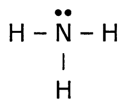
Chapter 56 ACID-BASE EQUILIBRIA, Part 3

We've completed a number of examples of acid dissociation problems, and we now turn to base dissociation. These calculations simply follow the same general steps. After that, we will work with conjugates, and then we will cover qualitatively some additional aspects of acid and base relationships.

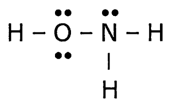
56.1 Back to basics

Ammonia is by far the most important and the most common of the molecular weak base compounds. There are yet many others, and many of those others are also compounds containing a nitrogen atom which has a lone pair. There is some parallel between being basic and being a hydrogen bond acceptor, as repeated and illustrated for NH_3 in Section 54.1. Although there is some parallel, it does take more to be basic than to simply accept a hydrogen bond, so not every hydrogen bond acceptor is basic in water. For NH_3, the lone pair is in an sp^3 hybrid; in general, lone pairs in sp^3 or sp^2 hybrids on a nitrogen tend to be basic. Lone pairs in *sp* hybrids don't work as well for being basic although those can still be hydrogen bond acceptors. Nitrogen compounds are among the most numerous of neutral, weak bases. Here is NH_3 again, along with a few others.



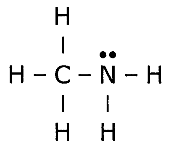
$$\begin{array}{ccccc} H & - & \ddot{N} & - & H \\ & & | & & \\ & & H & & \end{array}$$

NH_3
ammonia



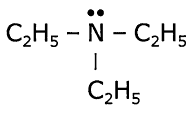
$$\begin{array}{ccccccc} H & - & \underset{\cdot\cdot}{\ddot{O}} & - & \ddot{N} & - & H \\ & & & & | & & \\ & & & & H & & \end{array}$$

$HONH_2$
hydroxylamine



$$\begin{array}{ccccccc} & & H & & & & \\ & & | & & & & \\ H & - & C & - & \ddot{N} & - & H \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

CH_3NH_2
methylamine



$$\begin{array}{ccccc} C_2H_5 & - & \ddot{N} & - & C_2H_5 \\ & & | & & \\ & & C_2H_5 & & \end{array}$$

$(C_2H_5)_3N$
triethylamine

Note the term "amine" for the other examples. That term can be written as a separate word or as part of a word: for example, methylamine is sometimes written as two words, methyl amine. Amines are an important class of weak bases and they have a nitrogen with an sp^3 lone pair. You should be able to recognize that term in a name as indicative of a weak base compound. While there are other weak bases besides the amines, we won't go further into the terminology for those.

Here is the dissociation equation for a generic weak base, designated as B.

$$B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq)$$

Compared to acid dissociation, note the role reversal for water. In acid dissociation, water dissociates the acid by pulling H^+ off the acid. In base dissociation, base dissociates the water by pulling H^+ off water. Again, water can go either way.

The equilibrium constant *K* for base dissociation is specifically designated K_b.

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

Like values for K_a, values of K_b have also been measured for many compounds and a selection is given in Appendix B. These show a wide range, typically 10^{-4} to 10^{-10}, although there are some outside this. Similar thermodynamic considerations apply for this range as noted for acids in Section 55.4, and small changes in $\Delta G°$ will give sizeable changes in K_b.

Problems involving weak base calculations closely follow those as done for weak acids. There is one thing you must remember, however, and that is K_b involves $[OH^-]$ directly, while K_a involves $[H^+]$. Thus, if you're looking for a pH in the end, you'll have an extra conversion via K_w or pK_w. Remember that.

By the way, there are monoprotic acids and there are polyprotic acids. The corresponding terms for bases are monobasic and polybasic. We will only do weak base calculations for monobasics.

Let's start an Example. We'll keep the numbering sequence from the prior Chapter.

……

Example 8. A solution of ammonia is prepared using 0.722 g NH_3 in a total solution volume of 400. mL. Find the concentrations at equilibrium of NH_3, NH_4^+ and OH^-. What are the pH of the solution and the percent dissociation of NH_3?

……

▸ Step 1. Equation. $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

▸ Step 2. K_b expression.

$$K_b = \frac{[NH_4^+]\,[OH^-]}{[NH_3]} = 1.8 \times 10^{-5}$$

▸ Step 3. Initial amount and a table. The provided amount for NH_3 is a mass, so you'll need the molar mass in order to get to moles and molar.

$$\text{initial } [NH_3] = \frac{0.722\text{ g}/(17.03\text{ g/mol})}{0.400\text{ L}} = 0.106\text{ M}$$

	$[NH_3]$	$[NH_4^+]$	$[OH^-]$
Initial:	0.106	-0-	-0-

▸ Step 4. Changes.

	$[NH_3]$	$[NH_4^+]$	$[OH^-]$
Initial:	0.106	-0-	-0-
Changes:	$-x$	$+x$	$+x$

▸ Step 5. Final equilibrium amounts.

	$[NH_3]$	$[NH_4^+]$	$[OH^-]$
Initial:	0.106	-0-	-0-
Changes:	$-x$	$+x$	$+x$
Equilibrium:	$0.106 - x$	x	x

▸ Step 6. Plug into K_b.

$$K_b = \frac{[NH_4^+]\,[OH^-]}{[NH_3]} = \frac{(x)\,(x)}{0.106 - x} = 1.8 \times 10^{-5}$$

Solve for x. How would you like to do that? If quadratic, then you will need to get to

$$x^2 + 1.8 \times 10^{-5}\,x - 1.9 \times 10^{-6} = 0$$

and for approximation/iteration, you would need the usual assumption to start.

$$K_b = \frac{x^2}{0.106 - x} \approx \frac{x^2}{0.106} = 1.8 \times 10^{-5}$$

Either way, you will get $x = 0.0014$. Be sure you can do so.

▸ Step 7. Take 0.0014 back into the final equilibrium line of the table.

