Acids, Bases and pH

Preliminary Course

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Outline

- What are acids and bases?
- Can we provide a general definition of acid and base?
- How can we quantify acidity and basicity?
- Can we classify acid and base strength?
- pH concept and pH scale.
- Acid/base reactions: neutralization
- How can we monitor an acid/base reaction in real time?
Acids and Bases: Common examples

**Acids**
- Citrus fruits
- Coffee
- Fertilizer
- Vinegar
- Coca-Cola

**Bases**
- Soap
- Bleach
- Baking Soda
- Antacid Tablets
# Uses of Common Acids and Bases

## 18.1 Some Common Acids and Bases and Their Household Uses

<table>
<thead>
<tr>
<th>Substance</th>
<th>Formula</th>
<th>Use</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Acids</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetic acid (vinegar)</td>
<td>CH₃COOH (or H₅C₂O₂)</td>
<td>Flavoring, preservative</td>
</tr>
<tr>
<td>Citric acid</td>
<td>H₃C₆H₅O₇</td>
<td>Flavoring</td>
</tr>
<tr>
<td>Phosphoric acid</td>
<td>H₃PO₄</td>
<td>Rust remover</td>
</tr>
<tr>
<td>Boric acid</td>
<td>B(OH)₃ or H₃BO₃</td>
<td>Mild antiseptic; insecticide</td>
</tr>
<tr>
<td>Aluminum salts</td>
<td>NaAl(SO₄)₂·12H₂O</td>
<td>In baking powder, with sodium hydrogen carbonate</td>
</tr>
<tr>
<td>Hydrochloric acid</td>
<td>HCl</td>
<td>Brick and ceramic tile cleaner</td>
</tr>
<tr>
<td>(muriatic acid)</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Bases</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium hydroxide (lye)</td>
<td>NaOH</td>
<td>Oven cleaner, unblocking plumbing</td>
</tr>
<tr>
<td>Ammonia</td>
<td>NH₃</td>
<td>Household cleaner</td>
</tr>
<tr>
<td>Sodium carbonate</td>
<td>Na₂CO₃</td>
<td>Water softener, grease remover</td>
</tr>
<tr>
<td>Sodium hydrogen carbonate</td>
<td>NaHCO₃</td>
<td>Fire extinguisher, rising agent in cake mixes (baking soda), mild antacid</td>
</tr>
<tr>
<td>Trisodium phosphate</td>
<td>Na₃PO₄</td>
<td>Cleaner for surfaces before painting or wallpapering</td>
</tr>
</tbody>
</table>

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Trinity College Dublin, The University of Dublin
Acids and Bases

**Acids**

1. Have sharp or sour taste
2. React with metals to produce hydrogen gas
3. React with (bi)carbonates to produce $\text{CO}_2$ gas
   - This results in weathering of buildings, etc.

**Bases**

1. Have bitter taste
2. React with acids to make salts
3. React with oil to make soaps
   - They feel slippery on your hands
Classical Acid-Base definition

- An acid is a neutral substance that contains hydrogen and dissociates or ionizes in water to yield hydrated protons or hydronium ions $H_3O^+$.
  
  \[ HCl \rightarrow H^+ (aq) + Cl^- (aq) \]

- A base is a neutral substance that contains the hydroxyl group and dissociates in water to yield hydrated hydroxide ions $OH^-$.  
  
  \[ NaOH \rightarrow Na^+ (aq) + OH^- (aq) \]

- Neutralization is the reaction of an $H^+(H_3O^+)$ ion from the acid and the $OH^-$ ion from the base to form water, $H_2O$.
  
  \[ HCl (aq) + NaOH (aq) \rightarrow NaCl (aq) + H_2O (aq) \]

  acid base salt water

- These definitions although correct are limited in that they are not very general and do not give a comprehensive idea of what acidity and basicity entails.
A note on “hydronium”

The $\mathrm{H}_3\mathrm{O}^+$ hydronium ion is often represented simply as “$\mathrm{H}^+$”

This is simpler and easier to write, but “$\mathrm{H}^+$” is simply a proton – and an isolated proton simply cannot exist by itself in solution.

