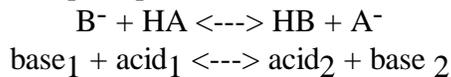


4. Acid Base Chemistry

4.1. Terminology:

4.1.1. Bronsted / Lowry Acid:

"An acid is a substance which can donate a hydrogen ion (H⁺) or a proton, while a base is a substance that accepts a proton.



Where HB = the conjugate acid

A⁻ = the conjugate base

Examples: HCl + water; carbonate + water; H₂S in Water

Note that water can act as either an acid or a base. Such substances are called **ampholytes**, and are **amphoteric**.

4.1.2. Lewis Acid:

This is a broader definition that is stated as a substance that accepts an electron, while a Lewis base donates a proton. All Bronsted/Lowry acids are Lewis acids, not all Lewis acids are Bronsted acids.

4.1.3. Acids in Aqueous Solution:

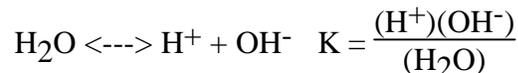
--Acids are usually referred to as donating *protons*, or H⁺, while bases donate OH⁻, or hydroxyls

--The proton is strongly bound to water forming the basic unit of H₃O⁺, the Hydronium ion. This species in turn binds to other waters forming H₉O₄⁺

--A similar structure is formed with OH, H₇O₄⁻

--the usage of H₃O⁺ is usually reserved to reactions involving water.

- The reaction for water:



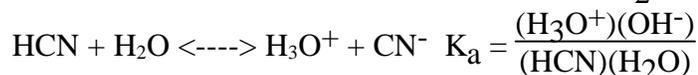
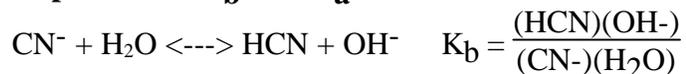
$$K_a = (H^+)(OH^-) = K_w \quad (\text{Dilute solution})$$

--We derived the value for K_{eq} from ΔG[°]_f; ΔG[°]_r = +19.09 kcal/mol, K_{eq} 25°C 10⁻¹⁴

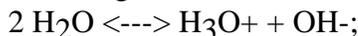
4.1.4. The Dissociation (Equilibrium) Constant, K_a:

- The **K_a** refers to the K_{eq} for the reaction where an acid **donates** a proton to water;
- The **K_b** is the reaction in which a base **accepts** a proton from a water molecule.
- The value of K_a or K_b is the **strength** of the acid or base. Large numbers are strong acids, small numbers are weak acids
 - A strong acid has a *stronger* tendency to donate a proton
 - A strong base has a greater tendency to accept a proton.
- K_a is usually expressed in log. **pK_a** is the *negative log of the equilibrium constant*
- A strong acid has a pK_a that is >0.8, a weak acid is <0.8. The K_a of HI is 10^{0.8}
- A strong base has a pK_b of greater than 1.4
- A very strong acid dissociates completely at almost all concentrations
- A very weak acid does not dissociate completely, leaving HA in solution
- Borderline acids have HA present at high total A concentrations.
- **Rule of Thumb:** Strong acids produce weak conjugate bases; weak acids produce strong conjugate bases: e.g. HCl v. HCO₃⁻

4.1.5. Relationship between K_b and K_a :



By adding these two expressions, we get



$$K = K_a K_b = \frac{(\text{H}_3\text{O}^+)(\text{CN}^-)(\text{HCN})(\text{OH}^-)}{(\text{HCN})(\text{H}_2\text{O})(\text{CN}^-)(\text{H}_2\text{O})} = \frac{(\text{H}_3\text{O}^+)(\text{OH}^-)}{(\text{H}_2\text{O})}$$

**This is a legal and useful approach. Remember, the K is an algebraic, numerical constant. Because the activity of water is 1:

$$K_a K_b = (\text{H}_3\text{O}^+) (\text{OH}^-) = K_w = 10^{-14}$$

Where K_w is the equilibrium constant water. This relationship allows the calculation of

either K_a or K_b if the other is known by: **$\text{pH} + \text{pOH} = \text{p}K_w = 14$**

--therefore, in pure water when the $(\text{H}^+) = (\text{OH}^-)$, the $\text{pH} = 7$, the $\text{pOH} = 7$

--Acid solution have a $\text{pH} < 7$, basic solutions have a $\text{pH} > 7$, or a $\text{pOH} < 7$

4.1.6. Neutrality, and the affect of temperature:

--Neutral solutions are $\text{pH} 7$ only at 25°C , where the K_w is 10^{-14}

--At other temperatures, the pH changes because the equilibrium changes. As temperature increases, since there is a positive ΔH , dissociation increases.