$[NH_3] = (0.106 - 0.0014)\text{ M} = 0.105\text{ M}$
$[NH_4^+] = 0.0014\text{ M}$
$[OH^-] = 0.0014\text{ M}$

▸ Step 8. K-check is close enough.

We still need pH and percent dissociation. Whenever you have $[OH^-]$ and you need pH, there are two possible routes.

Convert $[OH^-]$ to $[H^+]$ via K_w and then convert $[H^+]$ to pH.

OR

Convert $[OH^-]$ to pOH and then to pH via pK_w.

Here are the two routes for the present case.

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{0.0014} = 7.1 \times 10^{-12}$$

$$\text{pH} = -\log(7.1 \times 10^{-12}) = 11.15$$

OR

$$\text{pOH} = -\log(0.0014) = 2.85$$

$$\text{pH} = \text{p}K_w - \text{pOH} = 14.00 - 2.85 = 11.15$$

Either of the two routes is fine, although sometimes you can end up ±1 different in the final sigfig for the two ways. Both answers are valid. Now, for the percent dissociation, it's the same calculation as usual.

$$\%\text{diss} = \frac{\text{amount which dissociated}}{\text{starting amount}} \times 100\% = \frac{0.0014\ \text{M}}{0.106\ \text{M}} \times 100\% = 1.3\%$$

Done.

Your turn.

. . . .

Example 9. 0.00312 mol of hydroxylamine, $HONH_2$, is dissolved to make 100. mL solution. What is the pH of the solution?

. . . .

By the way, the hydroxyl part of the name does not imply a hydroxide ion. This compound is entirely covalent. The lone pair on N is the base part. Here's the balanced equation.

$$HONH_2(aq) + H_2O(l) \rightleftharpoons HONH_3^+(aq) + OH^-(aq)$$

Take it from there.

K_b expression:

Initial amount:

Fill in a table:

	$[HONH_2]$	$[HONH_3^+]$	$[OH^-]$
Initial:			
Changes:			
Equilibrium:			

Plug into K_b:

Solve for x:

Quadratic via $$x^2 + 9.1 \times 10^{-9}\,x - 2.8 \times 10^{-10} = 0$$

Approximation gives

$$\frac{(x)\,(x)}{0.0312 - x} \approx \frac{x^2}{0.0312} = 9.1 \times 10^{-9}$$

For this approximation, note that the value of x which you first obtain will not change the number in the denominator to the correct sigfigs. That means the iteration will give you the same number, so there's no need to continue the iteration.

K-check:

pH:

As a middle check for your work, $[OH^-]$ is 1.7×10^{-5} M.

56.2 Weak conjugates

All of our acid and base Examples 1 - 9 have started with neutral molecules and the products of their dissociations have been two ions. One ion derives from water and the other ion is the conjugate partner of the starting acid or base. Now we consider the acid/base properties of those conjugate ions. There are two things you need to know.

For every weak acid, its conjugate base is also weak.
For every weak base, its conjugate acid is also weak.

Thus, the conjugate partner of anything weak is also weak. This will also apply when you make a solution with a salt which contains such an ion. Let's elaborate on this a bit.

Acetic acid is a weak acid because its conjugate, acetate, pulls back (Section 54.1).

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons CH_3CO_2^-(aq) + H_3O^+(aq)$$

Since acetate is capable of pulling off H^+, it is a base. It can also be a base to other acids including water itself.

$$CH_3CO_2^-(aq) + H_2O(l) \rightleftharpoons CH_3CO_2H(aq) + OH^-(aq)$$

Thus, if you dissolve an acetate salt such as sodium acetate into water, the solution will be basic. (The sodium cation has no pH effect and it is a spectator to the acid/base equilibrium.) The equilibrium written above for an acetate solution is just another version of base dissociation. The K_b expression is derived in the usual manner.

$$K_b = \frac{[CH_3CO_2H]\,[OH^-]}{[CH_3CO_2^-]}$$

Although the K_b expression can be derived in the usual manner, you won't find its value in the usual manner. It's not in Appendix B and it's not in your typical reference books. You must calculate it, and here's how you do that. For simplicity, I'll use generic formulas for a conjugate pair, HA and A^-. The relevant equations are then the following.

HA acid dissociation: $HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$

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

A^- base dissociation: $A^-(aq) + H_2O(l) \rightleftharpoons HA(aq) + OH^-(aq)$

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

The sum of the two dissociations gives the autoionization equation.

$$\begin{array}{lr} \text{HA acid dissociation:} & HA(aq) \rightleftharpoons H^+(aq) + A^-(aq) \\ A^- \text{ base dissociation:} & \underline{A^-(aq) + H_2O(l) \rightleftharpoons HA(aq) + OH^-(aq)} \\ \text{Autoionization:} & H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq) \end{array}$$

Since we are adding the first two equations, we multiply their K's for the third equation

$$K_a \times K_b = K_w$$

which can also be shown by writing everything out.

$$\frac{[H^+]\,[A^-]}{[HA]} \times \frac{[HA]\,[OH^-]}{[A^-]} = [H^+]\,[OH^-]$$

$$K_a \quad \times \quad K_b \quad = \quad K_w$$

Know that relationship. The value for K_w is a constant; if you also have either of K_a or K_b, then you can calculate the other. For CH_3CO_2H, $K_a = 1.8 \times 10^{-5}$. That will get you K_b for $CH_3CO_2^-$.

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

With $K_b = 5.6 \times 10^{-10}$, we can see that $CH_3CO_2^-$ is a pretty lousy base on its own, but it's still a base.

The conjugate acid of a weak base receives analogous treatment. Consider the ammonium ion in some salt, such as NH_4Cl. (The chloride anion has no pH effect and it is a spectator to the acid/base equilibrium.) Ammonia is a weak base because its conjugate acid can lose H^+.

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

Since NH_4^+ is capable of losing H^+, it is also capable of losing it to any base, including water itself.

