8-1 What are Acids and Bases

Let’s start with the simple Arrhenius concept of acid and base. ACIDS are substances that increase the concentration of $H_3O^+$ when added to water. BASES decrease the concentration of $H_3O^+$ (Hence increase the concentration of $OH^-$).

The word PRO Tic refers to any chemistry involving the transfer of $H^+$ from one molecule to another.

The Bronsted-Lowry concept of acids and bases is also useful. Here an ACID is a proton donor and a BASE is a proton acceptor. The difference between this definition and the one above is that this doesn’t include water, so it is more general (can extend into non-aqueous solvent and gas phase).

The product of acid and base reaction are also acids and bases called conjugate acids and bases. A deprotonated acid is the conjugate base and a protonated base is a conjugate acid.

Take the case of acetic acid and Methyl amine

$$CH_3COOH + CH_3NH_2 \rightarrow CH_3COO^- + CH_3NH_3^+$$

Acid Base CJ Base CJ Acid

SALTS are any ionic solid.. In most cases the product of an acid-base reaction is a Salt. Many salts are strong electrolytes meaning that they completely dissociate into component ions in water. In the above reaction the $CH_3COO^-CH_3NH_3^+$ is the salt product.

8-2 Relation Between $[H^+]$, $[OH^-]$ and pH

Water can act as a base or an acid.

When it reacts with an acid it is a base

and when it reacts with a base it is an acid.

Autoproteolysis refers to water acting as both a base and an acid to react with itself.

$$H_2O + H_2O \rightarrow H_3O^+ + OH^-$$

Because this reaction goes on in water constantly, and most of our reaction are performed in water, this equilibrium is very important and has its own special designation and an easy to remember value

$K_w = 1 \times 10^{-14}$ (This does vary with temp, see Table 5-1 but we won’t worry about that here) Autoproteolysis occurs in all protic solvents, so this is not a special property of water.

This also means that in water if you know $H^+$ you know $OH^-$ Because $K_w = [H^+][OH^-]$.
Let's reinforce this concept with some calculations:

The \([\text{H}^+]\) of a solution is 6.7x10^{-9} is this solution acidic or basic, and what is the \([\text{OH}^-]\) of the solution?

\[
K_w = 1 \times 10^{-14} = [\text{H}^+][\text{OH}^-] = 6.7 \times 10^{-9} \times X
\]

\[
X = 1 \times 10^{-14} / 6.7 \times 10^{-9} \Rightarrow X = [\text{OH}^-] = 1.5 \times 10^{-6}
\]

\([\text{H}^+] < 10^{-7}, [\text{OH}^-] > 10^{-7}\) Basic

Now what is the definition of \(\text{pH}\) and \(\text{pOH}\)?

\[
\text{pH} = -\log[\text{H}^+], \text{pOH} = -\log[\text{OH}^-]
\]

What is the \(\text{pH}\) and \(\text{pOH}\) of the above solution?

\[
-\log(6.7 \times 10^{-9}) = 8.17
\]

\[
-\log(1.5 \times 10^{-6}) = 5.83
\]

\(\text{pH} > 7, \text{pOH} < 7;\) still basic

Note the useful relationship between \(\text{pH}\) and \(\text{pOH}\)

\(\text{pH} + \text{pOH} = 14\)

(Can derive this from \(K_w = [\text{H}^+][\text{OH}^-]\) but won’t to that here)

8-3 Strengths of acids and bases

Acids and bases are classed as ‘strong’ or ‘weak’ depending on how completely they react with water.

Because some of you don’t have a lot of exposure to chemicals, one question I frequently get is ‘how can I tell a strong acid or base’ Look at table 8-1 and memorize if you have to. The other clue is that if I give you a \(K_a\) or a \(K_b\) it must be a weak acid or base.

