Slide 1

Chemical Equilibrium

Acids & Bases in Aqueous Solution

Slide 2

K is K is K is K

No matter what type of reaction you are talking about – equilibrium properties remain the same.

K_c, K_p, K_a, K_b, K_w, K_{sp}, K_f

The subscripts refer to certain specific TYPES of equilibria, but…

Slide 3

K is K is K is K

Slide 4

What is an acid?

Bronsted-Lowry definition: An acid is a proton donor.

So, what's a base?

Bronsted-Lowry definition: A base is a proton acceptor.

Slide 5

They go together…like carrots and peas, Forrest.

If you are going to donate a proton, something must accept it.

You can't really be an acid without a base.

Slide 6

What's the most common acid?

Water!!

H-OH, it has a proton it can donate.

Slide 7

What's the most common base?

Water!

```
   ° °
H - O - H
    ° °
```

It has extra electrons on the oxygen, so a proton can stick to it.

7

Slide 8

Water is special…

…it is amphoteric: it can act as an acid or a base.

It's not the only compound that can, we'll see other's later.

It also means that most Bronsted-Lowry acids or bases can dissolve in water.

8

Slide 9

We like water…

Acids and bases like water…

So, acids and bases are mostly found as aqueous solutions here.

Like all solutions, the concentration is a critical parameter.

9

Slide 10

All solutions are created equal…

Like any other aqueous solution, a solution of either an acid or base is defined by its concentration.

So what's this thing called pH?

10

Slide 11

pH is concentration

The pH scale is just a logarithmic scale for the Molarity of the protons in the solution.

The pH scale is logarithmic (the difference between pH=1 and pH=2 is a factor of 10)

pH is concentration

11

Slide 12

Damn those logs

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

[x] always means "concentration of x"

$[H^+]$ should be in M.

pH is ONLY the concentration of H^+.

12

Slide 13

Example

0.1 M HCl solution. What's the pH?

Implicitly, you must recognize that:

$HCl_{(aq)} \rightarrow H^{+}_{(aq)} + Cl^{-}_{(aq)}$

Or, $HCl_{(aq)} + H_2O_{(l)} \rightarrow H_3O^{+}_{(aq)} + Cl^{-}_{(aq)}$

13

Slide 14

What is pH?

pH = - log $[H_3O^+]$=-log$[H^+]$

H_3O^+ is just an H^+ + H_2O

Protons don't float around freely in water, they ALWAYS hook up with a water molecule.

14

Slide 15

Example

0.1 M HCl solution. What's the pH?

Implicitly, you must recognize that:

$HCl_{(aq)} \rightarrow H^{+}_{(aq)} + Cl^{-}_{(aq)}$

Or, $HCl_{(aq)} + H_2O_{(l)} \rightarrow H_3O^{+}_{(aq)} + Cl^{-}_{(aq)}$

pH = - log $[H^+]$ = - log $[H_3O^+]$

pH = - log (0.1 M) = 1.0

15

Slide 16

We made an assumption?

We assumed 100% of the HCl dissociated!

$HCl_{(aq)} \rightarrow H^{+}_{(aq)} + Cl^{-}_{(aq)}$

That's why 0.1 M HCl gave me 0.1 M H^{+}

Suppose only 75% of the HCl dissociated?

Slide 17

75% dissociated means…?

$HCl_{(aq)} \rightarrow H^{+}_{(aq)} + Cl^{-}_{(aq)}$

I	0.1 M		0 M	0 M
C				
E				

Slide 18

100% dissociated means…?

$HCl_{(aq)} \rightarrow H^{+}_{(aq)} + Cl^{-}_{(aq)}$

I	0.1 M		0 M	0 M
C	-x		+x	+x
E	0		0.1	0.1

Slide 19

75% dissociated means…?

$HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$

I	0.1 M	0 M	0 M
C	-x	+x	+x
E	25% left	x	x

19

Slide 20

75% dissociated means…?

$HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$

I	0.1 M	0 M	0 M
C	-x	+x	+x
E	0.025 M	x	x

0.1-x=0.025 M
X=0.075 M

20

Slide 21

75% dissociated means…?

$HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$

I	0.1 M	0 M	0 M
C	-x	+x	+x
E	0.025 M	0.075 M	0.075 M

So pH = $-\log[H^+] = -\log(0.075\ M) = 1.1$

21

Slide 22

What's my point?