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$$

OR

$$NH_4^+(aq) \rightleftharpoons NH_3(aq) + H^+(aq)$$

Thus, if you dissolve NH_4Cl into water, the solution will be acidic. This equilibrium is just another version of acid dissociation, for which there is a K_a.

$$K_a = \frac{[NH_3]\,[H^+]}{[NH_4^+]}$$

You won't find the value for this K_a listed; you need the K_w connection and the K_b for NH_3.

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

Thus, NH_4^+ is a fairly lousy acid but it's still an acid.

Curiously, we just obtained the same numerical value for K_b of $CH_3CO_2^-$ as for K_a for NH_4^+. That's just a coincidence, so don't expect that to be any kind of generality. Acetic acid's K_a and ammonia's K_b just happen to be the same number to two sigfigs, 1.8×10^{-5}, so their conjugate K's will also be the same.

Let's take a look at an Example along these lines.

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Example 10. Calculate the pH of a solution of 0.00700 mol ammonium chloride dissolved in a solution volume of 300. mL.

……

As noted earlier, the Cl^- anion is spectating and we can ignore it. The ammonium ion is the conjugate acid of the weak base, NH_3. Set up the usual acid dissociation equilibrium, starting with NH_4^+.

Equation $NH_4^+(aq) \rightleftharpoons NH_3(aq) + H^+(aq)$

K_a expression

$$K_a = \frac{[NH_3]\,[H^+]}{[NH_4^+]} = 5.6 \times 10^{-10}$$

Initial amount

$$\text{initial } [NH_4^+] = \frac{0.00700 \text{ mol}}{0.300 \text{ L}} = 0.0233 \text{ M}$$

Table (with just the bottom line)

	$[NH_4^+]$	$[H^+]$	$[NH_3]$
Equilibrium:	$0.0233 - x$	x	x

Go into K_a.

$$K_a = \frac{[NH_3]\,[H^+]}{[NH_4^+]} = \frac{(x)\,(x)}{0.0233 - x} = 5.6 \times 10^{-10}$$

Pick your path.

Re-arrange. $x^2 + 5.6 \times 10^{-10}\,x - 1.3 \times 10^{-11} = 0$

Plug and chug. $x = 3.6 \times 10^{-6}$

OR

Approximate.

$$K_a = \frac{x^2}{0.0233 - x} \approx \frac{x^2}{0.0233} = 5.6 \times 10^{-10}$$

Plug and chug. $x = 3.6 \times 10^{-6}$

Iterate? Notice that the value for x starts in the sixth decimal place. That won't change the number in the denominator. You're done.

You have $x = 3.6 \times 10^{-6}$

from which you get the pH. pH = 5.44

The solution pH is 5.44 which is slightly acidic, as expected for a weak acid.

Let's do another.

. . . .

Example 11. Sodium benzoate, $NaC_6H_5CO_2$, is commonly used in many foods and other goods as a preservative. The benzoate ion, $C_6H_5CO_2^-$, is the conjugate base of benzoic acid, $C_6H_5CO_2H$. A 100. mL solution of sodium benzoate was prepared using 0.00521 mol of the salt. What is the pH of the solution?

. . . .

The Na^+ cation is again spectating and will not affect the pH. The benzoate ion is a weak base and that will determine the pH. Set up the usual base dissociation equilibrium, starting with $C_6H_5CO_2^-$.

Equation $C_6H_5CO_2^-(aq) + H_2O(l) \rightleftharpoons C_6H_5CO_2H(aq) + OH^-(aq)$

K_b expression

$$K_b = \frac{[C_6H_5CO_2H]\,[OH^-]}{[C_6H_5CO_2^-]}$$

You'll need K_a for benzoic acid in order to get K_b for benzoate.

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{6.3 \times 10^{-5}} = 1.6 \times 10^{-10}$$

Initial amount

$$\text{initial } [C_6H_5CO_2^-] = \frac{0.00521 \text{ mol}}{0.100 \text{ L}} = 0.0521 \text{ M}$$

Table (bottom line)

	$[C_6H_5CO_2^-]$	$[C_6H_5CO_2H]$	$[OH^-]$
Equilibrium:	$0.0521 - x$	x	x

Go into K_b.

$$K_b = \frac{[C_6H_5CO_2H]\,[OH^-]}{[C_6H_5CO_2^-]} = \frac{(x)\,(x)}{0.0521 - x} = 1.6 \times 10^{-10}$$

Pick your path.

Re-arrange. $x^2 + 1.6 \times 10^{-10}\,x - 8.3 \times 10^{-12} = 0$

Plug and chug. $x = 2.9 \times 10^{-6}$

OR

Approximate.

$$K_b = \frac{x^2}{0.0521 - x} \approx \frac{x^2}{0.0521} = 1.6 \times 10^{-10}$$

Plug and chug. $x = 2.9 \times 10^{-6}$

Iterate? What do you think?

You have $x = 2.9 \times 10^{-6}$

which means $[OH^-] = 2.9 \times 10^{-6}$ M

which leads to pOH = 5.54

and finally to pH. pH = 8.46

That's it. The solution pH is 8.46, basic.

OK, this will end the fundamental acid/base equilibrium calculations for now. Again, the calculations for acids and bases are very similar although you may need to convert between $[H^+]$ and $[OH^-]$ or pH and pOH.

Before closing this Section, let me repeat something and bring in something new. Here is the repeat part, from earlier.

> For every weak acid, its conjugate base is also weak.
> For every weak base, its conjugate acid is also weak.

Thus, the conjugate partner of anything weak is also weak.

