

General Chemistry II

Chapter 15 Lecture Notes

Acids and Bases

Brønsted Acids and Bases

Arrhenius (classical) acids are proton donors. Arrhenius bases are hydroxide ion donors

Brønsted acids are defined as proton donors but in a more general definition, Brønsted bases are *proton acceptors*.

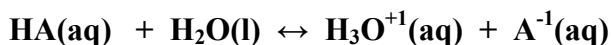
This leads to the concept of Acid-base conjugate pairs.

The removal of a proton from any species (a Brønsted acid) produces its conjugate base (a proton acceptor).

The addition of a proton to any acceptor species (a Brønsted base) produces its conjugate acid (a proton donor).

All acid-base reactions now become the reaction of an acid-base pair to produce another acid-base pair (the conjugate base and the conjugate acid of the first pair).

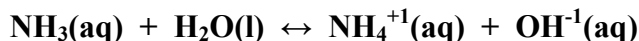
The dissociation of an acid in water produces a hydronium ion (the conjugate acid of water), not a bare proton.



(Hydrogen ion does not have a free existence in water and can only exist as the hydronium ion, $\text{H}_3\text{O}^{+1}(\text{aq})$. It is often still represented as just H^{+1} .)

Many substances which do not contain hydroxide ion can now be classed as bases, such as fluoride ion, cyanide ion, phosphate ion, bicarbonate ion, ammonia, etc. All are proton acceptors to some degree and all produce some hydroxide ion in aqueous solution.

Ammonia is the classic example of a base that does not have hydroxide in its molecular formula.



Exs: Identify conjugate acids of bases and conjugate bases from acid formulas.

Acid-Base Properties of Water

Water can donate a proton to a stronger base and become hydroxide ion or can accept a proton from a stronger acid and become the hydronium ion.

Exs: ammonia, carbonate ion (washing soda), phosphate ion (TSP), HCl, HOAc

Water also *autoionizes* to a very small (but very important) extent to produce low concentrations of hydronium ion and hydroxide ion. This is also a Brønsted acid-base reaction.



The Ion Product of Water

The autoionization of *pure* water produces *equal* concentrations of hydronium ion and hydroxide ion $\sim(10^{-7}\text{M}$ at 24 °C). Autoionization occurs at any temperature and with any concentration of added acid or base.

$$K_c = [\text{H}^+] \cdot [\text{OH}^-]/[\text{H}_2\text{O}]$$

Since $[\text{H}_2\text{O}]$ is a constant in most aqueous systems, equal to 55.55M, it is incorporated into the K term and the equilibrium expression now becomes the ion product constant expression:

$$K_w = [\text{H}^+] \cdot [\text{OH}^-] = 10^{-14} \text{ at } 25^\circ\text{C}$$

(The values of K_w and K_c differ by a factor of 55.55M but $[\text{H}^+]$ and $[\text{OH}^-]$ would be the same whichever version of the equation is used, because $K_c = 1.80 \times 10^{-16}$)

$[\text{H}^+]$ and $[\text{OH}^-]$ can be varied independently by the addition of acids or bases, but their product must always equal 10^{-14} . This enables the calculation of any $[\text{H}^+]$ or $[\text{OH}^-]$ given the $[\text{OH}^-]$ or $[\text{H}^+]$.

(Note that when $[\text{H}^+] = [\text{OH}^-]$, they both equal 10^{-7}M . this is defined as a *neutral* solution.)

Exs: $[\text{H}^+] = 6 \times 10^{-5}\text{M}$, $[\text{OH}^-] = 2 \times 10^{-10}\text{M}$.
 $[\text{OH}^-] = 2.5 \times 10^{-9}\text{M}$, $[\text{H}^+] = 4.0 \times 10^{-6}\text{M}$

The pH Concept

A more concise way to express the acidity or basicity of any aqueous solution.

Important to know $[\text{H}^+]$ of any aqueous system, organic, inorganic or biochemical.

