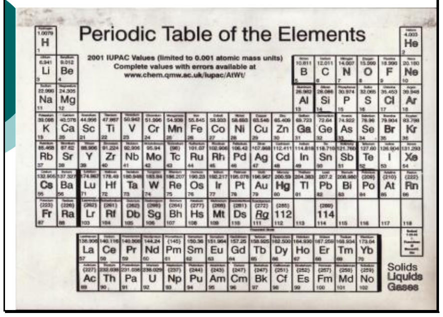
Slide 1



Slide 2

Solution Equilibria

Of Buffers, Ions and Solubility Products I sing!!!!

Slide 3

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 4

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.

Slide 5

An Old Friend – A Familiar Problem

What is the pH of a 0.100 M HOAc solution?

What's the 1st thing we need?

Slide 6

A Balanced Equation

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

And next we need….???

Slide 7

An ICE Chart & a K

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

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

Slide 8

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 9

An ICE Chart & a K

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

$K_a = \frac{[x][x]}{[0.100-x]} = 1.8 \times 10^{-5}$

How do we solve it?

Slide 10

An ICE Chart & a K

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

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

How do we solve it?

Always try our simplifying assumption

Slide 11

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

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

X<<0.100

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

$X^2 = 1.8x10^{-6}$

$x = 1.34x10^{-3}$ M

Slide 12

pH = - log $[H_3O^+]$

pH = - log ($1.34x10^{-3}$ M)

pH = 2.87

Slide 13

Test

1. pH (strong acids/bases)
2. Nomenclature – indirectly on the test.
3. Units! - indirectly
4. Alkalinity – CO_3^{2-}, HCO_3^- and OH^-
5. General Equilibrium
6. Special Equilibrium –acids/bases
7. pH of salts
8. General titration

Slide 14

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 15

A Balanced Equation

But what's going on here?

Is this a familiar reaction or something completely new?

Slide 16

Critical Judgement

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

How would you know this?

HOAc and NaOAc have only a couple possible products if they were to react….

Slide 17

Critical Judgement

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

HOAc is an ionic compound.
NaOAc is an ionic compound

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

Slide 18

Critical Judgement

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

If new compounds were to from, 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!

Slide 19

Critical Judgement

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

$HOAc + OAc^- \rightarrow HOAc + OAc^-$

The only possible products are:

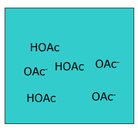
HOAc and OAc^- which is what you started with!

They cannot react with each other!

Slide 20

So – is there no reaction…

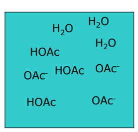
Well, there is actually one other thing in the beaker:



Slide 21

So – is there no reaction…

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



Slide 22

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: K_a or K_b

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

Slide 23

Returning to the Problem

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

Next on the list of things we need is…

Slide 24

Returning to the Problem

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

Next on the list of things we need is…

The Equilibrium Constant Expression

And maybe an ICE chart

Slide 25

The Equilibrium Constant Expression

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

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

The value is from the table in the book.

Slide 26

ICE ICE, BABY, ICE ICE

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

I

C

E

What goes where?

Slide 27

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?

Slide 28

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 $Fe(OAc)_3$

Slide 29

Why NaOAc?

Slide 30

Why NaOAc?

You see Na salts used a lot.

It's because they are very soluble in water and, therefore, easy to get into solution!!!

(K salts also work, things like Fe, Ca etc not so much.)

Slide 31

ICE ICE, BABY, ICE ICE

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

	HOAc	H_2O	OAc^-	H_3O^+
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?

Slide 32

The Equilibrium Constant Expression

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

$$K_a = \frac{[OAc^-][H_3O^+]}{[HOAc]} = 1.8\times10^{-5}$$

$$K_a = \frac{[0.100+x][x]}{[0.100-x]} = 1.8\times10^{-5}$$

Can we make our assumption?

Slide 33

The Equilibrium Constant Expression

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

$$K_a = \frac{[OAc^-][H_3O^+]}{[HOAc]} = 1.8\times10^{-5}$$

$$K_a = \frac{[0.100+x][x]}{[0.100-x]} = 1.8\times10^{-5}$$

Can we make our assumption?

