I will try to structure our tour of chemistry in 3150:153 around three Big Questions:
1. What’s in a solution? How far does a reaction “go”?  
2. What factors influence how far a reaction “goes” and how fast it gets there?  
3. How do atomic and molecular structure influence observed properties of substances?  
As chemistry is very integrated, it’s possible that sometimes we will think about something that deals with more than one question at a time.

**Big Question #1**
What’s in a solution? How far does a reaction “go”?  

**Review (Chapter 4) & Section 13.5**  
**Solutions: Components and Proportions**

<table>
<thead>
<tr>
<th>Air</th>
<th>Common aspects?</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sterling silver</td>
<td></td>
</tr>
<tr>
<td>Mountain Dew</td>
<td></td>
</tr>
</tbody>
</table>

- **solute:**
- **solvent:**

**Quantitative Expressions (Units) of Concentration**

<table>
<thead>
<tr>
<th>Concentration Definitions</th>
<th>Concentration Term</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molarity ((M))</td>
<td>amount (mol) of solute</td>
<td>volume (L) of solution</td>
</tr>
<tr>
<td>Molality ((m))</td>
<td>amount (mol) of solute</td>
<td>mass (kg) of solvent</td>
</tr>
<tr>
<td>Parts by mass</td>
<td>mass of solute</td>
<td>mass of solution</td>
</tr>
<tr>
<td>Parts by volume</td>
<td>volume of solute</td>
<td>volume of solution</td>
</tr>
<tr>
<td>Mole fraction ((X))</td>
<td>amount (mol) of solute</td>
<td>amount (mol) of solute + amount (mol) of solvent</td>
</tr>
</tbody>
</table>

**PROTIP**
Chemistry style for units with denominators uses negative exponents. For example, “meters per second” would be written m·s⁻¹.

- What is the molarity of a 28% by mass solution of ammonia with a density of 0.90 g·mL⁻¹?
What is the molality of a 15% by mass solution of sodium chloride? (NaCl: 58.44 g·mol⁻¹)

**Saturation and Solubility; Equilibrium in Saturated Solutions**
Chapter 17
Chemical Equilibrium

Consider 1.00 mol of N₂O₄ in a 1.00-liter flask at 25 °C and this equation:  \( \text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g) \)

What will be the concentration of NO₂ when the reaction reaches completion?

Analysis reveals that after a very long time, \([\text{N}_2\text{O}_4] = 0.85\) M and \([\text{NO}_2] = 0.30\) M. Years later, the concentrations are unchanged at the same temperature. “Completion” in the 3150:151 sense does not work for lots of reactions!

Many reactions achieve a dynamic chemical equilibrium.

- a state where the concentrations of products and reactants remain constant over time
- a dynamic state microscopically—not static
- a state where the rates of the forward and reverse reactions are equal

So, what is the equilibrium position? How far does the reaction “go”?

In general, for \( a\ A + b\ B \rightleftharpoons c\ C + d\ D \)

\[
K = \frac{[C]^c[D]^d}{[A]^a[B]^b}
\]

where \([X]\) \(\equiv\) the equilibrium concentration of \(X\)

The value of the equilibrium constant for a reaction depends on the temperature.

For the reaction discussed above, \( K = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{[0.30]^2}{[0.85]} = 0.106 @ 25 °C \)

Strictly speaking, \(K\) for the reaction comes out to 0.106 mol·L⁻¹ using molarities, but equilibrium constants don’t really have units. They are actually expressed in terms of activities instead of molarities. In solutions that are dilute enough, molarity \(\approx\) activity. The same argument applies to the use of partial pressures in \(K\) expressions (see text) where the partial pressures are divided by a reference value (1 atm). Furthermore, the distinction in the text between \(K_C\) and \(K_P\) is really artificial—for reactions that involve both gaseous and aqueous substances, it’s possible to write a \(K\) that includes pressures and molarities.

\(K\) small: mostly reactants at equilibrium
\(K\) large: mostly products at equilibrium

- \(K\) describes the ratio of products to reactants.
- \(K\) can be measured experimentally.
- \(K\) has predictive power—tied to how favorable a reaction is.
- \(K\) can be used to predict which way a reaction would need to “go” to reach equilibrium if it’s not there.

Reaction Quotient, \(Q\)
The reaction quotient expresses the ratio of products to reactants at any time (not just at equilibrium). \(Q\) is written the same way as \(K\) (“products over reactants”).

For the reaction discussed above, \(Q = \frac{(\text{NO}_2)^2}{(\text{N}_2\text{O}_4)} \) where \((X) \equiv\) the concentration of \(X\) at any time.
Q vs. K

- If $Q < K$, the reaction must shift to the right (toward products) to reach equilibrium.
- If $Q > K$, the reaction must shift to the left (toward reactants) to reach equilibrium.
- If $Q = K$, the reaction is at equilibrium.

### K (and Q) Expressions for Heterogeneous Equilibria

Pure solids and liquids do not appear in $K$ (or $Q$) expressions.