I have several – but one main one:

1. pH is NOT NOT NOT the concentration of the acid. It's the concentration of the H^+ (or H_3O^+ - same thing) that fell off the acid.
2. To determine the actual pH, I need to know how much acid dissociated.
3. ICE charts are good for a lot of different things!

22

Slide 23

So if I'm looking for pH…

…I need to know the H_3O^+ concentration.

The H_3O^+ concentration WHEN…?

At equilibrium, of course. Before that, the system isn't stable and it is constantly changing.

23

Slide 24

Acid Dissociation Reactions

- This is just a specific type of reaction.
- Referring to Bronsted-Lowry acids: proton donors
- An acid is only an acid when in the presence of a base
- Water is the universal base

24

Slide 25

General K_a Reaction

The general form of this reaction for any generic acid (HA) is:

$HA_{(aq)}$ + $H_2O_{(l)}$ ↔ $A^-_{(aq)}$ + $H_3O^+_{(aq)}$

Acid   Base   Conjugate base   Conjugate acid

25

Slide 26

$$K_a = \frac{[A-][H_3O^{+]}}{[HA]}$$

26

Slide 27

Shorthand Notation

Sometimes the water is left out:

$HA_{(aq)}$ ↔ $A^-_{(aq)}$ + $H^+_{(aq)}$

This is simpler, but somewhat less precise. It looks like a dissociation reaction, but it doesn't look like an acid/base reaction.

27

Slide 28

A sample problem

What is the pH of a 0.100 M HOAc solution?

The K_a of HOAc = 1.8×10^{-5}

Kind of an equilibrium giveaway

But pH is USUALLY a K problem.

28

Slide 29

A sample problem

What is the pH of a 0.100 M HOAc solution?

The K_a of HOAc = 1.8×10^{-5}

It's just an equilibrium problem. Equilibrium problems have…???

3 FRIGGING PARTS!!!!!!!!!!

29

Slide 30

Old Familiar solution

1st we need a balanced equation:

30

Slide 31

Old Familiar solution

1st we need a balanced equation:

$HOAc_{(aq)} + H_2O_{(l)} \leftrightarrow H_3O^+_{(aq)} + OAc^-_{(aq)}$

Then we need to construct an ICE chart

Slide 32

All K_a look alike

It's always:

Water with proton

$ACID_{(aq)} + H_2O_{(l)} \leftrightarrow H_3O^+_{(aq)}$ + acid - proton $_{(aq)}$

H_2O MUST MUST MUST MUST BE THE BASE.

Acid without proton

Slide 33

ICE ICE Baby ICE ICE

$HOAc_{(aq)} + H_2O_{(l)} \leftrightarrow H_3O^+_{(aq)} + OAc^-_{(aq)}$

I	???	???	???	???
C	???	???	???	???
E	???	???	???	???

This is the pH box

What do we know, what do we need to know?

Slide 34

ICE ICE Baby ICE ICE

$HOAc_{(aq)} + H_2O_{(l)} \leftrightarrow H_3O^+{}_{(aq)} + OAc^-{}_{(aq)}$

I	???	???	???	???
C	-x	-x	+x	+x
E	???	???	???	???

What do we know, what do we need to know?

34

Slide 35

A peek back at the problem.

What is the pH of a 0.100 M HOAc solution?
The K_a of HOAc = 1.8×10^{-5}

What do we know?

What do we need to know?

35

Slide 36

A peek back at the problem.

What is the pH of a 0.100 M HOAc solution?
The K_a of HOAc = 1.8×10^{-5}

What do we know? The INITIAL CONCENTRATION of HOAc

What do we need to know? The EQUILIBRIUM CONCENTRATION of H_3O^+ (Recall, that's what pH is:

$pH = - \log [H_3O^+]$

36

Slide 37

ICE ICE Baby ICE ICE

$HOAc_{(aq)} + H_2O_{(l)} \leftrightarrow H_3O^+_{(aq)} + OAc^-_{(aq)}$

I	0.100 M	-	0	0
C	-x	-	+x	+x
E	0.100 – x	-	x	x

How do we solve for x?

37

Slide 38

Use the Equilibrium Constant Expression

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

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

How do we solve this?