Remember this. Now consider something new, although it does follow from the conjugate relationships. Since a conjugate pair is related by $K_a \times K_b = K_w$, then K_a and K_b change inversely. When comparing different acids and bases, a higher K_a for an acid will result in a lower K_b for its conjugate base, while a lower K_a for an acid will result in a higher K_b for its conjugate base. Here're a few comparisons.

conjugate acid	HF	CH_3CO_2H	HClO	HCN
K_a	6.8×10^{-4}	1.8×10^{-5}	3.0×10^{-8}	6.2×10^{-10}
conjugate base	F^-	$CH_3CO_2^-$	ClO^-	CN^-
K_b	1.5×10^{-11}	5.6×10^{-10}	3.3×10^{-7}	1.6×10^{-5}

As K_a goes down, the K_b goes up and vice versa. The acids get weaker to the right; the bases get weaker to the left. For example, CH_3CO_2H is a better acid than HClO, but ClO^- is a better base than $CH_3CO_2^-$. This relationship comes in handy for making qualitative comparisons without calculating actual K's for conjugates. For example, which is the better acid: NH_4^+ or $HONH_3^+$? You can answer this question by looking up the K_b values for the bases. The K_b for NH_3 is 1.8×10^{-5} while the K_b for $HONH_2$ is 9.1×10^{-9}. NH_3 is the better base but that means that $HONH_3^+$ will be the better acid.

Keep these relationships in mind.

56.3 Acid-base effects of salts

The discussion and Examples above regarding acid/base properties of ions illustrate a very important point when it comes to solutions of ionic compounds in water: some salt solutions are acidic, some are basic, and some are neutral. The outcome is determined by the relative properties of the cation and anion, each of which can be acidic, basic or of no pH effect. Whether an ion has a pH effect depends on whether it derives from a weak or strong acid or base. The reason for that lies in the explanation behind why something is weak or strong, which goes back to the refresh in Section 54.1. For weaks, there is an equilibrium pull which is exerted by both members of the conjugate pair. Because of this, both members of the conjugate pair will have a pH effect. For strongs, one member of the conjugate pair does not pull to a significant extent, so it does not have a pH effect.

We will now summarize the various types of ions in terms of what pH effect they have, if any. These are presented in six Categories as follows. These won't cover every possible variation, but it will cover enough for our purposes.

- CATEGORY I. Anions from monoprotic, strong acids and cations from strong bases have no pH effect.

HCl, HBr, HI, HNO_3 and $HClO_4$ are your five examples to know within our coverage of monoprotic strong acids. Accordingly, Cl^-, Br^-, I^-, NO_3^- and ClO_4^- do not have a pH effect. Remember those five anions specifically for having no pH effect. The strong bases include the hydroxides and oxides of Group 1 and of Group 2 except for Be and Mg. Accordingly, the metal cations of Group 1 along with Ca^{2+} and the lower cations in Group 2 are of no pH effect.

Notice that HSO_4^- is not mentioned here, even though it derives from H_2SO_4 which is also a strong acid. It does not fit here because H_2SO_4 is diprotic. The anion from the first dissociation step of every polyprotic is a hydrogen anion. Hydrogen anions are in the next two Categories.

- CATEGORY II. Hydrogen anions from strong acids are weak acids.

HSO_4^- is the most common example. There are others but they are nowhere near as common. You need to know that HSO_4^- is a weak acid.

- CATEGORY III. Hydrogen anions from weak acids can be acidic or basic overall.

All of these are amphoteric, so they can act as an acid or as a base. Although they can act in both directions, they are not equal in both directions. In solution, the outcome will be acidic or basic depending on which property is better. That outcome is determined by comparing the ion's K_a to its K_b. Whichever is bigger wins.

- CATEGORY IV. All other anions are weak bases.

This is a very extensive Category which includes all anions from monoprotic weak acids, such as $CH_3CO_2^-$, F^-, ClO^-, $C_6H_5CO_2^-$, etc. This Category also includes the final anion in any polyprotic dissociation string, such as CO_3^{2-} or PO_4^{3-}. This is a "none-of-the-above" Category: if an anion is not in the above Categories I - III, then it's here. This means if an anion is not a hydrogen anion and it's not Cl^-, Br^-, I^-, NO_3^- or ClO_4^-, then it's in this Category and it's basic. Remember this, even if you can't tell what acid the anion derives from.

- CATEGORY V. Cations which are the conjugate acid of a weak base are weak acids.

Weak bases include ammonia and amines. Their conjugates, NH_4^+ and protonated amines, are weak acids. As a point of naming, ammonium is the conjugate acid of ammonia. Similarly, many names of protonated amines and related compounds end in "*-nium*". For our purposes here, we will use this ending for ions which are weak acids. (The "*-nium*" ending also occurs for some other types of compounds and not all of those are acids. Those are not in our coverage here, so we will assume "*-nium*" refers to a weak acid cation.)

This ends the first five Categories. There is a Category VI but we need to cover a few things before we get there.

Let's do a few examples with Categories I - V and see how this works. The task is to evaluate whether a particular salt gives an acidic, basic or neutral solution upon dissolving in water. This depends on whether the cation and the anion are acidic, basic or of no effect. There are three Outcomes which we will consider.

OUTCOMES

A. If both the cation and the anion are of no pH effect, then the solution is neutral. In real life, the solution will be close to pH 7.0 if dilute.
B. If only one ion has a pH effect, then the solution will be acidic or basic according to that ion.
C. If both ions have a pH effect, then the outcome is determined by comparing the relative effects of the cation versus the anion.

We will now do a number of examples to illustrate this process.

▸ lithium perchlorate

Li^+ derives from the strong base LiOH and it falls under Category I for no pH effect.
ClO_4^- derives from the strong acid $HClO_4$ and it also falls under Category I for no pH effect.

Neither ion has a pH effect. This leads to Outcome A, and a solution of $LiClO_4$ is neutral.

▸ calcium acetate

Ca^{2+} derives from the strong base $Ca(OH)_2$ and it falls under Category I for no pH effect.
$CH_3CO_2^-$ derives from the weak acid CH_3CO_2H and it falls under Category IV for basic anions.

The cation has no pH effect; the anion is basic. This leads to Outcome B, and a solution of $Ca(CH_3CO_2)_2$ is basic.