However, “$\mathrm{H}_3\mathrm{O}^+$” is also a simplification – acidified water is EXTREMELY complicated, with large and dynamic conglomerates of water molecules really stabilising the extra protons.

It’s probably best to write “$\mathrm{H}_3\mathrm{O}^+$”, but don’t be confused if you see “$\mathrm{H}^+$”.
Defining acids and bases

1. **Arrhenius (1884)**
   - **Acid**: a species that dissolves to give *proton concentration*
   - **Base**: a species that dissolves to give *hydroxide concentration*

2. **Brønsted-Lowry (1923)**
   - **Acid**: a species that *donates a proton*
   - **Base**: a species that *accepts a proton*

3. **Lewis (1923)**
   - **Acid**: a species able to *accept an electron pair*
   - **Base**: a species able to *donate an electron pair*
Arrhenius Acid-Base definition

Arrhenius acid is a H-containing substance that dissociates in water to produce hydronium ions ($\text{H}_3\text{O}^+$).

Arrhenius base is an OH-containing substance that dissociates in water to produce hydroxide ions, $\text{OH}^-$.

NaOH $\rightleftharpoons$ Na$^+$ + OH$^-$
The problems with Arrhenius

For example, ammonia (NH₃) has all the properties of a base, but doesn’t contain any OH groups, so doesn’t fit Arrhenius’s definition

\[ \text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^- \]

Similarly, Boric Acid (BO₃H₃) produces hydronium ions, but by taking on an OH, not by losing a H, so it doesn’t fit Arrhenius’s definition

\[ \text{BO}_3\text{H}_3 + \text{H}_2\text{O} \rightarrow \text{BO}_4\text{H}_4^- + \text{H}_3\text{O}^+ \]
Bronsted – Lowry definition

• **Bronsted – Lowry Acid (HA):** An acid is a species which **donates** a proton.

• **Bronsted – Lowry Base (B):** A base is a species which **accepts** a proton.

• These definitions are quite general and refer to the reaction between an acid and a base.

• An acid must contain H in its formula; HNO₃ and H₂PO₄⁻ are two examples.

• A base must contain a lone pair of electrons to bind the H⁺ ion; a few examples are NH₃, CO₃²⁻, F⁻, as well as OH⁻.

In the Bronsted-Lowry perspective: one species donates a proton and another species accepts it: an acid-base reaction is a proton transfer process.
General Definition

Does this match Arrhenius’s definition?

If I put an acid in water, it can donate a proton to form hydronium:

\[ \text{HA} + \text{H}_2\text{O} \rightarrow \text{A}^- + \text{H}_3\text{O}^+ \]

If I put an base in water, it can accept a proton to form hydroxide:

\[ \text{B} + \text{H}_2\text{O} \rightarrow \text{BH}^+ + \text{OH}^- \]

So Bronsted and Lowry repeat Arrhenius’s observations, but with more general rules:

- Water does not need to be present
- More things fit the definitions of acid and base (eg. \( \text{NH}_3 \) and \( \text{BO}_3\text{H}_3 \))
General Definition

How does water fit in to these definitions of acid/base?

With acid:

\[ \text{HA} + \text{H}_2\text{O} \rightarrow \text{A}^- + \text{H}_3\text{O}^+ \]

Accepted a proton

So water is acting as a base

And with base:

\[ \text{B} + \text{H}_2\text{O} \rightarrow \text{BH}^+ + \text{OH}^- \]

Donated a proton

So water is acting as an acid

Water is known as an **AMPHOTERIC** or **AMBIPROTIC** substance, since it can act as an acid and as a base.
• Proton donation and acceptance are dynamic processes for all acids and bases. Hence a proton transfer equilibrium is rapidly established in solution.