**Strong acids and bases**

When you have a strong acid or base in solution you can assume it dissociates completely.

\[
\text{HCl(aq)} \rightarrow \text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \quad \text{(100% dissociation)}
\]

No HCl exists in solution, only H\(^+\) and Cl\(^-\)
NaOH(aq) → Na⁺(aq) + OH⁻ (aq) 100%
No NaOH exists in solution, only Na⁺ and OH⁻

*Weak Acids and Bases*

These do not dissociate completely and, instead come to an equilibrium involving the acid or base and it conjugate and water. For an acid we have

\[
HA = H^+ + A^- \quad K_a = [H^+][A^-]/[HA]
\]

Actually

\[
HA + H_2O \rightarrow H_3O^+ + A^-\]

and for bases

\[
B + H_2O \rightarrow BH^+ + OH^- \quad K_b = [BH^+][OH^-]/[B]
\]

How do you tell a stronger weak acid or base form a weaker weak acid or base?

Larger K, larger dissociates, the stronger the acid or base!

*Carboxylic acids are weak acids, and Amines are weak bases*

For those who have had, or are having organic, What are the acids and bases most commonly found in organic (and therefore biochemical) applications?

COOH and CNH₂R₁R₂NH R₁R₂R₃N (1,2, and 3° amines)

Reaction of carboxylic acid easy to see

\[
\text{COOH} \rightarrow \text{COO}^- + H^+
\]

Noteing our earlier bronstead-lowry, what can you say about the acid/base properties of the carboxylate anion (CB or a weak acid, it is a base)

What about amines?

\[
\text{H} \quad \text{CH}_3\text{N}^+: + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{NH}_3^+ + \text{OH}^- \quad \text{H}
\]

And the Acid/Base properties of the ammonium cation? (BA or a weak base, its an acid)
Just pointed out that a carboxylic acid is a weak acid, and its carboxylate anion is a weak base. Conversely amines are weak bases and their ammonium cations are weak acids. So there are pairs of weak acids and conjugate bases, but you knew that already. More importantly is that there is a direct mathematical relationship between the $K_a$ of a weak acid and the $K_b$ of it conjugate (or $K_b$ of a weak base and $K_a$ of its conjugate)

\[ HA \rightarrow H^+ + A^-; \quad Ka = [H^+][A^-]/[HA] \]

Acid            Conjugate base

Using the conjugate base in a base reaction

\[ A^- + H_2O = HA + OH^-; \quad Kb = [HA][OH^-]/[A^-] \]

Adding these two reactions together we get

\[ HA + A^- + H_2O = HA + OH^- + H^+ + A^- \quad K = Ka \times Kb \]

Removing common terms

\[ H_2O = H^+ + OH^- \]

The above equation is our Kw equation so

\[ Kw = Ka \times Kb \text{ for a conjugate acid/base pair} \]

or, in the -log form

\[ pK_a + pK_b = Kw = 14! \]

Example 1

What is the $K_b$ of the acetate anion?

\[ K_a K_b = Kw \]

\[ K_a = 1.75 \times 10^{-5} \]

\[ K_b = 1 \times 10^{-14}/1.75 \times 10^{-5} = 5.7 \times 10^{-10} \]

What is the $K_b$ of Methylamine

Hold it. Isn’t this too easy? Can’t I just look that one up in the back of the book? NO! The book only lists $K_a$, not $K_b$, even if you are dealing with a base! SO YOU HAVE TO DO THIS CALCULATION FOR ALL BASES!

\[ K_a K_b = Kw \]
\[ \text{K}_A = 2.3 \times 10^{-11} \]
\[ \text{K}_B = \frac{1 \times 10^{-14}}{2.3 \times 10^{-11}} = 4.3 \times 10^{-4} \]

Which is the stronger base the acetate anion, or methylamine? (Methylamine)

8- 4 pH of Strong Acids and Bases

What is the pH of a 5.4 \times 10^{-3} \text{ M solution of NaOH}?

5.4 \times 10^{-3} \text{ M NaOH}, is more correctly 5.4 \times 10^{-3} \text{F NaOH}, because it completely dissociates so [NaOH] = 0, [Na^+] = 5.4 \times 10^{-3}, [OH^-] = 5.4 \times 10^{-3}

pOH = -\log 5.4 \times 10^{-3}

= 2.3

pH = 14 - pOH

= 11.7

Now try a tricky one

What is the pH of a 0.5 \times 10^{-7} \text{ M KOH solution}?