Always worth a try! $x << 0.100$

Slide 34

The Equilibrium Constant Expression

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

$x = 1.8x10^{-5}$

Looks like a pretty good assumption.

Slide 35

ICE ICE, BABY, ICE ICE

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

	HOAc	H_2O	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	$1.8x10^{-5}$

Slide 36

Calculating the pH

$pH = - \log[H_3O+]$

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

pH = 4.74

Slide 37

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?

Slide 38

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

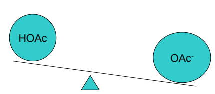
Does this make sense?

Of course! It's the see-saw!

Slide 39

Buffer

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



If you have a big heavy weight at both ends of the equilibrium, it is hard to move it. You make very little H_3O^+.

Slide 40

Le Chatelier's Principle!

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

By introducing a second source of OAc-, we force the K_a 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!

Slide 41

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 42

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!

Slide 43

What's a Buffer?

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?

Slide 45

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?

Slide 46

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?

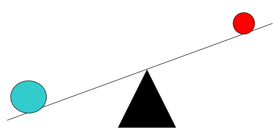
A buffer resists changes in its pH!

How?
Le Chatelier's Principle, Common Ion Effect, 2 fat kids on the playground…

Slide 47

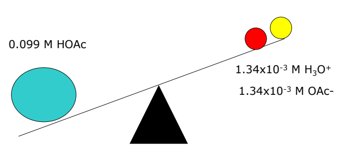
Two fat kids on the playground

Remember "equilibrium" is all about balancing the see-saw!

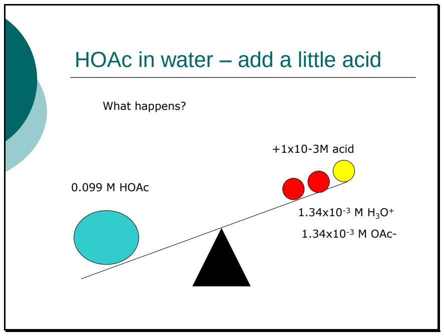


Slide 48

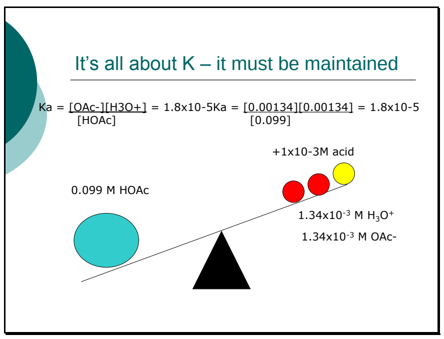
0.100 M HOAc in water



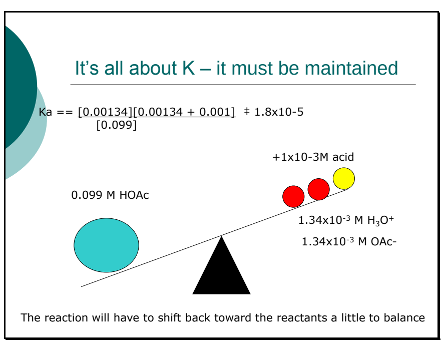
Slide 49



Slide 50



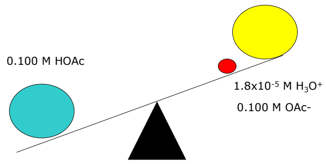
Slide 51



Slide 52

0.100 M HOAc in water + the other Fat Kid

A small addition of acid (or base) isn't going to move the Fat Kids very much!



Slide 53

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.

Slide 54

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…

Slide 55

Henderson-Hasselbach

pH= pK_a + log [base]/[acid]

This is actually just the ICE chart.

Recall the equilibrium expression we just used:

K_a = [OAc-][H_3O+]/[HOAc]

Could I write it more generally for any acid?

Slide 56

Acid + H_2O ↔ Conj Base + H_3O^+

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

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

Slide 57

A little algebra

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

Remember log A*B = log A + log B

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

Slide 58

A little algebra

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

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

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

Slide 59

Rearranging a little

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

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

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

You can also write it as:

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

Slide 60

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_4Cl?

1^{st} thing you need is…

Slide 61

Balanced Equation!

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

Do I need to do an ICE chart?

Not with H-H!

Slide 62

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_4Cl?

