

Lecture 3: Acid-Base Equilibria & Buffers

Reading in Campbell: Chapter 2.3-2.6

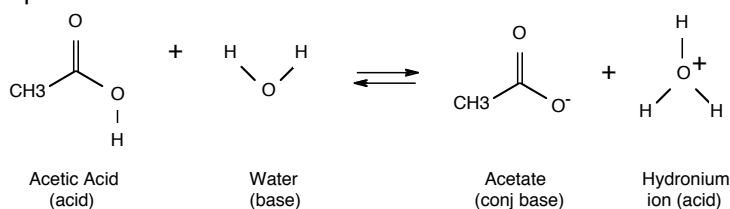
Key Terms:

- Acid strength
- Equilibrium constant
- Acid-base properties of H₂O
- Acid dissociation constant
- $\text{pH} = -\log[\text{H}^+]$
- $\text{pH} = \text{pKa} + \log[\text{A}^-]/[\text{HA}]$
- Titration: pKa determination
- Equivalence point, Inflection point
- Calculation of degree of protonation

3.1 Acids and Bases and Acid Strength

- Acid: can donate protons
- Base: can accept protons

Example:



Acid strength:

A compound is an acid if it loses its proton, and it is a base if it takes up a proton. For a simple acid like X-H, acid strength depends on the strength of the X-H bond and the stability of the charged anion X⁻.

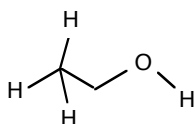
Weaker bonds generally lead to greater acidity.

12.011	6	14.0074	7	15.9994	8	18.9984032	9	20.1797	10
4602*	C	14.00306	N	15.00306	O	18.9984032	F	18.9984032	Ne
12.011	Carbon	14.00306	Nitrogen	15.00306	Oxygen	18.9984032	Fluorine	18.9984032	Neon
28.0855	14	30.973762	15	32.06	16	35.4527	17	36.9658	18
14.01	Si	30.973762	P	32.06	S	35.4527	Cl	36.9658	Ar
28.0855	Silicon	30.973762	Phosphorus	32.06	Sulfur	35.4527	Chlorine	36.9658	Argon
72.61	32	74.921595	33	75.94	34	79.904	35	83.80	36
72.61	Ge	74.921595	As	75.94	Se	79.904	Br	83.80	Kr
72.61	Germanium	74.921595	Arsenic	75.94	Selenium	79.904	Bromine	83.80	Krypton

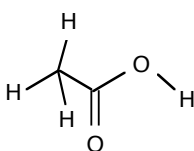
H₂O < H₂S < H₂Se
HF < HCl < HBr

HF > H₂O
HCl > H₂S

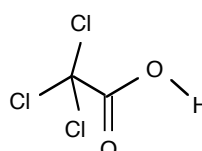
Consider the following three compounds:



ethanol



acetic acid

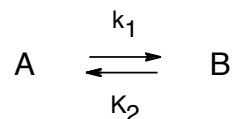


trichloroacetic acid

The negative charge on the ionized acid can be further stabilized by resonance structures that distribute the negative charge as well as by nearby electron withdrawing groups. The nearby presence of formal positive and negative charges also affects acidity.

3.2 General Equilibrium Reactions:

Consider first a very simple reaction and its equilibrium features:



The following rate equations can be used to describe the reaction:

$$\frac{d[A]}{dt} = -k_1[A] + k_2[B] \quad \frac{d[B]}{dt} = +k_1[A] - k_2[B]$$

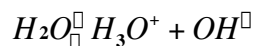
At equilibrium there is no change in the concentration of A or B, therefore:

$$\frac{d[A]}{dt} = \frac{d[B]}{dt} = 0$$

At equilibrium the reaction has not stopped, but rather, the rates of the forward reaction ($k_1[A]$) and the reverse reaction ($k_2[B]$) are equal. Thus:

$$K_{eq} = \frac{k_1}{k_2} = \frac{[B]}{[A]} = \frac{[products]}{[reactants]}$$

3.3 Ionization of H₂O and definition of pH:



The equilibrium constant for the dissociation of H₂O can be written:

$$K_{eq} = \frac{[H^+][OH^-]}{[H_2O]}$$

Since the concentration of H₂O is high (55.5 M) and practically constant, we can incorporate it into the equilibrium constant and define a dissociation constant for H₂O:

$$K_w = K_{eq}(55.5 M) = [H^+][OH^-] = 1 \times 10^{-14} M^2$$

Pure H₂O is neutral. Therefore ionization produces equal concentrations of H⁺ and OH⁻, and

$$[H^+] = [OH^-] = 1 \times 10^{-7} M$$

There is a reciprocal relationship between [H⁺] and [OH⁻]. In solutions that are acidic, [H⁺] is high and [OH⁻] is low. Conversely, in solutions that are alkaline, [H⁺] is low and [OH⁻] is high. Note that the ion product is always 1×10^{-14} .