Well, Duh, pOH = -\log(0.5 \times 10^{-7}) = 7.3, pH = 6.7

But...but...but 6.7 is acidic!! If I start with a base, shouldn’t t be basic?

That is the trick. We must have missed something. What did me miss?

In very dilute solutions of acids and bases we have to think about the other source of H^+ or OH^-, water itself.

We missed the fact that in water we already have 1 \times 10^{-7} \text{ OH^-}

The quick and dirty answer is to simply add the OH^- from these two sources together

\[ [\text{OH}^-] = 1 \times 10^{-7} \text{ (from water)} + 0.5 \times 10^{-7} \text{ (from the base)} \]

\[ = 1.5 \times 10^{-7} \]

pOH = -\log (1.5 \times 10^{-7}) = 6.82; pH=7.18

Which is more correct

Actually it is still not right, but at least it is closer.

The OH^- from the base and the OH^- from the water are not independent of each other, so this simple treatment where we just add them up is not exactly correct. You will have to wait until chapter 12, however before you can do this problem correctly

Note that this happens with both acids and bases, so you might try the problem
'What is the pH of $1 \times 10^{-8}$ H HNO$_3$ just to see if you understand the system.

*Water almost never produces* $10^{-7}$ H* and OH*.
You all know that water should be pH 7, but is it?
Almost never
Why?
Most water not pure usually some trace impurity to change pH
Acid rain (Nitric and Sulfuric acids)
Around here Creek water comes from limestone aquifers that make basic
Even distilled water has low pH
As is distilled, picks up CO$_2$, and CO$_2$ + H$_2$O → H$_2$CO$_3$ and acid!

**8-5 Tools for dealing with Weak Acids and bases**

**Tool 1**
- $pK_a = -\log K_A$
- $pK_b = -\log K_B$
- $pK_a + pK_b = 14$ for a conjugate pair

**Tool 2**
Appendix B in back of book page 540
As noted earlier
All chemicals shown in fully protonated form
Tables lists only $K_a$ and $pK_a$ (even if it's a base)
Some indication what functional group pKa is associated with

**8-6 Weak-Acid Equilibrium**

Let's find the pH of a solution containing a weak acid, say hydrofluoric acid, $K_a$ = $6.8 \times 10^{-4}$ at a .05M F concentration

Since this is a weak acid, we need to use the weak acid equilibrium expression:

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

Setting up a reaction table

<table>
<thead>
<tr>
<th></th>
<th>HA</th>
<th>A$^-$</th>
<th>H$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>.05</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Want to find $[H^+]$ so $X$-[H$^+$]

Reaction .05-$X$ x x
Plugging in to equilibrium

\[ 6.8 \times 10^{-4} = X^2/(0.05-X) \]

More general form

\[ K_a = X^2/(f-X) \]

How do we solve?

I. Exact using calculator (Ti 83 or equivalent)

Use solver function

- Hit solver
- Put in equation
- Hit enter
- Make a guess for X and hit solve

X = 0.0055

II. Exact calculation using quadratic

If equation in the form 0 = aX^2 + bx + c, then

\[ \frac{-b \pm \sqrt{b^2-4ac}}{2a} \]

will give you two roots, one negative and one positive.

Can't have a negative conc so you can throw this answer out

\[ 6.8 \times 10^{-4} = X^2/(0.05-X) \]
\[ 6.8 \times 10^{-4}.05-X = X^2 \]
\[ 3.4 \times 10^{-5} - 6.8 \times 10^{-4} X = X^2 \]
\[ 0 = X^2 + 6.8 \times 10^{-4} X - 3.4 \times 10^{-5} \]

\[ -6.8 \times 10^{-4} \pm \sqrt{(6.8 \times 10^{-4})^2 + 4(1)3.4 \times 10^{-5}} / 2 \]
\[ -6.8 \times 10^{-4} \pm \sqrt{4.62 \times 10^{-7} + 1.36 \times 10^{-4}} / 2 \]
\[ -6.8 \times 10^{-4} \pm \sqrt{1.365 \times 10^{-4}} / 2 \]
\[ -6.8 \times 10^{-4} \pm 1.17 \times 10^{-2} / 2 \]
\[ (1.17 \times 10^{-2} - .0068 \times 10^{-2}) / 2 \]
\[ 1.10 \times 10^{-2} / 2 \]
\[ 5.5 \times 10^{-3} \]
\[ .0055 \]