Acidic solutions are defined as $[\text{H}^+] > [\text{OH}^-]$ or $[\text{H}^+] > 10^{-7}\text{M}$

Basic solutions are defined as $[\text{H}^+] < [\text{OH}^-]$ or $[\text{OH}^-] > 10^{-7}\text{M}$

Neutral solutions are defined as $[\text{H}^+] = [\text{OH}^-] = 10^{-7}\text{M}$.

pH is a concise term, devised by Arrhenius, to express $[\text{H}^+]$ without units or exponents.

$$\text{pH} = -\log[\text{H}^+]$$

Why log? Why negative log? Wide range of $[\text{H}^+]$ values possible

pH easy to calculate from simple exponential $[\text{H}^+]$ values as 10^{-1}M , 10^{-12}M , 10^{-7}M , 10^0M , 10^{-5}M , etc.

resulting range of possible pH values.

Use a calculator for terms with significant parts other than one.

(Dissection of negative log terms.)

How are sig. figs. handled in common log problems?

Exs: $[H^{+1}] = 6 \times 10^{-5}M$, pH = 4.2
 $[H^{+1}] = 3.7 \times 10^{-11} M$, pH = 10.43
 pH = 9.7, $[H^{+1}] = 2 \times 10^{-10}M$
 pH = 2.90, $[H^{+1}] = 1.3 \times 10^{-3}M$

Alternative, but rarely used, **pOH = $-\log[OH^{-1}]$**

Since $[H^{+1}] \cdot [OH^{-1}] = 10^{-14}$, then pH + pOH = 14

Exs: pOH = 12.60, pH = 1.40, $[H^{+1}] = 4.0 \times 10^{-2}M$, $[OH^{-1}] = 2.5 \times 10^{-13}M$

Exs of Specific Solutions:

What are the $[H^{+1}]$, pH, pOH and $[OH^{-1}]$ of a 0.0023 M HCl solution?
 $[H^{+1}] = 0.0023M$, pH = 2.64, pOH = 11.36, $[OH^{-1}] = 4.3 \times 10^{-12}$.

What are the $[H^{+1}]$, pH, pOH and $[OH^{-1}]$ of a 0.00065 M Ba(OH)₂ solution?
 $[OH^{-1}] = 1.3 \times 10^{-3}M$, pOH = 2.89, pH = 11.11, $[H^{+1}] = 7.8 \times 10^{-12}M$

Acid and Base Strengths

Define acid and base *strength*.

Most acids are weak.

Memorize the short list of strong acid formulas, names and anions (conjugate bases).

All other acids are weak!

All strong acids are strong electrolytes.

Their conjugate bases have negligible base strength. Why?

Memorize the short list of strong acid formulas, names and anions (conjugate bases).

All weak acids are weak electrolytes.

Their conjugate bases are fairly strong proton acceptors. Why?

Some examples of well-known weak acids:

Memorize the short list of strong base formulas and names.

All other bases are weak, including all other metal hydroxides, ammonia.

Hydronium ion is the strongest acid that can exist in water. Why?

Any acid such as HCl immediately dissociates and donates its proton to water to form hydronium ion.

Hydroxide ion is the strongest base that can exist in water.

Ex: dissociation of perchloric acid. (Also nitric, HCl, etc.)

Stronger bases such as oxide ion or amide ion react with water to form hydroxide ion.

Ex: Potassium oxide or sodium amide.

Weak Acids and Acid Ionization Constants

All weak acids have an associated acid dissociation constant, K_a .
(K_a values for strong acids are "large" and have no useful meaning.)

K_c applies to the "true" reaction $\text{HA(aq)} + \text{H}_2\text{O(l)} \leftrightarrow \text{H}_3\text{O}^+(\text{aq}) + \text{A}^-(\text{aq})$

K_a applies to the simplified equation $\text{HA(aq)} \leftrightarrow \text{H}^+(\text{aq}) + \text{A}^-(\text{aq})$ where $[\text{H}_2\text{O(l)}]$ is 55.55M and incorporated into K_c .

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

K_a is an index of acid strength and can be calculated easily because $[\text{HA}]$, $[\text{H}^+]$ and $[\text{A}^-]$ are usually measurable. It is sometimes more work to calculate *equilibrium* $[\text{HA}]$, $[\text{H}^+]$ and $[\text{A}^-]$ values from a given K_a . Some equations are easily solved. Some require the quadratic formula or the method of successive approximations.

Ex: What is the expected pH of a 0.300M HNO_2 solution given $K_a = 4.5 \times 10^{-4}$?