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

$$pOH = -\log(1.8\times10^{-5}) + \log \frac{(1.5\ M)}{(1.5\ M)}$$

Why 1.5 M?

Dilution!

$pOH = -\log(1.8\times10^{-5}) + \log 1 = 4.74 + 0$

$pOH = 4.74$

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

Slide 63

New problem

A buffer solution is made by mixing 500 mL of 3.0 M NH_3 and 500 mL of 3.0 M NH_4Cl. What is the pH of the solution after addition of 10 mL of 1.0 M HCl?

What kind of problem is this?

Slide 64

IT'S A BUFFER!

So, H-H still rules!

But what's with the HCl?

HCl is an acid, so what's it going to do?

Neutralize some base, that's what!

Slide 65

HCl is the acid, what's the base?

NH_3!!!

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

So every mole of acid eliminates a mole of NH_3 and creates one of NH_4^+

Slide 66

ICE charts make light work

	NH_3	$+ H_2O \leftrightarrow$	NH_4^+	$+ OH^-$
I	1.5 M		1.5 M	
C				
E				

But, it's usually easier to use moles than M in this case!

Slide 67

ICE charts make light work

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

$1.0 \frac{\text{mol HCl}}{\text{L HCl sol}} * 0.010 \text{ L HCl solution} = 0.010 \text{ moles}$

	NH_3 + H_2O ↔	NH_4^+ + H_3O^+
I	1.5 mol	1.5 mol
C	-0.01 mol	+ 0.01 mol
I	1.49 mol	1.51 mol
C		
E		

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

Slide 68

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

$[acid] = \frac{1.51 \text{ mol}}{1.01 \text{ L}} = 1.495 \text{ M}$

$[base] = \frac{1.49 \text{ mol}}{1.01 \text{ L}} = 1.475 \text{ M}$

$pOH = 4.74 + \log \frac{1.495}{1.475}$

$pOH = 4.74 + \log 1.015$

$pOH = 4.746 = 4.75$

pH = 14 – 4.75 = 9.25 (as opposed to 9.26 before addition of the HCl)

Slide 69

Compare that to a non-buffer

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

Slide 70

1^{st} the baseline

	NH_3	+ H_2O ↔	NH_4^+	+ OH^-
I	1.5 M	-	0	0
C	-x		x	x
E	1.5-x		x	x

$1.8\times10^{-5} = \frac{x^2}{1.5-x} = \frac{x^2}{1.5}$

$X = 5.196\times10^{-3}$

pOH = -log (5.196×10^{-3}) = 2.28

pH = 14 – 2.28 = 11.72

Slide 71

Compare that to a non-buffer

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

Slide 72

Now add the acid!

	NH_3	+ H_2O ↔	NH_4^+	+ OH^-
I	1.485 M	-	0	0
C	-0.0099		+0.0099	0
I	1.4751		.0099	0
C	-x		+x	+x
E	1.4751-x		.0099+ x	x

$1.8\times10^{-5} = \frac{x(0.0099 + x)}{1.4751-x} = \frac{x\,(0.0099)}{1.4751}$

$X = 2.68\times10^{-3}$

pOH = -log (2.68×10^{-3}) = 2.57

pH = 14 – 2.57 = 11.43 (vs. 11.72 for the original)

Slide 73

Acidity

Most natural waters are buffered as a result of a carbon dioxide(air)-bicarbonate (limestone – $CaCO_3$) buffer system.

Slide 74

Buffer

Mixture of an acid (or base) and its conjugate base (or acid)

Think of chemical equilibrium as a see-saw:

$CO_2 + H_2O \leftrightarrow H_2CO_3$

$H_2CO_3 \leftrightarrow HCO_3^- + H^+$

$HCO_3^- \leftrightarrow CO_3^{2-} + H^+$

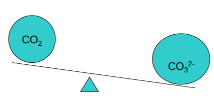
$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow HCO_3^- + H^+ \leftrightarrow CO_3^{2-} + 2 H^+$

You need to put 2 fat kids on the see-saw!

Slide 75

Buffer

$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow HCO_3^- + H^+ \leftrightarrow CO_3^{2-} + 2 H^+$



The carbonate comes from limestone. The CO_2 comes from the air. They meet in the water and buffer the lake (or river or pond or…)