Long, involved, prone to error

III Successive approximation

\[ 6.8 \times 10^{-4} = X^2/(0.05-X) \] Assume 0.05 - X \approx 0.05 (Our approximation) and solve
6.8x10^-4 = X^2 / .05
X = √(6.8x10^-4 x .05)
X = .00583

Now try again plugging this in for X in the .05-X term
6.8x10^-4 = X^2 / (.05 - .00583)
6.8x10^-4 = X^2 / .04417
X = √(6.8x10^-4 x .04417)
X = .00548

Keep at it until the answer doesn’t change
6.8x10^-4 = X^2 / (.05 - .00548)
6.8x10^-4 = X^2 / .04452
X = √(6.8x10^-4 x .04452)
X = .00550

6.8x10^-4 = X^2 / (.05 - .00550)
6.8x10^-4 = X^2 / .04450
X = √(6.8x10^-4 x .04450)
X = .00550 You’re there

To summarize
\([H^+][A^-] = .0055; pH = 2.56\)
\([A^-] = .05 - .0055 = .0445M\)

A little less error prone than the quadratic method, but sometimes it takes a while, and every once in a while you can hit a problem that doesn’t work

*Fraction Dissociation*
Another term that is used in the discussion of weak acids and bases is

Fraction Dissociation = \([A^-]/ total acid (all forms)\)
= \([A^-]/([HA]+[A^-])\)

What is the fraction Dissociation in the last problem?

\([A^-] = .0055\)
total acid = \([A^-] + [HA] = F acid = .05\)

Fraction dissociation = .0055/.05 = .11 or 11%!

Other problems for you to try
from fraction dissociation determine $K_a$

(If an acid is 1% dissociated when the formal concentration is .1M, what is the $K_a$?)

from pH at a given $[$ of weak acid determine the $K_a$

(If the pH of a .1M solution of acid is 2, what is the $K_s$ of the acid?)
8-7 Weak Base Equilibrium

Weak bases are almost the same as weak acids

\[ B + H_2O \rightarrow BH^+ + OH^- \]

\[ K_B = [BH^+][OH^-]/[B] \]

\[ F = [B] + [BH^+] \]

\[ [B] = F-X \]

\[ K_B = X^2/(F-x) \]

Example

What is pH of a solution of .25M Triethylamine (\( CH_3CH_2)_3NH^+ \)

\[ K_a = 1.93 \times 10^{-11} \]

First convert from \( K_a \) to \( K_b \)

\[ K_aK_b = K_w; K_B = K_w/K_A; = 1 \times 10^{-14}/1.93 \times 10^{-11} = 5.18 \times 10^{-4} \]

\[ 5.18 \times 10^{-4} = X^2/(.25-x) \]

Exact solution (calculator)

\[ [BH^+] = [OH^-] = .0111 \]

Successive Aprox

\[ 5.18 \times 10^{-4} \approx X^2/.25 \]

\[ X \approx \sqrt{5.18 \times 10^{-4}.25} \]

\[ X \approx .0114 \]

Next try

\[ 5.18 \times 10^{-4} \approx X^2/(.25-.0114) \]

\[ X \approx \sqrt{5.18 \times 10^{-4}.2386} \]

\[ X = .0111 \]

Next try

\[ 5.18 \times 10^{-4} \approx X^2/(.25-.0111) \]

\[ X \approx \sqrt{5.18 \times 10^{-4}.2389} \]

\[ X = .0111 \text{ Same as last answer, so I’m done} \]
if \([\text{OH}^-] = 0.0111\), \(p\text{OH} = 1.95\), \(p\text{H} = 14 - 1.95 = 12.05\)