Assume $[\text{H}^+] = [\text{NO}_2^-] = X$ $[\text{HNO}_2] = 0.300\text{M} - X$

Is X small enough to ignore in relation to the initial $[\text{HNO}_2]$? Do a trial calculation

Set $4.5 \times 10^{-4} = X^2/(0.300)$.

$X^2 = 1.35 \times 10^{-4}$. $X = 1.2 \times 10^{-2}$, too large to ignore in relation to 0.300M.

To get a better value for the new equilibrium $[\text{HNO}_2]$ value, try the method of successive approximation.

Set $X^2 = 4.5 \times 10^{-4} (0.300 - 0.012)$. Now $X = 1.14 \times 10^{-2} \approx 1.1 \times 10^{-2}$. $[\text{H}^+] = [\text{NO}_2^-] = 1.1 \times 10^{-2}\text{M}$ and $[\text{HNO}_2] = 0.289\text{M}$. Substituting the new $[\text{H}^+]$, $[\text{NO}_2^-]$ and $[\text{HNO}_2]$ values back into the K_a equation gives $K_a = 4.5 \times 10^{-4}$, the correct original value.

Only one approximation step was needed to get the correct answer.

Try the same problem using the quadratic formula.

$4.5 \times 10^{-4} = X^2/(0.300 - X)$ gives the quadratic equation $X^2 + 4.5 \times 10^{-4}X - 1.35 \times 10^{-4} = 0$

Plugging into the quadratic formula gives $X = 1.1 \times 10^{-2}$.

The equilibrium concentration values are the same as with the approximation method.

Weak Bases and Base Ionization Constants

In general,



$$K = \frac{[\text{BH}^+] \cdot [\text{OH}^-]}{[\text{B}] \cdot [\text{H}_2\text{O}]}$$

$$K_b = K[\text{H}_2\text{O}] = \frac{[\text{BH}^+] \cdot [\text{OH}^-]}{[\text{B}]}$$

Typical K_b values range from 0.1 to 10^{-10} .

Ex: Calculate pH, pOH, $[\text{OH}^-]$, $[\text{H}^+]$, $[\text{BH}^+]$ and $[\text{B}]$ for a 0.200 M ethylamine solution.

K_b of ethylamine = 5.6×10^{-4} .

$$K_b = \frac{[\text{BH}^+] \cdot [\text{OH}^-]}{[\text{B}]} \quad [\text{BH}^+] = [\text{OH}^-] = x$$

Try the assumption that $[B] = 0.200 - x \approx 0.200$

$$K_b = 5.6 \times 10^{-4} = \frac{[BH^{+1}] \cdot [OH^{-1}]}{[B]} = \frac{X^2}{(0.200 - X)}$$

$$X^2 = 5.6 \times 10^{-4} / (0.200) = 1.12 \times 10^{-4}$$

$$X = 1.06 \times 10^{-2} \text{ (Temporarily carry three significant figures to avoid rounding errors.)}$$

$$[BH^{+1}] = [OH^{-1}] = 1.06 \times 10^{-2} \text{ M} \approx 1.1 \times 10^{-2} \text{ M}$$

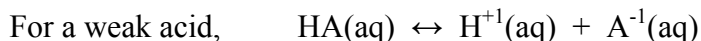
$$\text{pOH} = 1.97 \quad \text{pH} = 12.03 \quad [H^{+1}] = 9.4 \times 10^{-13} \text{ M}$$

$$[B] = 0.200 - x = 0.200 - 1.06 \times 10^{-2} = 0.189 \text{ M. Cannot ignore change in [B].}$$

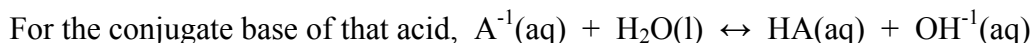
To get a better answer, either start by using the quadratic equation, or use $[B] = 0.189 \text{ M}$ instead of 0.200 M when solving the equation to get $X = 1.03 \times 10^{-2} \text{ M}$, a better value. Then pOH changes to 1.99 , etc.

K_a Values of Weak Acids and K_b Values of Their Conjugate Bases

A simple relationship:



$$K_a = \frac{[H^{+1}] \cdot [A^{-1}]}{[HA]}$$



$$K_b = \frac{[HA] \cdot [OH^{-1}]}{[A^{-1}]}$$

Multiplying K_a and K_b gives $[H^{+1}] \cdot [OH^{-1}]$, the ion product of water,

It is now possible to calculate any K_a from the K_b of its conjugate base and vice-versa.