• They are not one way streets – the products can turn back into the reactants. This is known as an EQUILIBRIUM PROCESS, denoted by ⇌

\[
\text{HA} + \text{H}_2\text{O} \quad \overset{\text{⇌}}{\rightarrow} \quad \text{A}^- + \text{H}_3\text{O}^+
\]

Therefore:

After an acid donates its proton, it is known as a CONJUGATE BASE

After an base accepts its proton, it is known as a CONJUGATE ACID
• A conjugate acid has one more proton than the base has, and a conjugate base one less proton than the acid has.

• If the acid of a conjugate acid/base pair is strong (good tendency to donate a proton) then the conjugate base will be weak (small tendency to accept a proton) and vice versa.

\[
\text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{A}^- + \text{H}_3\text{O}^+
\]

Acid \hspace{1cm} Base \hspace{1cm} Conjugate Base \hspace{1cm} Conjugate Acid

Another example:

\[
\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-
\]

Base \hspace{1cm} Acid \hspace{1cm} Conjugate acid \hspace{1cm} Conjugate base

**Acid: Proton donor**  
**Base: Proton acceptor**
Quantifying acid/base strength

Strong acid or base

Weak acid or base

• Key concept is degree of ionization or dissociation

• Correlation exists between acid/base strength, degree of ionization in solution and extent to which solution exhibits ionic conductivity.
Degree of dissociation

1. Acid/base strength quantified in terms of degree of dissociation

2. **Strong acid/base**: An acid or base is classified as strong if it is fully ionized in solution (e.g. HCl, NaOH).

3. **Weak acid/base**: An acid or base is classified as weak if only a small fraction is ionized in solution (e.g. CH₃COOH, NH₃).
Examples

**Strong Electrolyte**: 100% dissociation

NaCl (s) $\rightarrow$ Na$^+$ (aq) + Cl$^-$ (aq)

**Weak Electrolyte**: not completely dissociated

CH$_3$COOH $\rightleftharpoons$ CH$_3$COO$^-$ (aq) + H$^+$ (aq)

**Strong Acids** are strong electrolytes

HCl (aq) + H$_2$O (l) $\rightarrow$ H$_3$O$^+$ (aq) + Cl$^-$ (aq)
HNO$_3$(aq) + H$_2$O (l) $\rightarrow$ H$_3$O$^+$ (aq) + NO$_3^-$ (aq)

Nitric acid

**Weak Acids** are weak electrolytes

HF (aq) + H$_2$O (l) $\rightleftharpoons$ H$_3$O$^+$ (aq) + F$^-$ (aq)
HNO$_2$ (aq) + H$_2$O (l) $\rightleftharpoons$ H$_3$O$^+$ (aq) + NO$_2^-$ (aq)

Nitrous acid
**Strong bases** are strong electrolyte

\[ \text{NaOH (s) + H}_2\text{O (l)} \rightarrow \text{Na}^+(\text{aq}) + \text{OH}^-(\text{aq}) \]
\[ \text{KOH (s) + H}_2\text{O (l)} \rightarrow \text{K}^+(\text{aq}) + \text{OH}^-(\text{aq}) \]

**Weak Bases** are weak electrolytes

\[ \text{NO}_2^- (\text{aq}) + \text{H}_2\text{O (l)} \rightleftharpoons \text{OH}^- (\text{aq}) + \text{HNO}_2 (\text{aq}) \]
\[ \text{F}^- (\text{aq}) + \text{H}_2\text{O (l)} \rightleftharpoons \text{OH}^- (\text{aq}) + \text{HF (aq)} \]
Dissociation constant, $K$

We can quantify the extent of dissociation of a weak acid or a weak base in aqueous solution by introducing:

\[ \text{The acid dissociation constant } K_a \]

or

\[ \text{The base dissociation constant } K_b \]

These are numbers which reflect acid or base strength and are computed by determining the equilibrium concentrations of all relevant species in the solution, and inputting this data into a theoretical expression for the relevant dissociation constant.
Acid strength: the acid dissociation constant, $K_a$

• It is easy to quantify the strength of strong acids since they fully dissociate to ions in solution.