▸ methylammonium bromide

Note the "*-nium*" ending on the first word, so this is telling you that the cation is a weak acid and it falls under Category V. You would be able to recognize this even without knowing the cation formula. (The cation formula is $CH_3NH_3^+$ and it is the conjugate acid of the weak base methylamine, CH_3NH_2.)

Br^- derives from the strong acid HBr and it falls under Category I for no pH effect.

The cation is acidic; the anion has no effect. This leads to Outcome B, and a solution of methylammonium bromide is acidic.

- potassium arsenate

  K^+ derives from the strong base KOH and it falls under Category I for no pH effect.
  AsO_4^{3-} is the final anion in the triprotic series for H_3AsO_4 and it falls under Category IV for basic anions.

The cation has no pH effect; the anion is basic. This leads to Outcome B, and a solution of K_3AsO_4 is basic.

- NaIO

  Na^+ derives from the strong base NaOH and falls under Category I for no pH effect.
  IO^- may not be familiar, but it doesn't really matter. It's not a hydrogen anion and it's not Cl^-, Br^-, I^-, NO_3^- or ClO_4^-, so it falls under Category IV, basic. (It's the conjugate base of hypoiodous acid, HIO. The anion's name is hypoiodite.)

The cation has no effect but the anion is basic. This leads to Outcome B, and a solution of NaIO is basic.

- potassium hydrogen oxalate

  K^+ derives from the strong base KOH and it falls under Category I for no pH effect.
  $HC_2O_4^-$ is a hydrogen anion from a weak acid and it falls under Category III for amphoterics. This means that you must look both ways and compare hydrogen oxalate's K_a to its K_b. For that, we need some numbers.

K_a for $HC_2O_4^-$ is the same as K_{a2} for $H_2C_2O_4$ and that value is 5.4×10^{-5}. K_b for $HC_2O_4^-$ is derived using K_w/K_a but which K_a? Do we want K_{a1} or K_{a2} for oxalic acid? Good question. When dealing with polyprotics and amphoterics, you have to be very careful with this.

For this purpose, let me introduce a conjugate line diagram. A conjugate line diagram is simply a way of representing the dissociation steps without spelling out the balanced equations. For oxalic acid, we can write

$$H_2C_2O_4 \quad \leftrightarrow \quad HC_2O_4^- \quad \leftrightarrow \quad C_2O_4^{2-}$$

and this shows each dissociation with a double-headed arrow which connects the conjugate pair of each step. Acid dissociations are read forward, left to right, with each step losing H^+.

$$H_2C_2O_4 \quad \rightarrow \quad HC_2O_4^- \quad \rightarrow \quad C_2O_4^{2-}$$

Each acid step has a K_a.

$$\begin{array}{lccccc} K_a\text{'s:} & & K_{a1} & & K_{a2} & \\ & H_2C_2O_4 & \rightarrow & HC_2O_4^- & \rightarrow & C_2O_4^{2-} \end{array}$$

We need the K_a of $HC_2O_4^-$. For that, you begin at $HC_2O_4^-$ and read right: the K_a is K_{a2} of oxalic acid, which is 5.4×10^{-5}.

Base dissociations are read backwards, right to left, with each step gaining H^+.

$$H_2C_2O_4 \quad \leftarrow \quad HC_2O_4^- \quad \leftarrow \quad C_2O_4^{2-}$$

Each base step has a K_b which is K_w divided by the corresponding K_a.

$$\begin{array}{lccccc} & H_2C_2O_4 & \leftarrow & HC_2O_4^- & \leftarrow & C_2O_4^{2-} \\ K_b\text{'s:} & & K_w/K_{a1} & & K_w/K_{a2} & \end{array}$$

We need the K_b of $HC_2O_4^-$. Begin at $HC_2O_4^-$ and read left: the K_b is K_w/K_{a1}.

$$K_b = \frac{K_w}{K_{a1}} = \frac{1.0 \times 10^{-14}}{5.4 \times 10^{-2}} = 1.9 \times 10^{-13}$$

So now, overall, is the hydrogen oxalate ion acidic or basic? Well, the K_a is 5.4×10^{-5} and the K_b is 1.9×10^{-13}. The K_a is larger than the K_b so $HC_2O_4^-$ is a better acid than it is a base. The anion is acidic. The ultimate answer for the salt as a whole is that this is Outcome B and a solution of potassium hydrogen oxalate is acidic.

In summary, the overall conjugate diagram is the following

$$\begin{array}{lccccc} K_a\text{'s:} & & K_{a1} & & K_{a2} & \\ & H_2C_2O_4 & \leftrightarrow & HC_2O_4^- & \leftrightarrow & C_2O_4^{2-} \\ K_b\text{'s:} & & K_w/K_{a1} & & K_w/K_{a2} & \end{array}$$

and this is a shorthand way of figuring out what K goes with what step for a polyprotic series. Just remember to read it to the right for acid steps and to the left for base steps. This is useful in other applications also, as we will see in the next Chapter.

This was a fairly involved procedure just to determine if hydrogen oxalate ion is acidic or basic, but the amphoterics take a bit of figuring. Make sure you put K_w over the correct K_a to get the K_b or you can screw this up royally.

Care to take a stab at this? Why is a solution of baking soda basic? Baking soda is sodium bicarbonate. Na^+ has no pH effect (Category I). Bicarbonate ion is amphoteric (Category III). Here's the line diagram which involves bicarbonate.

$$\begin{array}{lccccc} K_a\text{'s:} & & K_{a1} & & K_{a2} & \\ & CO_2 & \leftrightarrow & HCO_3^- & \leftrightarrow & CO_3^{2-} \\ K_b\text{'s:} & & K_w/K_{a1} & & K_w/K_{a2} & \end{array}$$

We use CO_2 and not H_2CO_3 as the original acid, as discussed in Section 55.3. K_{a1} for CO_2 is 4.5×10^{-7} and K_{a2} is 4.7×10^{-11}.