The ΔH° of the dissociation of water is $+13.36 \text{ kcal/mole}$

$$\ln K_w @ 50^\circ\text{C} = \ln K_w, 25^\circ\text{C} + \frac{\Delta H^\circ}{R} \left(\frac{1}{298} - \frac{1}{323} \right) = 5.73 \times 10^{-14}$$

So at 50°C , neutrality is at $\text{pH} = 6.62$.

4.1.7 Multiprotic acids:

- A *monoprotic* acid has one proton that can be donated under normal circumstances (i.e. environmental conditions. A diprotic acid has 2, a triprotic 3, etc.)
- For groundwater systems, triprotic acids are the most complicated to deal with, and there are several of these, e.g. phosphoric acid, boric acid, and citric acid.
- Each proton has a unique K_a , or acid dissociation constant, with names of $K_{a,1}$, $K_{a,2}$, etc.
- A general rule for Bronsted acids is that the first proton to be donated from a multiprotic acid is *much* more acidic than the second, the second more acidic than the third, etc. In organic acids, the second and third may be similar.
- The conjugate base of the first deprotonation of a diprotic acid is *amphoteric*, and is both a proton donor *and* a proton acceptor.

4.2. Equilibrium Calculations

This is a systematic approach to solving acid-base equilibrium that uses 4 equations. The goal is to use enough equations, and the right equations, to solve the specific problem being examined. An important consideration, and one of the most difficult to master, is the use of specific *assumptions*, used to simplify the equations. This a trial and error approach.

4.2.4. Mass Balance:

In acid-base reactions the reacting species are conserved, assuming a closed system. When HA is added to water, the acid ionizes (partly or completely):

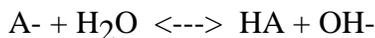
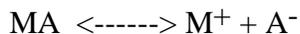


A mass balance equation would be:

$$C_{T,A} = [\text{HA}] + [\text{A}^-]$$

$C_{T,A}$ is the analytical concentration of all species containing A, with units being moles per liter. Note that concentration is used.

When C moles of the salt MA are added to a liter of solution:



$C_{T,M} = [\text{M}^+] + [\text{MA}]$, or if MA dissociates completely, $C_{T,M} = [\text{M}^+]$

4.2.4. Equilibrium Relationships

This utilizes the known equilibrium constant of the acids involved to help solve for concentration of an unknown species. The first equation is K_w .

$$K_w = (\text{H}^+)(\text{OH}^-) = 10^{-14} \text{ at } 25^\circ\text{C}$$

Note that here activity *must* be used, and the difference between activity and concentration used in the mass balance equation must be reckoned.

The dissociation of HA is described by :

$$K_a = \frac{(\text{H}^+)(\text{A}^-)}{(\text{HA})} \quad K_b = \frac{(\text{HA})(\text{OH}^-)}{(\text{A}^-)}$$

Since $K_w = K_a K_b$, both of these equations can not be used since they are not independent.

4.2.4. Charge Balance (electroneutrality)

All solutions are electrically neutral. Unlike the analytical charge balance equation, the CB equation used here is an absolute equality – The total molar concentration of cations is always equal to the total anions.

$$[\text{M}^+] + 2[\text{M}^{2+}] + [\text{H}^+] = [\text{A}^-] + 2[\text{A}^{2-}] + [\text{OH}^-]$$

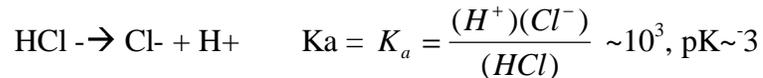
NOTE: **concentration** is used, not activity. Also, note that [HA] is not used, as it is a neutral species.

4.2.4. Proton Condition:

- The proton condition is a mass balance on protons, and is essential part of solving for protons involved in equilibria.
- The proton mass balance is established with reference to a "zero level" or reference level for protons, called the PRL. The PRL is established as the species with which the solution was prepared, and species having protons in excess of the PRL are equated with species having less than the PRL.
- This means that protons are conserved, and if protons are transferred from the initial reactants, that the result is some species gain protons (>PRL), while others lose protons (<PRL).

4.3. Strong Acid-Base Calculations.

- Examples of strong acids in ground water are nitric and sulfuric acid from acid rain or industrial discharge, hydrochloric acid used to open up a well (dissolve calcite)
- Strong acids have a large K_a , indicating that there are more products than reactants, i.e. that the reaction proceeds very far toward to products.
- The dissociation of strong acids in water is exothermic and has a large positive entropy. The release of heat is from the hydration of proton by water to make hydronium ion.