• The situation with respect to weak acids is more complex since they only dissociate to a small degree in solution.

• The question is how small is small?

• We quantify the idea of incomplete dissociation of a weak acid HA by noting that the dissociation reaction is an equilibrium process and introducing the acid dissociation constant, $K_a$. 
Weak acids

\[ \text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+ \]

Acetic acid
Weak acids

\[ \text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+ \]

\[ K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}][\text{H}_2\text{O}]} \]

But, \([\text{H}_2\text{O}] = \text{constant}\)

\[ K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]} \]

\[ K_a = 1.8 \times 10^{-5} \]

[...] represents the concentration of relevant species in Molar (can be represented as mol/L, mol/dm³ or M)
Therefore:

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

\[
K_a = \frac{[A^-][H_3O^+]}{[HA][H_2O]} = \text{Constant}
\]

- \( K_a \) is a measure of the acid strength.
- When \( K_a \) is \textbf{large} there is considerable \textbf{dissociation} and the \textbf{acid is strong}.
- When \( K_a \) is \textbf{small} there is a \textbf{small degree of dissociation}, and the \textbf{acid is weak}. 
$K_a$ values vary over a wide range so it is best to use a log scale.

$$pK_a = -\log_{10}K_a$$

<table>
<thead>
<tr>
<th>Acid Name (Formula)</th>
<th>$K_a$ at 298 K</th>
<th>pK$_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen Sulfate ion (HSO$_4^-$)</td>
<td>$1.02 \times 10^{-2}$</td>
<td>1.99</td>
</tr>
<tr>
<td>Nitrous acid (HNO$_3$)</td>
<td>$7.1 \times 10^{-4}$</td>
<td>3.15</td>
</tr>
<tr>
<td>Acetic acid (CH$_3$COOH)</td>
<td>$1.8 \times 10^{-5}$</td>
<td>$K_A \downarrow$</td>
</tr>
<tr>
<td>Hypobromous acid (HBrO)</td>
<td>$2.3 \times 10^{-9}$</td>
<td>8.64</td>
</tr>
<tr>
<td>Phenol (C$_6$H$_5$OH)</td>
<td>$1.0 \times 10^{-10}$</td>
<td>10.00</td>
</tr>
</tbody>
</table>

When $K_a$ is small $pK_a$ is large and the acid does not dissociate in solution to a large extent. A change in 1 $pK_a$ unit implies a 10 fold change in $K_a$ value and hence acid strength.
The ion product of water

\[ \text{H}_2\text{O (l)} \rightleftharpoons \text{H}^+ \text{(aq)} + \text{OH}^- \text{(aq)} \]

\[ K_C = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} \; ; \; K_C = \text{Equilibrium constant and } [\text{H}_2\text{O}] = \text{constant} \]

\[ K_C [\text{H}_2\text{O}] = [\text{H}^+][\text{OH}^-] \]

\[ K_W = [\text{H}^+][\text{OH}^-] \]

The **ion-product constant** \( (K_W) \) is the product of the molar concentrations of \( \text{H}^+ \) and \( \text{OH}^- \) ions at a particular temperature.

At 25°C:

\[ K_W = [\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14} \]

<table>
<thead>
<tr>
<th>Solution is</th>
<th>([\text{H}^+] = [\text{OH}^-])</th>
<th>Neutral</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{H}^+] &gt; [\text{OH}^-])</td>
<td>Acidic</td>
<td></td>
</tr>
<tr>
<td>([\text{H}^+] &lt; [\text{OH}^-])</td>
<td>Basic</td>
<td></td>
</tr>
</tbody>
</table>
Basicity Constant, $K_b$

- The proton accepting strength of a base is quantified in terms of the basicity constant $K_b$.

- The larger the value of $K_b$, the stronger the base.