Now, what is the value of K_a of bicarbonate?

What is the value of K_b of bicarbonate?

How do the numbers compare? I already said the solution is basic. Your numbers should show that K_b is larger than K_a.

This can get more complicated when dealing with a triprotic series. Just be careful and set up your conjugate line diagram. For example, consider the H_3PO_4 series. If you had to determine the pH effect of dihydrogen phosphate ion, how would you do that? $H_2PO_4^-$ is amphoteric. Here's the whole kit and caboodle for the K's.

$$\begin{array}{lccccccc} K_a\text{'s:} & & K_{a1} & & K_{a2} & & K_{a3} & \\ & H_3PO_4 & \leftrightarrow & H_2PO_4^- & \leftrightarrow & HPO_4^{2-} & \leftrightarrow & PO_4^{3-} \\ K_b\text{'s:} & & K_w/K_{a1} & & K_w/K_{a2} & & K_w/K_{a3} & \end{array}$$

Starting at $H_2PO_4^-$, its K_a goes to the right and that is K_{a2} for H_3PO_4. The K_b for $H_2PO_4^-$ goes to the left and it is K_w/K_{a1}. You would compare those two values. What about hydrogen phosphate ion? For the pH effect of HPO_4^{2-}, you compare K_{a3} versus K_w/K_{a2}. What about phosphate ion? Well, PO_4^{3-} is not amphoteric and you wouldn't necessarily need the line diagram; it's only basic (Category IV) with $K_b = K_w/K_{a3}$.

OK, let's get back to general examples.

‣ $CsHSO_4$

Cs^+ derives from the strong base CsOH and it falls under Category I for no pH effect.
HSO_4^- is a hydrogen anion of a strong acid and it falls under Category II for acidic.

Again, be mindful of bisulfate. Although it is a hydrogen anion, you must remember that it is not amphoteric so you don't need a line diagram. It's only acidic. This is Outcome B. A solution of cesium bisulfate is acidic.

‣ NH_4F

NH_4^+ derives from the weak base NH_3 and it falls under Category V for acidic.
F^- derives from the weak acid HF and it falls under Category IV for basic.

The cation is acidic and the anion is basic. They're opposites. Now what? This is Outcome C, and we need to compare the acidity of NH_4^+ to the basicity of F^-. We do this by comparing K_a of NH_4^+ versus K_b of F^-. The K_a for NH_4^+ is found using the K_b for NH_3.

$$NH_4^+: \qquad K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

The K_b for F^- is found using the K_a for HF.

$$F^-: \qquad K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{6.8 \times 10^{-4}} = 1.5 \times 10^{-11}$$

The numbers tell us that NH_4^+ is a better acid than F^- is a base. Acid wins. A solution of ammonium fluoride is acidic.

You could also have done this one by the inverse K relationship mentioned at the end of the last Section. Since the value of K_b for NH_3 (1.8×10^{-5}) is less than the value of K_a for HF (6.8×10^{-4}), then the conjugate K's will be reversed in the comparison: the value of K_a for NH_4^+ will be larger than the value of K_b for F^-. The calculations show this to be true, but you wouldn't need to do the calculations if you used this relationship.

Your turn. For each of the following salts, will their aqueous solution be acidic, basic or neutral?

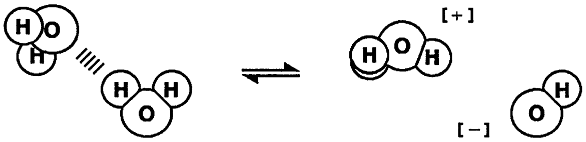
- triethylammonium chloride
- potassium nitrate
- calcium dihydrogen phosphate
- lithium sulfate
- methylammonium cyanide

The answers are two solutions are acidic, two are basic and one is neutral. You figure out which is what and why.

We still need Category VI. That's next.

56.4 Acid effects of metal cations

We now turn to a different kind of acid behavior, one which is associated with metal cations. We know from Category I above that metal cations from Group 1 and metal cations from Group 2, Ca^{2+} and lower, have no pH effect. Most other metal cations are weak acids when dissolved in water. In order to understand this, we must return to autoionization. Chapter 54:

> ❝ Water molecules can pull on each other and compete for H^+ from each other.
>
> 
>
>
> On the left, water molecules do their usual hydrogen bonding thing. Again, the hydrogen bonding acts somewhat as a pull by one water molecule operating on its neighbor. If the pull is sufficient, you get some ionization as given on the right side of the equation. Those ions could recombine to form neutral water molecules or they can become separated from each other and stay as such until they run into another opposite somewhere else. You have opposing processes overall, and an equilibrium. ❞

Now we bring a metal cation into the picture and consider its hydration. The hydration is dominated by ion-dipole interaction. This was described in Chapter 39 but it actually went back to Chapter 10.

> ❝ Opposite charges always attract each other. Those charges can be whole ion charges or they can be the fractional, partial charges of polar things. The net result is that a water molecule's

> partial charges will attract ions. The δ− portion of the water molecules will attract cations. The δ+ portion of the water molecule will attract anions. The illustration on the left shows the O side of one water molecule interacting with a generic cation (labeled C^+ for cation, not to be taken for carbon). On the right, the illustration shows the δ+ on one H interacting with a generic anion (labeled A^-)... Notice how the ion charges and the partial charges are interacting, either with the polarity of the molecule overall or with the polarity of one bonded atom. These interactions are an essential feature of the hydration of ions.
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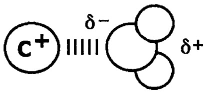
> 
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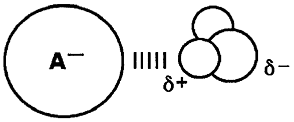
> 
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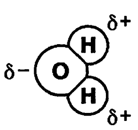
>
> The attractions between a polar molecule and an ion can be good but they're not always great. Some are better than others, but that depends on which ions are involved. For example, a water molecule is more attracted to a 3+ cation than to a 1+ cation. Even so, the attractions are often not as strong as full chemical bonds. However, they work very well for water for two reasons. First, because water's polarity is stronger than the polarity of most other liquids, each of these attractions is stronger in water than in most other solvents. Second, it's not just one water molecule which is interacting, it's a bunch. Each dissolved ion is surrounded by a bunch of water molecules, all piling around, even in layers, trying to get in on the charge attraction. There could be 10, 15 or even more total water molecules attracted to each and every single ion. Although one interaction is not so great, the grand sum of all interactions can be great. ❞

We'll pick it up from there. I used C^+ for a generic cation back then but we are now focusing specifically on metal cations, so I will use M for metal at this time.