38

Slide 39

2 Possibilities

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

1. Assume x <<0.100
2. Don't assume x<<0.100 and use quadratic formula

39

Slide 40

The long way

$$1.8 \times 10^{-5} = \frac{(x)(x)}{(0.1-x)} = \frac{x^2}{(0.1-x)}$$

$x^2 = 1.8 \times 10^{-5} (0.1-x) = 1.8 \times 10^{-6} - 1.8 \times 10^{-5} x$

$x^2 + 1.8 \times 10^{-5} x - 1.8 \times 10^{-6} = 0$

Recall the quadratic formula:

$x = \frac{-b +/- \mathrm{SQRT}(b^2-4ac)}{2a}$

40

Slide 41

The long way

$x^2 + 1.8 \times 10^{-5} x - 1.8 \times 10^{-6} = 0$

$x = \frac{-b +/- \mathrm{SQRT}(b^2-4ac)}{2a}$

$x = \frac{-1.8 \times 10^{-5} +/- \mathrm{SQRT}((1.8 \times 10^{-5})^2-4(1)(-1.8 \times 10^{-6}))}{2(1)}$

$x = \frac{[-1.8 \times 10^{-5} +/- \mathrm{SQRT}(7.200 \times 10^{-6})]}{2}$

$x = \frac{[-1.8 \times 10^{-5} +/- 2.68 \times 10^{-3}]}{2}$

41

Slide 42

2 roots - only 1 makes sense

$x = \frac{[-1.8 \times 10^{-5} +/- 2.68 \times 10^{-3}]}{2}$

$X = 1.33 \times 10^{-3}$ or -1.35×10^{-3}

The negative root is clearly non-physical

$x = 1.33 \times 10^{-3}$ M

We can now put this back into the ICE chart

42

Slide 43

ICE ICE Baby ICE ICE

$HOAc_{(aq)} + H_2O_{(l)} \leftrightarrow H_3O^+_{(aq)} + OAc^-_{(aq)}$

I	0.100 M	-	0	0
C	-x = $-1.33x10^{-3}$ M	-	+x= $1.33x10^{-3}$ M	+x=$1.33x10^{-3}$ M
E	0.100 M – $1.33x10^{-3}$ = 0.0987 M	-	$1.33x10^{-3}$ M	$1.33x10^{-3}$ M

This is the pH box

43

Slide 44

pH = - log [H_3O^+]

pH = - log [H_3O^+]
= - log ($1.33x10^{-3}$)
= 2.88

Was all of that work necessary?
Let's look at making the assumption!

44

Slide 45

Assume x<<0.100

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

If x<<0.100, then 0.100-x≈0.100

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

$1.8x10^{-6} = [x][x] = x^2$
x = $1.34x10^{-3}$ M

45

Slide 46

Was the assumption good?

We assumed that x<<0.100, is 1.34×10^{-3} M << 0.100?

$$\frac{0.100}{20} = 0.005$$

$1.34\times10^{-3} < 0.005$

It passes the 5% rule. Notice how little difference it makes in the final answer.

And if I calculate the pH = - log (1.34×10^{-3})
pH = 2.87

This compares well with pH = 2.88 calculated the long way. Look at all the work we saved!

46

Slide 47

ALL acid dissociation reactions are the same!

Acid + $H_2O \leftrightarrow H_3O^+$ + protonless acid

The ONLY thing that happens in an acid dissociation reaction is that the acid donates its proton to water to make H_3O^+.

A single proton hops from the acid to the water.

That's it. ALWAYS.

Anything else, even if there's an acid, is not a K_a reaction.

47

Slide 48

Base Dissociation Reactions

- Acids and bases are matched sets.
- If there is a K_a, then it only makes sense that there is a K_b
- The base dissociation reaction is also within the Bronsted-Lowry definition
- Water now serves as the acid rather than the base.

48

Slide 49

General K_b Reaction

The general form of this reaction for any generic base (B) is:

$B_{(aq)}$ + $H_2O_{(l)}$ ↔ $HB^+_{(aq)}$ + $OH^-_{(aq)}$

Base Acid Conjugate acid Conjugate base\

Looks just like the K_a only the H^+ goes the opposite direction (from the water rather than to the water).

49

Slide 50

K_b

It is, after all, just another "K"

$$K_b = \frac{[HB^+][OH^-]}{[B]}$$

And this gets used just like any other equilibrium constant expression.

50

Slide 51

Question

What is the pH of 0.250 M NH_3?

K_b (NH_3) = 1.79×10^{-5} at 298 K

51

Slide 52

It's an equilibrium question…

…it's got THREE PARTS!

52

Slide 53

Question

What is the pH of 0.250 M NH_3?