So the product of proton and chloride concentration is 1000 times the concentration of free HCl. This leads to the basic assumption used to simplify acid-base calculations: **STRONG ACIDS DISSOCIATE COMPLETELY** in dilute solutions. This results simplification of the mass balance calculation as:

$$[\text{Cl}^-] \gg [\text{HCl}]$$

$$C_{\text{T,Cl}} = \text{[HCl]} + [\text{Cl}^-]$$

Strong and intermediate acids important in natural systems:

Acid Name	Formula	pK
Perchloric	HClO ₄	-7
Hydrogen Chloride	HCl	-3
Sulfuric	H ₂ SO ₄	-3 (pK ₁)
Nitric	HNO ₃	-1
Hydronium	H ₃ O ⁺	0
Bisulfate	HSO ₄ ⁻	1.9 (pK ₂)
Phosphoric	H ₃ PO ₄	2.1 (pK ₁)
Aquo ferric ion**	Fe(H ₂ O) ₆ ³⁺	2.2 (pK ₁)
Arsenic Acid	H ₃ AsO ₄	2.25 (pK ₁)

**The ferric iron ion in solution is coordinated to 6 waters of hydration, and you can think of these waters as having acidic protons. Another way of thinking of it is the exchange of a water for a hydroxyl ion – that decreases the hydroxyl activity, thus decreasing pH – i.e. an acid. So adding FeCl₃ to water decreases pH. Aluminum acts in the same way.

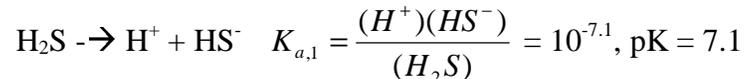
4.4. Weak Acid-Base Calculations

- Weak acids and bases do not dissociate completely, so while the approach to solving the equations is similar to strong-acid systems, the complication of the K_a is added. The use of simplifying assumptions is even more important for this system.

Acid Name	Formula	pK
Hydrofluoric	HF	3.45
Acetic	CH ₃ COOH	4.7
Arsenic Acid	H ₂ AsO ₄ ⁻	6.77
Hydrogen Sulfide	H ₂ S	7.1
Dihydrogen Phosphate	H ₂ PO ₄ ⁻	7.2 (pK ₂)
Hypochlorous Acid	HOCl	7.6
Hydrogen Cyanide	HCN	9.2
Boric Acid	H ₃ BO ₃	9.3
Ammonium Ion	NH ₄ ⁺	9.3
Bicarbonate Ion	HCO ₃ ⁻	10.3
Arsenic Acid	H ₂ AsO ₄ ⁻	11.6 (pK ₃)
Bisulfide	HS ⁻	14 (pK ₂)
Water	H ₂ O	14

- The small pK values mean that the concentration of the reactants is greater than the products, and the reaction does not proceed very far to the right.

Example: Hydrogen sulfide is produced by sulfate reducing bacteria in some anaerobic groundwater, and is common in water wells east of Austin. Hydrogen sulfide is a very weak acid...



The fundamental relationship with weak acids is that the extent of the reaction, or the amount of acid that dissociates, is directly related to the pH. When $\text{pH} < \text{pK}$, little acid dissociates. *As pH increases, more acid must dissociate to maintain equilibrium.* The relationship between pH and weak acids is also expressed as:

$$\text{pH} = \text{pK}_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

Rule of Thumb: With weak acids, *When the $\text{pK} = \text{pH}$, the activity of the acid is equal to the conjugate base.* **This is a critical relationship that you must remember!!** i.e. For H₂S, at pH 7.1, (H₂S) = (HS⁻)

4.5. Strong Acid-Strong Base Mixtures

- For this system we need to examine the *changes* that occur when acids and bases are mixed, rather than simply solving a static system.
- The general approach is to write equations that describe the solution after the acid and base are mixed, make simplifying assumptions, then solve as usual.
- Forget using the equilibrium equation – there is no appreciable undissociated acid or base left. The proton condition equation is possible, but difficult.
- In this case, you assume that both the acid and base dissociate completely (with much heat evolved...), and you now have a salt solution at some new pH. The best equations to use are the mass balance and charge balance equations. If you know the anion concentration, and the metal cation concentration (e.g. add HCl to a NaOH solution), then solve for proton
- When the system is going to change across pH 7 (e.g. acid to base) try to use the mixture to first get to neutral, and then to the final pH. It is conceptually easier than going directly from acid to base conditions.