- If $K_b$ is large then $pK_b$ will be small, and the stronger will be the base.

- Solve weak base problems like weak acids except solve for $[\text{OH}^-]$ instead of $[\text{H}^+]$.

\[ \text{B} + \text{H}_2\text{O} \rightleftharpoons \text{BH}^+ + \text{OH}^- \]

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

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

\[ pK_b = -\log_{10} K_b \]

\[ K_a K_b = K_w \]

\[ pK_a + pK_b = K_w \]
The pH concept

- The **best** quantitative measure of acidity or alkalinity rests in the determination of the concentration of hydrated protons \([H_3O^+]\) present in a solution.

- The \([H_3O^+]\) varies in magnitude over quite a large range in aqueous solution, typically from 1 M to \(10^{-14}\) M.

- Hence to make the numbers meaningful \([H_3O^+]\) is expressed in terms of a logarithmic scale called the **pH scale**.

- The higher the \([H_3O^+]\), the more acidic the solution and the lower is the solution pH.

- The pH of a solution can be defined as the negative base 10 logarithm of the hydronium ion concentration.

\[
pH = -\log_{10} [H_3O^+] \\
[H_3O^+] = 10^{-pH}
\]
pH scale

- pH is expressed on a numerical scale from 0 to 14.
- When \([H_3O^+] = 1.0 \text{ M} \) (i.e. \(10^0 \text{ M}\)), pH = 0.
- When \([H_3O^+] = 10^{-14} \text{ M}\), pH = 14.
- Hence a change in one pH unit represents a change in concentration of \(H_3O^+\) ions by a factor of 10.

<table>
<thead>
<tr>
<th>pH</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>Neutral</td>
</tr>
<tr>
<td>&lt;7</td>
<td>Acidic</td>
</tr>
<tr>
<td>&gt;7</td>
<td>Alkaline</td>
</tr>
</tbody>
</table>

- pH 0 = Battery Acid
- pH 2 = Lemon Juice
- pH 2.5 = Soda
- pH 4.3 = Acid Rain
- pH 5.6 = Clean Rain
- pH 7 = Distilled Water
- pH 7.4 = Blood
- pH 8.1 = Sea Water
- pH 9 = Baking Soda
- pH 11 = Ammonia
- pH 12.6 = Bleach
- pH 14 = Liquid Drain Cleaner
pH and pOH scale

\[ pH = -\log_{10} [H_3O^+] \]

Similarly:

\[ pOH = -\log_{10} [OH^-] \]

Therefore:

\[ pH + pOH = 14 \]
Summary: pH – a measure of acidity

\[ pH = -\log_{10} [H_3O^+] = -\log_{10} [H^+] \]

<table>
<thead>
<tr>
<th>Solution is</th>
<th>At 25°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neutral</td>
<td>[H⁺] = [OH⁻]</td>
</tr>
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</tr>
<tr>
<td>Basic</td>
<td>[H⁺] &lt; [OH⁻]</td>
</tr>
</tbody>
</table>

pH ↑ \[H^+\] ↓
pH measurement: pH meter

- More accurate pH values determined using an electronic instrument called a pH meter.

- The device (consisting of a probe electrode made of glass and associated electronics) measures the electrical potential generated across a glass membrane (which separates an internal solution of known $[\text{H}_3\text{O}^+]$ from the external test solution of unknown $[\text{H}_3\text{O}^+]$ ) located at the electrode tip.

- This membrane potential is proportional to the pH of the test solution.

- A digital readout of solution pH is obtained.
Methods for Measuring the pH of an Aqueous Solution

- pH meter
- Litmus papers
pH measurements: Indicators

- Approximate pH of a solution determined by use of acid/base indicators.

- Indicators are substances (weak acids) which change colour over a specific pH range when they donate protons.

- We add a few drops of indicator (which changes colour over the required pH range) to the test solution and record the colour change produced.