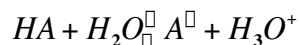
pH Definition: pH is measured as the $-\log_{10}[H^+]$. The lower the pH, the more acidic the solution. Neutral pH is 7.0. At this pH there are an equal number of H⁺ and OH⁻ ions in solution.

Relation of [H⁺] to [OH⁻] to pH

pH	[H ⁺], M	[OH ⁻], M	
0	10 ⁰	10 ⁻¹⁴	--- Hydrochloric Acid (1 M)
1	10 ⁻¹	10 ⁻¹³	
2	10 ⁻²	10 ⁻¹²	--- Human gastric contents
3	10 ⁻³	10 ⁻¹¹	
4	10 ⁻⁴	10 ⁻¹⁰	--- Tomato juice
5	10 ⁻⁵	10 ⁻⁹	
6	10 ⁻⁶	10 ⁻⁸	--- Cow's milk
7	10 ⁻⁷	10 ⁻⁷	--- Human blood plasma
8	10 ⁻⁸	10 ⁻⁶	--- Human pancreatic juice
9	10 ⁻⁹	10 ⁻⁵	
10	10 ⁻¹⁰	10 ⁻⁴	
11	10 ⁻¹¹	10 ⁻³	--- Ammonia (1 M)
12	10 ⁻¹²	10 ⁻²	
13	10 ⁻¹³	10 ⁻¹	
14	10 ⁻¹⁴	10 ⁰	--- Sodium hydroxide (1 M)

3.4 Characterization of Acid Strength using pK_a.

When an acid HA is added to H₂O,



The equilibrium constant for its dissociation is defined:

$$K_{eq} = \frac{[H^+][A^-]}{[HA][H_2O]}$$

$$K_a = K_{eq}[H_2O] = \frac{[H^+][A^-]}{[HA]}$$

The acidity constant, K_a, is a fundamental property of the acid and does not depend on the pH of the solution. **Stronger acids have larger K_a values since they are more fully dissociated.**

The Henderson-Hasselbalch Equation: Since the proton concentration is always measured in units of pH, it is useful to modify the above equation by taking the negative log*:

$$pK_a = -\log \frac{[H^+][A^-]}{[HA]} = pH - \log \frac{[A^-]}{[HA]}$$

which gives rise to the Henderson-Hasselbalch equation:

$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$

* Remember that pX is the negative log of X: e.g. pH = -log[H⁺].

Also recall that log(ab) = log a + log b and log(a/b) = log a – log b.

The pKa is the $-\log K_a$. **Therefore strong acids have small pKa values.**

Monoprotic acids (release only one proton):

Acid	pKa	Type
HCl	-7	Very strong
Acetic Acid	4.76	Weak
Ammonium (NH_4^+)	9.25	Very weak
Methanol	16	Extremely weak

3.5 Solving pH Problems:

The H&H equation has predictive value. Once you know the pK_a of an acid and the pH, you can predict $[\text{A}^-]/[\text{HA}]$. One particular case is routinely used in biochemistry: Given a pH and pK_a of an acid, calculate the fraction of the acid that is protonated: $f_{\text{HA}} = ([\text{HA}]/A_T)$ and the fraction that is deprotonated: $f_{\text{A}^-} = ([\text{A}^-]/A_T)$, where A_T is the total concentration of acid: $A_T = [\text{HA}] + [\text{A}^-]$.

Defining $R = [\text{A}^-]/[\text{HA}]$

$$\text{pH} = \text{pK}_a + \log([\text{A}^-]/[\text{HA}])$$

$$\text{pH} = \text{pK}_a + \log(R)$$

$$\text{pH} - \text{pK}_a = \log(R)$$

$$10^{(\text{pH} - \text{pK}_a)} = R$$

Once R is found, the fraction protonated and deprotonated is obtained as follows:

$$[\text{A}^-]/[\text{HA}] = R$$

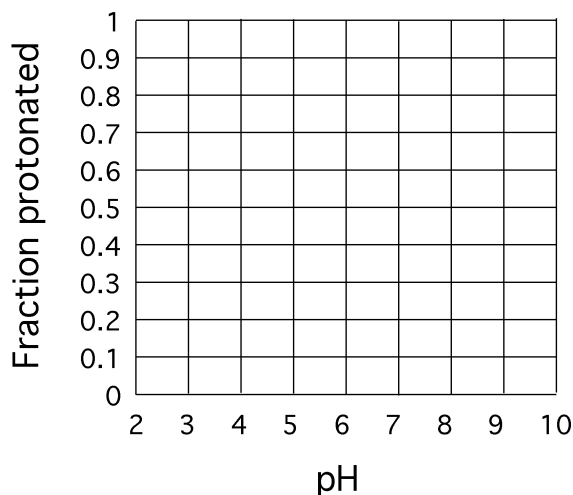
$$[\text{A}^-] = [\text{HA}]R$$

$$[A_T] = [\text{A}^-] + [\text{HA}]$$

$$[A_T] = [\text{HA}](1+R)$$

$$f_{\text{HA}} = \frac{[\text{HA}]}{[A_T]} = \frac{1}{(1+R)}$$

$$f_{\text{A}^-} = \frac{[\text{A}^-]}{[A_T]} = \frac{R}{(1+R)}$$



Using the ionization of the side chain of the amino acid Histidine as an example ($\text{pK}_a = 6.0$)

pH	(i) R	F_{HA}
4	$R = 10^{(4-6)} = 10^{-2}$	$F_{\text{HA}} = 1/(1+0.01) = 0.99$
5	$R = 10^{(5-6)} = 10^{-1}$	$F_{\text{HA}} = 1/(1+0.1) = 0.91$
6	$R = 10^{(6-6)} = 10^0$	$F_{\text{HA}} = 1/(1+1) = 0.5$
7	$R = 10^{(7-6)} = 10^1$	$F_{\text{HA}} = 1/(1+10) = 0.091$
8	$R = 10^{(8-6)} = 10^2$	$F_{\text{HA}} = 1/(1+100) = 0.01$

There are four general statements that are useful to remember:

1. When the $\text{pH} = \text{pK}_a$, $[\text{HA}] = [\text{A}^-]$.
1. When the pH is lower than the pK_a , $[\text{HA}] > [\text{A}^-]$.
1. When the pH is higher than the pK_a , $[\text{HA}] < [\text{A}^-]$.
1. A pH change of 1 leads to a 10 fold change in the ratio of $[\text{A}^-]/[\text{HA}]$.

3.6 Titration Curves

K_a values are usually measured by direct experiment, usually with a pH titration. Known amounts of a strong base (NaOH) are added to a solution of a weak acid and the pH is measured as the amount of NaOH is added. As the base is added it removes the proton from the acid, as well as increasing the pH.

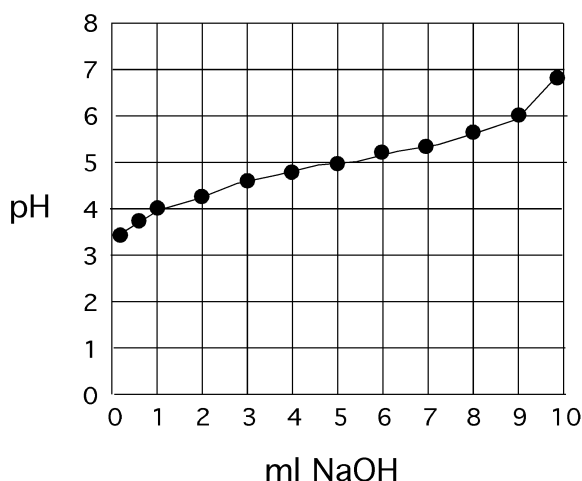
Inflection point ($\text{pH} = \text{p}K_a$): You can prove from the Henderson-Hasselbalch equation that the smallest change in pH due to addition of base occurs when the $\text{pH} = \text{p}K_a$; at this inflection point, the pH of the solution is the $\text{p}K_a$ of the acid.

Equivalents: moles of base/moles of acid, the x-axis for titrations. Varies from 0 to 1 for monoprotic acids.

Equivalence point: Complete deprotonation of the weak acid occurs when the molar amount of base is equal to, or equivalent to, the molar amount of weak acid. This point in the titration is referred to as the equivalence point.

Example titration curve:

<u>ml NaOH</u>	<u>measured pH</u>
0.25	3.20
0.5	3.80
1	4.07
2	4.44
3	4.62
4	4.87
5	4.96
6	5.17
7	5.33
8	5.64
9	5.96
10	7.00



Facts: Concentration of NaOH = 1 M
Volume of solution that is titrated = 100 ml

Possible acids (from Campbell table 2.6)

Pyruvate	$\text{p}K_a = 2.5$
Acetic Acid	$\text{p}K_a = 4.8$
Tris	$\text{p}K_a = 8.3$

Questions:

1. What is the $\text{p}K_a$ of the acid?
2. Which acid is it?
3. Give the x-axis scale in equivalents.