Diprotic and Polyprotic Acids

Common examples are: sulfuric acid, oxalic acid, phosphoric acid, carbonic acid, and sulfurous acid.

Why is the second K_a always smaller than the first?

Usually the contribution that the second ionization step makes to $[H^{+1}]$ can be ignored.

Molecular Structure and Acid Strengths

Define "Acid Strength" again



The strength of an acid depends on the strength of the bond and the polarity (the difference in electronegativity of the anion atom and the hydrogen) of the bond.

The more electronegative the anion atom(s), the more polar the H-X bond and the easier it is for the H to leave as a proton.

The hydrohalic acid series is an exception to this rule. HF is a weak acid while HCl, HBr and HI are all strong. (HI is the strongest, but this does not make any difference in aqueous solution because they all form hydronium ion.) HF is a weak acid because of the small size of the fluoride ion, which makes the H-F bond very short and therefore strong.

Oxyacids are easier to understand. Consider the structure Z—O—H. The more electronegative Z is or the higher its oxidation state is, the more polar the H—O bond will be and the easier it is for H to leave without its electrons.

Compare HNO₂ and HNO₃; H₂SO₄ and H₂SO₃.
Compare H₂SO₄ and H₂SeO₄.

Acid-base Properties of Salts

Salts are ionic compounds that result for the reaction of an acid or a base. (Excluded ions are H⁺, OH⁻ and O²⁻. *If* a salt is soluble in water, it dissociates completely into its constituent cations and anions. Salts, however, do not generally produce neutral solutions. Some cations and some anions undergo hydrolysis in water to produce excess H⁺ or OH⁻ in the solution.

A Negative Example: Salts That Do Not Undergo Hydrolysis

KCl is soluble salt and dissociates into K⁺ and Cl⁻ ions in solution. A solution of KCl in water is neutral. Neither constituent ion produces an acidic or basic solution.

Remember that potassium ion is the cation of a strong base; it cannot covalently hold onto hydroxide ion.



Therefore we say potassium ion does not hydrolyze. It does not react with water to produce hydrogen ion.

Chloride ion also does not hydrolyze because it is the anion of a strong acid, and as such, it does not have the ability to bond tightly to a proton or take one away from water..

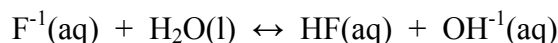


Chloride does not react with water to produce hydroxide ion in solution.

Salts That Produce Basic Solutions:

The majority of anions hydrolyze in aqueous solution to produce hydroxide. This is because the majority of anions (F⁻, SO₃⁻², CH₃COO⁻, CO₃⁻², etc.) are derived from weak bases. (Remember, most acids are

weak.) These anions by definition form strong bonds with hydrogen ion (as in HF, H₂SO₃, CH₃COOH, HCO₃⁻¹, etc.) and are able to abstract a proton away from water, producing a small but significant amount of hydroxide ion, making the solution basic.



The K_b of this reaction is given as $K_b = [HF] \cdot [OH^{-1}]/[F^{-1}]$

Calculate the parameters of the equation as usual.

Ex: What is the pH of a 0.300 M NaHCO₃ solution. (Remember, Na⁺¹ is merely a spectator ion.)

$$K_b = 2.4 \times 10^{-8} = [H_2CO_3] \cdot [OH^{-1}]/[HCO_3^{-1}] = X^2/(0.300 - X) \quad \text{Can we ignore X?}$$

$$X^2 = 2.4 \times 10^{-8} \times (0.300) = 7.2 \times 10^{-9} \quad X = 8.5 \times 10^{-5} \quad [OH^{-1}] = 8.5 \times 10^{-5} \text{ M}$$

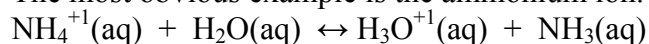
(The value of X can be ignored relative to 0.300M)

$$pOH = 4.07$$

$$pH = 9.93$$

Salts that Produce Acidic Solutions

The most obvious example is the ammonium ion.



Ammonium in itself the product of the neutral molecule ammonia and a proton so it will have the ability to donate protons in aqueous solution.