4. Strong acid-weak base mixtures.

- These mixtures are more complicated because we lose the assumption of complete dissociation.
- Most natural waters, however, behave like a mixture of weak acids and bases.
- An understanding of these systems is essential to understanding pH buffers.

$$\text{Equivalent Fraction } f = \frac{\text{number of equivalents of NaOH added}}{C_{T,Ac}}$$

OVERHEAD: Fig. 4-12

1. When $f=0.5$, $\text{pH} = \text{pK}_a$. Any addition of base corresponding to $f < 0.5$ will produce a solution pH between that of the original HAc solution and the pK_a .
2. At $f=0.5$, the titration curve has an inflection point. At this pH ($=\text{pK}_a$) the change of pH for a given addition of strong base is small, and the solution is *well buffered*.
3. When $f=1.0$, the pH is that of a 0.001M NaAc solution, or the equiv of Na added is equal to the $[\text{Ac}^-]$ present. This pH is the *equivalence point*. At this pH value the curve has an inflection point in the opposite direction to that at $f=0.5$, and the resistance of the solution to pH change is small, or the system is *poorly buffered*.
4. The pH increases very slowly as it approaches the pH of the solution being added.

5. pH Buffers and Buffer Intensity:

- *A buffer solution is a solution that in some way has the ability to maintain a stable composition when various components are added or removed.*

- A solution buffered at a particular pH value will contain an acid that reacts with any strong base added to the solution and a base that reacts with any strong acid added to the solution.
- The pH of a buffer solution can be predicted by the equation (assuming infinite dilution):

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

Question: Which acid-conjugate base pair should be used to buffer a solution at pH 4.7 and at pH 7? What ratio of acid to conjugate base should be used in each of these buffers?

1. Examine a table of K_a values to choose an acid with a pK_a near the desired pH. Acetic acid has a pK_a of 4.7, and should be good at pH 4.7.
2. Simplifying assumptions:
 $[H^+]$ and $[OH^-] \ll [HAC]$ and $[NaAc]$

$$\frac{[H^+]}{K_a} = \frac{10^{-4.7}}{10^{-4.7}} = \frac{[HAC]}{[NaAc]} = 1$$

3. The $pH = pK$ therefore requires equal concentrations of salt and acid.
 - While this gives the *ratio*, it does not give the *concentration* of salt and acid.
 - The greater the concentration, the greater the buffer capacity.
- 4.. $H_2PO_4^-$ has a pK near 7.0, and can be used to buffer a system:

$$\frac{[Na_2HPO_4^-]}{[NaH_2PO_4]} = \frac{10^{-7.2}}{10^{-7.0}} = 0.63$$

4.2.4. Buffer Intensity

- Buffer capacity (β) or Buffer intensity is defined as the moles/l of strong base which when added to a solution causes a unit change in pH.:

$$\beta = \frac{d[OH^-]}{dpH} = -\frac{d[H^+]}{dpH}$$

- So the reciprocal of the slope of the titration curve is proportional to the buffer intensity.
- In general the buffer intensity is a maximum at $pH = pK$, and that β is at a minimum when $f=1$, at the equivalence point of the titration.

Figure 4-15 OVERHEAD

4.6. Carbonic Acid/Carbonate system

1. Gas Exchange:

- Gaseous carbon dioxide, $\text{CO}_2(\text{g})$ dissolves into water producing $\text{CO}_2(\text{aq})$. The equilibrium of this processes is the Henry's Law Constant for carbon dioxide:

$$K = K_H = \frac{(\text{CO}_2(\text{aq}))}{(\text{CO}_2(\text{g}))} = 10^{-1.5}$$

- This species has not yet reacted with anything

2. Hydrolysis of Carbon Dioxide:



- Based on the equilibrium constant, the extent of this reaction is small, so H_2CO_3 is only about 0.16% of the $\text{CO}_2(\text{aq})$ at 25°
- This reaction is also kinetically slow, slower than acid-base reactions.
- It is nearly impossible to analytically separate the two species, and it is difficult to determine the acidity constant of H_2CO_3 so the two are simply added to form the species H_2CO_3^*

3. First Acidity Constant:

$$K_{a,1} = \frac{(\text{H}^+)(\text{HCO}_3^-)}{(\text{H}_2\text{CO}_3^*)}; \quad K'_1 = \frac{(\text{H}^+)(\text{HCO}_3^-)}{(\text{H}_2\text{CO}_3)} = 10^{-3.5}$$