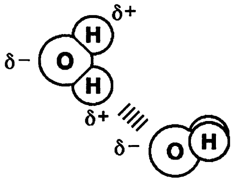
At its simplest, the hydration of a metal cation starts just as for any cation: a bunch of water molecules crawling all around the cation, trying to get in on the charge interaction. But for cases of medium-to-high charge density, this interaction can go further. Recall the importance of charge density on hydration, Section 39.4:

> ❝ A HIGHER CHARGE DENSITY gives a HIGHER LATTICE ENTHALPY and a STRONGER (MORE NEGATIVE) HYDRATION ENTHALPY. ❞

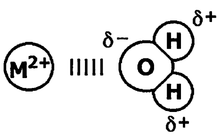
As the charge density on a metal cation increases, further effects become possible. The effect of our present concern is acidity. This effect traces to the dissociation of a water molecule which contacts the metal cation directly. Let's focus on one water molecule in contact with a generic $M^{2+}(aq)$ cation for illustration purposes.



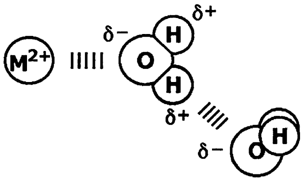
First, we start with a water molecule at left. Due to bond polarities, the O carries a δ− partial charge while each H carries a δ+ partial charge.



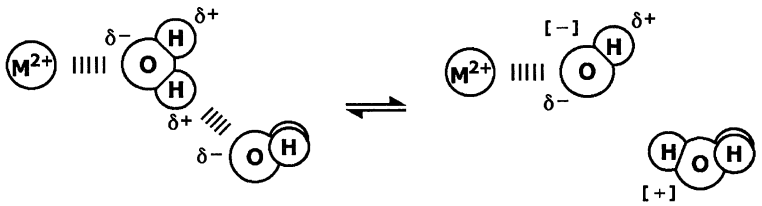
We add another water molecule in contact with the first, at right. (I did not label the δ+'s on the H's in the second molecule but they are there.) The second molecule interacts by hydrogen bonding which, as we have seen, acts as a pull. The picture so far is the same setup which leads to autoionization. If the pull is successful, then you get H_3O^+ and OH^-, but very little ionization is actually obtained.



Now we bring in one M^{2+} cation and start the picture over, at left. Many water molecules actually surround the cation, some in direct contact and others on top of those. Our focus is on one of the water molecules in direct contact, and that is all which I show at left. The metal cation's 2+ charge is strongly interacting with the oxygen of the water. This can attract electrons from O (from a lone pair) causing a shift (polarization) of negative charge toward M^{2+}. This causes O to draw more from the H's and this further polarizes the O–H bonds. This increases the O–H bond polarity and makes the δ+ charges on the H's even larger.



At right, we now bring in another water molecule which interacts by hydrogen bonding with the first. Again, this constitutes a pull between the water molecules. Now, however, the partial δ+ charges on H are greater than in plain water, so it is now easier for H^+ to be ripped off by the second water molecule. There will still be a pull in both directions, and this gives rise to a new dissociation equilibrium shown below.



Due to its full 1− charge, the OH^- formed in the process is very strongly attracted to M^{2+}, and, in fact, these are often chemically bonded. The overall result of all of these interactions is that H^+ is formed and this increases total $[H^+]$ in the solution, which decreases the pH. As long as the OH^- remains bonded to (or at least strongly interacting with) M^{2+}, then it is not free $OH^-(aq)$ in solution and it does not affect the pH of the solution. We can write this in either of the following ways.

$$M^{2+}(aq) + 2\,H_2O(l) \rightleftharpoons MOH^+(aq) + H_3O^+(aq)$$

OR

$$M^{2+}(aq) + H_2O(l) \rightleftharpoons MOH^+(aq) + H^+(aq)$$

Sometimes you will see these equations with a specific number of waters included in the formula for the metal cation. Those refer to waters in direct contact, and common numbers are 4 or 6 depending on the cation. For example, if M^{2+} starts off with 6 water molecules, we can write the dissociation as follows

$$M(H_2O)_6^{2+} + H_2O(l) \rightleftharpoons (H_2O)_5MOH^+(aq) + H_3O^+(aq)$$

OR

$$M(H_2O)_6^{2+} \rightleftharpoons (H_2O)_5MOH^+(aq) + H^+(aq)$$

and each of these formats conveys the acidity of the metal cation. Unfortunately, for many metal cations, there can then be other types of additional equilibria involved; as such, further complications can arise, but we will not go into those. The above covers our bottom line here: many metal cations are weak acids. Although a range of K_a values are known, we will not do calculations with them due to the further complications. Here are a few values of K_a for illustration.

M^{2+}	Be^{2+}	Fe^{2+}	Co^{2+}	Cu^{2+}	Zn^{2+}	Sn^{2+}
	4.0×10^{-6}	3.0×10^{-10}	2.2×10^{-10}	1.1×10^{-8}	1.1×10^{-9}	3.8×10^{-4}
M^{3+}	Al^{3+}	Cr^{3+}	Fe^{3+}	La^{3+}	Tl^{3+}	Bi^{3+}
	1.1×10^{-5}	9.8×10^{-5}	6.5×10^{-3}	3.0×10^{-9}	2.4×10^{-1}	8.1×10^{-2}

Our interest in this Section remains directed at the qualitative question as to whether a metal cation will be acidic or of no pH effect in water. For this much, we won't need calculations.