K_b (NH_3) = 1.79×10^{-5} at 298 K

$NH_{3\,(aq)} + H_2O_{(l)} \leftrightarrow NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$

$K_b = \frac{[OH^-][NH_4^+]}{[NH_3]}$

53

Slide 54

Question

	$NH_{3\,(aq)}$	+ $H_2O_{(l)}$	↔ $NH_4^+{}_{(aq)}$	+ $OH^-{}_{(aq)}$
I	0.250 M	-	0	0
C	−x	-	+x	+x
E	0.248	-	x	x

$K_b = \frac{[OH^-][NH_4^+]}{[NH_3]}$

$1.79 \times 10^{-5} = \frac{(x)(x)}{0.250-x}$

54

Slide 55

Question

$NH_{3\,(aq)} + H_2O_{(l)} \leftrightarrow NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$

	NH_3	H_2O	NH_4^+	OH^-
I	0.250 M	-	0	0
C	−.002	-	+.002	+0.002
E	0.248	-	0.002	0.002

$K_b = \frac{[OH^-][NH_4^+]}{[NH_3]}$

$1.79\times10^{-5} = \frac{(x)(x)}{0.250-x}$

55

Slide 56

Question

$1.79\times10^{-5} = \frac{(x)(x)}{0.250-x}$

Assume x<<0.250

$1.79\times10^{-5} = \frac{(x)(x)}{0.250}$ $4.47\times10^{-6} = x^2$

$x = 2.11\times10^{-3}$ = [OH-] (good assumption

pOH = - log (2.11×10^{-3}) = 2.67

pOH + pH = 14   (at room temperature)

14 – pOH = pH

14 – 2.67 = 11.33 = pH

56

Slide 57

Water, water everywhere

Both K_a and K_b reactions are made possible by the role of water.

Water acts as either an acid or a base. Water is **amphiprotic**.

If water is both an acid and a base, why doesn't it react with itself?

57

Slide 58

Water does react with itself

- Autoionization of water:

$$H_2O_{(l)} + H_2O_{(l)} \leftrightarrow H_3O^+_{(aq)} + OH^-_{(aq)}$$

58

Slide 59

Autoionization of water:

$H_2O_{(l)} + H_2O_{(l)} \leftrightarrow H_3O^+_{(aq)} + OH^-_{(aq)}$

- This is, in fact, the central equilibrium in all acid/base dissociations
- This is also the connection between K_a and K_b reactions.

59

Slide 60

The Equilibrium Constant Expression K_w

$H_2O_{(l)} + H_2O_{(l)} \leftrightarrow H_3O^+_{(aq)} + OH^-_{(aq)}$

$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$

K IS K IS K IS K – this is just another equilibrium constant.

Let's ICE

60

Slide 61

ICE ICE Baby ICE ICE

$H_2O_{(l)} + H_2O_{(l)} \leftrightarrow H_3O^+_{(aq)} + OH^-_{(aq)}$

I	???	???	???	???
C	???	???	???	???
E	???	???	???	???

61

Slide 62

ICE ICE Baby ICE ICE

$H_2O_{(l)} + H_2O_{(l)} \leftrightarrow H_3O^+_{(aq)} + OH^-_{(aq)}$

I	-	-	0	0
C	-	-	+x	+x
E	-	-	x	x

Solve for x

62

Slide 63

Evaluating K_w

$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$

$[x]\ [x] = 1.0 \times 10^{-14}$

$x^2 = 1.0 \times 10^{-14}$

$x = 1.0 \times 10^{-7}$

63

Slide 64

ICE ICE Baby ICE ICE

$H_2O_{(l)} + H_2O_{(l)} \leftrightarrow H_3O^+_{(aq)} + OH^-_{(aq)}$

I	-	-	0	0
C	-	-	$+x = 1.0x10^{-7}$	$+x = 1.0x10^{-7}$
E	-	-	$1.0x10^{-7}$	$1.0x10^{-7}$

What's the pH?

64

Slide 65

pH = - log $[H_3O^+]$

pH = - log $(1.0x10^{-7})$

pH = 7

This is why "7" is considered neutral pH. It is the natural pH of water. Neutral water doesn't have NO acid, it has the EQUILIBRIUM (K_w) amount!!!

65

Slide 66

K_b, K_a, and K_w

It is the Kw of water (1.0×10^{-14}) which is responsible for the observation that:

pOH + pH = 14

Since we've already established that pure water has $1x10^{-7}$ M concentrations of both H^+ and OH^-

In an aqueous solution, this relationship always holds because K_w must be satisfied even if there are other equilibria that also must be satisfied.