- This procedure is utilized in acid/base titrations. Universal indicator (mixture of pH indicators) often used for making approximate pH measurements in range 3 – 10.

- As solution pH increases, the indicator changes colour from red to orange to yellow to green to blue, and finally to purple.
COLOURS OF pH INDICATORS

0  2  4  6  pH  8  10  12  14

UNIVERSAL INDICATOR

PHENOLPHTHALEIN
RANGE: 8.3 - 10.0

METHYL ORANGE
RANGE: 3.1 - 4.4

THYMOL BLUE
RANGE: 1.2 - 2.8, 8.9 - 9.6

BROMOTHYMOL BLUE
RANGE: 6.0 - 7.6

PHENOL RED
RANGE: 6.4 - 8.3
Colors and Approximate pH Range of Some Common Acid-Base Indicators

Universal indicator is a mixture of indicators to give a full range of pH values.
Titrations

In a **titration**, a solution of accurately known concentration is added gradually to another solution of unknown concentration until the chemical reaction between the two solutions is complete.

\[ HA + MOH \rightarrow MA + H_2O \]

**Indicator:** Substance that changes color at (or near) the equivalence point

**Equivalence point or Stoichiometric point:** The point at which the reaction is complete

Slowly add base to unknown acid UNTIL The indicator changes color (pink)
Strong acid – strong base titrations

HCl (aq) + NaOH (aq) $\rightarrow$ NaCl (aq) + H$_2$O (aq)

At equivalence point:

Amount of acid = Amount of base

\[ n_A = n_B \]
\[ c_A V_A = c_B V_B \]

0.1 M NaOH added to 25 ml of 0.1 M HCl

Volume of NaOH added (mL) | pH
---|---
0.0 | 1.00
5.0 | 1.18
10.0 | 1.37
15.0 | 1.60
20.0 | 1.95
22.0 | 2.20
24.0 | 2.69
25.0 | 7.00
26.0 | 11.29
28.0 | 11.75
30.0 | 11.96
35.0 | 12.22
40.0 | 12.36
45.0 | 12.46
50.0 | 12.52
Weak acid – strong base titrations

\[
\text{CH}_3\text{COOH} \text{ (aq)} + \text{NaOH} \text{ (aq)} \rightarrow \text{CH}_3\text{COONa} \text{ (aq)} + \text{H}_2\text{O} \text{ (l)}
\]

\[
\text{CH}_3\text{COOH} \text{ (aq)} + \text{OH}^- \text{ (aq)} \rightarrow \text{CH}_3\text{COO}^- \text{ (aq)} + \text{H}_2\text{O} \text{ (l)}
\]

At equivalence point (pH > 7):

\[
\text{CH}_3\text{COO}^- \text{ (aq)} + \text{H}_2\text{O} \text{ (l)} \rightleftharpoons \text{OH}^- \text{ (aq)} + \text{CH}_3\text{COOH} \text{ (aq)}
\]
Summary

• The process involves the transfer of a hydrated proton from a donor species (the acid) to an acceptor species (the base).

• The degree of proton transfer can be quantified and enables a distinction between strong and weak acids/bases to be made.

• The degree of acidity or alkalinity of a solution may be quantified in terms of the logarithmic pH scale.

• Acidic solutions have a low pH and basic solutions have a high pH.

• The solution pH can be measured via use of indicators or via use of pH meter.

• An acid/base reaction is termed a neutralization reaction and can be monitored by measuring the pH during the reaction.
Reading Materials

   - Chapter 19 → Ionic equilibria in aqueous systems. pp.814 – 862.

   - Chapter 17&18, pp.760 – 859.


4. Lecture notes available after course on School of Chemistry website located at: http://www.tcd.ie/Chemistry/outreach/prelim/
Useful websites

1. http://www.shodor.org/unchem/basic/ab/

2. http://chemistry.about.com/od/acidsbases/


4. http://dbhs.wvusd.k12.ca.us/webdocs/AcidBase/AcidBase.html

Good luck!!