Therefore the salts ammonium chloride, ammonium nitrate, ammonium sulfate, ammonium iodide, etc. will give acidic aqueous solutions.

Metal cations hydrolyze in a more interesting manner. For instance, aluminum ion hydrolyzes extensively in water to give acidic solutions. How can this be when Al⁺³ contains no protons?

All metal cations are *hydrated*. They exist as the hexaquo species M(H₂O)₆⁺ⁿ. When the cation is small and n is larger than 1, the H-O bonds in water are highly polarized and the complex easily donates a proton to H₂O, making the solution acidic. Theoretically, any cation will generate protons in solution but some, such as Na⁺¹ and K⁺¹ do so at almost undetectable levels.

Ex: What is the pH of 0.045 M Al(NO₃)₃?



$$K_a = 1.3 \times 10^{-5} = [Al(H_2O)_5(OH)^{+2}] \cdot [H^{+1}]/[Al(H_2O)_6^{+3}]$$

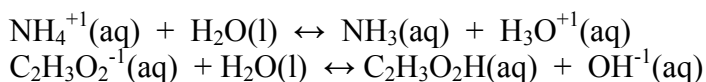
$$1.3 \times 10^{-5} = X^2/(0.045 - X) \quad X^2 = 5.85 \times 10^{-7} \quad X = 7.6 \times 10^{-4}$$

$$[H^{+1}] = 7.6 \times 10^{-4} \text{ M} \quad [Al(H_2O)_6^{+3}] \approx 0.044 \text{ M} \quad pH = 3.12$$

Salts in Which both the Cation and Anion Hydrolyze

The math is complicated so we will only do qualitative examples.

If $K_a = K_b$, the rate of hydrogen ion and hydroxide ion formation are the same and the solution is neutral. The classic example is ammonium acetate where K_b of acetate ion = K_a of ammonium ion = 5.6×10^{-10} .



Hydrogen ion and hydroxide ion are produced in equal amounts so the solution remains neutral.

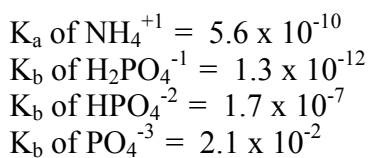
If $K_a > K_b$, the solution is acidic.

If $K_a < K_b$, the solution is basic.

Ex: The three ammonium phosphate salts. $(\text{NH}_4)_3\text{PO}_4$ $(\text{NH}_4)_2\text{HPO}_4$ $(\text{NH}_4)\text{H}_2\text{PO}_4$
(Uses as fertilizer or fire extinguishants)

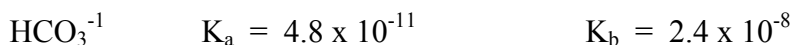
One can qualitatively rank the relative acidity of the salts without even looking at the relative acid and base constants.

Knowing the values gives a more confident prediction of their relative acidity or basicity.



The example of bicarbonate ion is interesting in that bicarbonate can act as an acid or a base. (Reaction as a stomach acid neutralizer.)

Bicarbonate is a stronger base than it is an acid.



Acid-Base Properties of Oxides and Hydroxides

General rule: Oxides of metals are basic, oxides of nonmetals are acidic. Metalloids and elements near them may have little acid-base character or may be **amphoteric**, capable of acting as an acid or a base.

Compare the acid-base character and the acid-base strength of the oxides of the third period elements Na, Mg, Al, Si, P, S and Cl. All the oxides react with water to form a potential acid or base.

The left-to-right base-to-acid trend can be explained by the electronegativity of the element and its effect on the polarity of the M-O-H bonds in the acid or base derived from each oxide.

Lewis Acids and Bases

A further extension of acid-base theory.

In the Lewis theory, a Lewis acid is any species that can accept an electron pair.

(Note that a proton fits this definition, so all Arrhenius and Brønsted acids fall under the Lewis category.)

A Lewis base is any species that can donate an electron pair. This definition includes hydroxide ion and all the Brønsted bases we have so far studied.

BF_3 (neither an Arrhenius nor a Brønsted base) and NH_3 (a Brønsted base but not an Arrhenius base) will react to form an adduct.

Also the reaction of Cu^{+2} ion and water to form the hexaquo species, the reaction of Cu^{+2} with ammonia, the reaction of a proton with water, the reaction of fluoride ion with a proton, etc.