66

Slide 67

$[H_3O^+][OH^-] = 1.0 \times 10^{-14}$
$-\log([H_3O^+][OH^-]) = -\log(1.0 \times 10^{-14})$
$-\log[H_3O^+] + (-\log[OH^-]) = 14$
$pH + pOH = 14$

67

Slide 68

K depends on…

…Temperature.

So the "neutral pH" of water is only 7 at STANDARD TEMPERATURE AND PRESSURE!

If the water is at a different temperature, K_w is NOT 1.0×10^{-14}

68

Slide 69

Backwards and forwards and forwards and back…

The general K_a reaction involves donating a proton to water.

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

The acid (HA) is the thing that donates the proton to the base (H_2O).

What if I consider the reverse reaction?

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

What is "A^-"?
Yup! It's a base! It got a proton from the H_3O^+

69

Slide 70

Backwards and forwards and forwards and back…

HA + H_2O ↔ H_3O^+ + A^-

What if I consider the reverse reaction?

A^- + H_3O^+ ↔ HA + H_2O

What is "A^-"?
Yup! It's a base! It got a proton from the H_3O^+
And so, that would make H_3O^+…?
Yup! It's an acid! It donated a proton.

70

Slide 71

K_b, K_a, and K_w

HA	+ H_2O ↔	H_3O^+	+	A^-
acid	base	conjugate acid		conjugate base

So, it's really a PAIR of acids and a PAIR of bases!

That means that A- has it's own K_b reaction!

71

Slide 72

K_b, K_a, and K_w

HA + H_2O ↔ H_3O^+ + A^-

A^- + H_2O ↔ HA + OH^-

Please note, this general notation can be confusing. I'm referring specifically to the conjugate base of a particular acid. For example:

$$HOAc\ (aq) + H_2O\ (l) \leftrightarrow OAc^-(aq) + H_3O^+(aq)$$

$$OAc^-\ (aq) + H_2O\ (l) \leftrightarrow HOAc\ (aq) + OH^- aq)$$

72

Slide 73

Writing the K for both reactions

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

$K_a = \frac{[H_3O+][A-]}{[HA]}$

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

$K_b = \frac{[HA][OH-]}{[A-]}$

73

Slide 74

Writing the K for both reactions

If you add these two reactions together

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

$\underline{A^- + H_2O \leftrightarrow HA + OH^-}$

$HA + A^- + H_2O + H_2O \leftrightarrow H_3O^+ + A^- + HA + OH^-$

$H_2O + H_2O \leftrightarrow H_3O^+ + OH^-$ OMG! IT'S K_W!!!

74

Slide 75

Add 2 reactions, you multiply the Ks

If you multiply K_a by K_b:

$K_a*K_b = \frac{[H_3O+][A-]}{[HA]} \frac{[HA][OH-]}{[A-]}$

$= [H_3O+][OH-]$

$=K_w$

So, if you know K_b, you know K_a and vice versa because:

$K_a*K_b=K_w$

75

Slide 76

Remember…

K_a and K_b refer to specific reactions. I can't just apply them to any old reaction I want.

$K_w = K_a*K_b$

BUT this relationship only holds if the K_a and the K_b are related. It is an acid and its CONJUGATE base (or a base and its CONJUGATE acid).

76

Slide 77

$K_a(HOAc)*K_b(?) = 1x10^{-14}$

It HAS to be the conjugate base.

The conjugate base is ALWAYS just the acid without the H+ it donated.

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

$?=OAc^-$

77

Slide 78

$K_a(?)*K_b(NH_3) = 1x10^{-14}$

It HAS to be the conjugate base.

The conjugate base is ALWAYS just the acid without the H+ it donated.

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

$?=NH_4^+$

78

Slide 79

Remember…

For example, consider the acid dissociation of acetic acid:

$HOAc_{(aq)} + H_2O_{(l)} \leftrightarrow H_3O^{+}_{(aq)} + OAc^{-}_{(aq)}$

This reaction has a K_a, it does not have a K_b. BUT, its sister reaction is a base dissociation that has a K_b:

$OAc^{-}_{(aq)} + H_2O_{(l)} \leftrightarrow OH^{-}_{(aq)} + HOAc_{(aq)}$

HOAc is an acid
OAC⁻ is the CONJUGATE base of HOAc

It is this reaction that you are calculating the K_b for if you use the relationship $K_w = K_a * K_b$