The K_a values cover a wide range and several factors are actually involved. One general trend for the acidity of metal cations involves its charge density. In general, a greater charge density can give a greater effect, and the cation is then more acidic. Notice in the table that Fe^{3+} is a better acid than Fe^{2+}; Fe^{3+} has a higher charge and is smaller than Fe^{2+}, both of which lead to a greater charge density. Other factors also get involved, however, so it's not so simple. For one example, increasing the electronegativity of the metal cation will also increase the polarization effects, and this will increase acidity. For a second example, the actual number of water molecules in direct contact with the original metal cation will also have an effect. For a third example, even the specific electron configuration of the metal cation can have an effect. Thus and overall, a number of factors come into play. Despite the various factors involved, for purposes of our coverage, we can give some general trends for simply gauging whether some metal cation is acidic or not.

Metal cations of 1+ charge are not very good at this. They don't have enough pull on the water molecules to cause enough polarization, so they do not give a significant acid effect. We've already covered the Group 1 cations as having no pH effect within Category I. There are a few other 1+ cations from other Groups which also have no pH effect or which are borderline, but we won't cover those cases.

Most metal cations of 2+ charge are acidic. The primary duds which do not display acidity are Ca^{2+} and lower elements in Group 2, which are already covered within Category I as having no pH effect. Mg^{2+} is actually borderline, while Be^{2+} is clearly acidic and is in the list above.

All metal cations of 3+ or higher charge are acidic.

With this, we can finally do Category VI.

- CATEGORY VI. 2+ metal cations except Ca^{2+} and lower Group 2, as well as metal cations of higher charge, are acidic.

Here are two examples for salt solutions.

▸ copper(II) nitrate

Cu^{2+} is acidic (Category VI).
NO_3^- has no pH effect (Category I).

The cation is acidic but the anion has no effect. This is Outcome B, and a solution of copper(II) nitrate is acidic.

▸ $ScCl_3$

Sc^{3+} is acidic (Category VI).
Cl^- has no pH effect (Category I).

The cation is acidic but the anion has no effect. This is Outcome B, and a solution of scandium(III) chloride is acidic.

This ends our six Categories for acid/base effects of ions, as well as the overall Outcomes for salt solutions.

Problems

1. True or false.
   a. Amines are weak bases.
   b. Protonated amines are weak acids.
   c. Anions of weak, monoprotic acids are weak bases.
   d. Acetate ion is a better base than cyanide ion.
   e. Ammonia is a better base than phosphate ion.
   f. Metal cations of 3+ charge are acidic.

2. Write the balanced equation for base dissociation and write the K_b expression for each of the following.
   a. methylamine, CH_3NH_2 b. aniline (phenylamine), $C_6H_5NH_2$

3. A solution was prepared using 0.00286 mol of the weak base pyridine, C_5H_5N, in a volume of 200. mL. At equilibrium, what are the concentrations of C_5H_5N, OH^- and $C_5H_5NH^+$? What are the pOH and the pH?

4. 0.00912 mol triethylamine, $(C_2H_5)_3N$, was dissolved into water to produce 300. mL of solution. What are the concentrations of $(C_2H_5)_3N$, OH^- and $(C_2H_5)_3NH^+$ at equilibrium? What are the pH and the percent dissociation?

5. How many grams of pyridine, C_5H_5N, must be dissolved into 1.00 L of solution to give pH = 9.08 at equilibrium?

6. Write the balanced equation and the appropriate K expression for each of the following.
   a. acid dissociation of hydroxylammonium ion, $HONH_3^+$
   b. base dissociation of cyanide ion

7. What is the value of the indicated K for each of the following?
   a. K_b of NO_2^- b. K_b of SO_4^{2-} c. K_a of $CH_3NH_3^+$ d. K_a of $C_5H_{10}NH_2^+$

8. What are the values of K_a and of K_b for each of the following amphoteric hydrogen anions?
   a. $H_2AsO_4^-$ b. $HSeO_3^-$ c. HPO_4^-

9. A solution was prepared by dissolving 0.00274 mol sodium hypochlorite in 500. mL solution. At equilibrium, what are the concentrations of ClO^-, OH^- and HClO? What are the pOH and the pH?

10. A solution was prepared by dissolving 0.00724 mol anilinium ($C_6H_5NH_3^+$) bromide in 1.00 L solution. What are the concentrations of $C_6H_5NH_3^+$, H^+ and $C_6H_5NH_2$ at equilibrium? What is the pH?

11. A solution of $NH_3(aq)$ was prepared and stored in a closed jar with some gas space at the top. At equilibrium at 25 °C, the pOH was 2.77. What was the pressure (in atm) of $NH_3(g)$ in the gas space? (Here's a start. Set up the solubility equilibrium for $NH_3(g)$ and also set up the base dissociation for $NH_3(aq)$. Add these two equations together. Find $\Delta G°$ for the sum equation from free energies of formation and use that to find K.)

12. Write the balanced equation for the acid dissociation of $Cr(H_2O)_6^{3+}$.

13. Consider separate solutions of each of the following salts. For each, is the solution acidic, basic or neutral?

    a. $Ba(NO_3)_2$ b. $AlCl_3$ c. Na_3PO_4 d. KNO_2 e. NH_4Cl

14. Consider separate solutions of each of the following salts. For each, is the solution acidic, basic or neutral?

    a. $RbClO_4$ b. $Sr(ClO)_2$ c. $Sn(NO_3)_2$ d. CsBr e. $KHSO_4$

15. Consider separate solutions of each of the following salts. For each, is the solution acidic, basic or neutral?

    a. $LiHSO_3$ b. methylammonium acetate c. FeI_2 d. $NH_4H_2PO_4$