By substituting the summation for our fictional carbonic acid species, we obtain

$$K_{a,1} = \frac{(\text{H}^+)(\text{HCO}_3^-)}{(\text{H}_2\text{CO}_3) + (\text{CO}_2(\text{aq}))}$$

Now multiplying the numerator and denominator by (H_2CO_3) , and knowing that:

$$(\text{CO}_2(\text{aq})) / (\text{H}_2\text{CO}_3) = 1/K_m:$$

$$\frac{(\text{H}^+)(\text{HCO}_3^-) / (\text{H}_2\text{CO}_3)}{(\text{CO}_2(\text{aq}) + (\text{H}_2\text{CO}_3)) / (\text{H}_2\text{CO}_3)} = \frac{K'_1}{(1/K_m) + 1} = K_{a,1}$$

Since $1/K_m \gg 1$,

$$K_{a,1} = K'_1 K_m = 10^{-3.5} 10^{-2.8} = 10^{-6.3}$$

- This means that while carbonic acid is a strong acid, the combination of the two species, and the slow kinetics, make it appear as a weak acid
- It actually is a fairly strong acid capable of dissolving silicates.

4.1.7 SYSTEMS APPROACH – carbonic acid system:

1. Case 1. Closed system, no solid

equations: K_w
Unknowns, (H^+) , (OH^-)
 $pH = 7$

2. Case 2. Open System, No Solid

Problem: Pure water in equilibrium with atmospheric carbon dioxide. No other solutes, assume infinite dilution, 25°C. What are the concentrations of the unknown species.

equations: K_H, K_1, K_2, K_w

Unknowns: (H^+) , (HCO_3^-) , (OH^-) , (H_2CO_3) , (CO_3^{2-})

Constants: $PCO_2 = 10^{-3.5}$ Atm.

Assumptions: $(H^+) \gg (OH^-)$; $(HCO_3^-) \gg (CO_3^{2-})$

Mass Balance: $C_{T,(CO_3)} = [CO_3^{2-}] + [HCO_3^-] + [H_2CO_3]$

assumptions...

Electroneutrality: $[H^+] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-]$

assumptions...

Solution:

$$1) (H_2CO_3) = K_H PCO_2 = (10^{-1.47})(10^{-3.5}) = 10^{-5} \text{ M}$$

$$2) (H_2CO_3) = \frac{(H^+)(HCO_3^-)}{K_1}; K_1(H_2CO_3) = (H^+)(HCO_3^-)$$

$$3) (10^{-5})(10^{-6.4}) = (H^+)^2$$

$$4) (H^+) = 10^{-5.67}, pH = 5.67$$

$$(HCO_3^-) = 10^{-5.67}$$

$$(OH^-) = 10^{-8.33}$$

$$5) (CO_3^{2-}) = K_2(HCO_3^-)/(H^+) = 10^{-10.3}$$

--In an open system, the $[H_2CO_3]$ remains constant, fixed by the PCO_2

--The pH of distilled water open to the air is 5.65

Case 6: Open System, Fixed pH

Problem: Water in equilibrium with atmospheric carbon dioxide. pH is fixed at 8.0, 25°C using NaOH. What are the concentrations?.

equations: K_H, K_1, K_2, K_w

Unknowns: $(\text{HCO}_3^-), (\text{OH}^-), (\text{H}_2\text{CO}_3), (\text{CO}_3^{2-})$

Constants: $\text{PCO}_2 = 10^{-3.5} \text{ Atm.}$

Assumptions: $(\text{H}^+) < (\text{OH}^-); (\text{HCO}_3^-) \gg (\text{H}_2\text{CO}_3)$

Mass Balance: $C_{T,(\text{CO}_3)} = [\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{H}_2\text{CO}_3]$
assumptions...

Electroneutrality: $[\text{H}^+] + [\text{Na}^+] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-]$
assumptions...

Solution:

$$1) (\text{H}_2\text{CO}_3) = K_H \text{PCO}_2 = (10^{-1.47})(10^{-3.5}) = 10^{-5} \text{ M}$$

$$2) (\text{H}_2\text{CO}_3) = \frac{(\text{H}^+)(\text{HCO}_3^-)}{K_1}; K_1(\text{H}_2\text{CO}_3) = (\text{H}^+)(\text{HCO}_3^-)$$

$$3) (10^{-5})(10^{-6.4})/10^{-7} = (\text{HCO}_3^-)$$

$$5) (\text{CO}_3^{2-}) = K_2(\text{HCO}_3^-)/(10^{-7})$$

--In an open system, even with fixed pH, **the $[\text{H}_2\text{CO}_3]$ remains constant, fixed by the PCO_2**