### Dealing with K values

- When an equation is reversed, the $K$ value for the reverse reaction is the reciprocal of the original.

  \[
  2\text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{OH}^-(aq) \quad K = 1.0 \times 10^{-14}
  \]

  \[
  \text{H}_3\text{O}^+(aq) + \text{OH}^-(aq) \rightleftharpoons 2\text{H}_2\text{O}(l)
  \]

- When an equation is multiplied by a coefficient, the $K$ value is raised to that power.

  \[
  2\text{KClO}_3(s) \rightleftharpoons 2\text{KCl}(s) + 3\text{O}_2(g) \quad K = 6.5 \times 10^7
  \]

  \[
  \text{KClO}_3(s) \rightleftharpoons \text{KCl}(s) + \frac{3}{2}\text{O}_2(g)
  \]

- When equations are added, the overall equation’s $K$ value is the product of the individual $K$ values.

  \[
  \text{Ag}^+(aq) + 2\text{CN}^-(aq) \rightleftharpoons \text{Ag(CN)}_2^- (aq) \quad K = 5.3 \times 10^{18}
  \]

  \[
  \frac{\text{Zn(CN)}_2(s) \rightleftharpoons \text{Zn}^{2+} (aq) + 2\text{CN}^-(aq)}{K = 3.0 \times 10^{-16}}
  \]

  \[
  \text{Ag}^+(aq) + \text{Zn(CN)}_2(s) \rightleftharpoons \text{Ag(CN)}_2^- (aq) + \text{Zn}^{2+}(aq)
  \]

### PROTIP

Usual excuse for solids and liquids not appearing in $K$ expressions: “they are constant in concentration.”
Actual reason: the activity of a solid or liquid equals exactly 1.
Influencing the Equilibrium Position

LeChatelier’s Principle: A change in one or more variables describing a system at equilibrium produces a shift in the equilibrium position that counteracts the effect of the change.

- Changes in Concentration
  - equilibrium position changed
  - $K$ unchanged
  
  e.g., $\text{Fe}^{3+}(\text{aq}) + \text{SCN}^-(\text{aq}) \rightleftharpoons \text{Fe(SCN)}^{2+}(\text{aq})$

- Changes in Pressure
  - equilibrium position usually changed
  - $K$ unchanged
  1. Add/remove gaseous reactant/product
     - same principle as for concentration change; equilibrium shifts to “use up” some of added substance or produce some of removed substance
  2. Add inert gas (not involved in reaction)
     - total pressure increases, but no change in equilibrium position
  3. Change volume of container
     - equilibrium position changes to favor side of reaction with fewer moles of gas if $V$ decreases, or to side of reaction with more moles of gas if $V$ increases.

  e.g., $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$

  $K = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$

  suppose that at some temperature, $K = 1.0$ and all $[\text{]} = 1.0$. Cut the volume in half...now

  $Q = \frac{(\frac{1.0 \text{ mol}}{0.5 \text{ L}})^2}{(\frac{1.0 \text{ mol}}{0.5 \text{ L}})(\frac{1.0 \text{ mol}}{0.5 \text{ L}})^3} = 0.25 < 1.0$. $Q < K$, so shift right

  - If the gaseous moles are the same on both sides of the reaction, a volume change will not cause any change in equilibrium position.

  e.g., $2\text{IBr}(\text{g}) \rightleftharpoons \text{I}_2(\text{g}) + \text{Br}_2(\text{g})$

  $K = \frac{[\text{I}_2][\text{Br}_2]}{[\text{IBr}]^2}$

  suppose that at some temperature, $K = 1.0$ and all $[\text{]} = 1.0$. Cut the volume in half...now

  $Q = \frac{(\frac{1.0 \text{ mol}}{0.5 \text{ L}})(\frac{1.0 \text{ mol}}{0.5 \text{ L}})}{(\frac{1.0 \text{ mol}}{0.5 \text{ L}})^2} = 1.0$. $Q = K$, so no change in equil. position
Changes in Temperature

- equilibrium position changed
- $K$ also changed

\[ \text{e.g., } \quad N_2O_4(g) \leftrightarrow 2NO_2(g) \quad \Delta H^\circ = +58 \text{ kJ} \quad \text{endothermic—heat is like a reactant} \]

When warmed, it’s as if a reactant is being added, so reaction shifts toward products.

---

Application: Haber-Bosch Process

\[ \text{N}_2(g) + 3\text{H}_2(g) \leftrightarrow 2\text{NH}_3(g) \quad \Delta H^\circ = -92 \text{ kJ} \quad \text{exothermic—product favored at lower T} \]

But, reaction is very S-L-O-W at low T

What other factors can be manipulated to maximize product yield?
Section 19.3
Aqueous Solubility Equilibria

Knowing that we do not include pure liquids or solids in $K$ expressions, write $K$ expressions for each of the following reactions of “insoluble” compounds slightly dissolving in water.

- $\text{AgCl}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq)$
- $\text{HgI}_2(s) \rightleftharpoons \text{Hg}^{2+}(aq) + 2\text{I}^-(aq)$
- $\text{Cr(OH)}_3(s) \rightleftharpoons \text{Cr}^{3+}(aq) + 3\text{OH}^-(aq)$
- $\text{Ca}_3(\text{PO}_4)_2(s) \rightleftharpoons 3\text{Ca}^{2+}(aq) + 2\text{PO}_4^{3-}(aq)$

The $K$ expressions written for “insoluble” compounds dissolving in water are called $K_{SP}$ expressions, after the name “Solubility Product.” Note that there is no denominator in any of the expressions—only the product of the terms for the cations and anions. In general, the smaller the value of $K_{SP}$ is, the less soluble a compound is. It’s not uncommon for $K_{SP}$ to have values of $10^{-20}$, $10^{-30}$, or even $10^{-50}$ or less for certain compounds.

Consider mercury(II) iodide in otherwise pure water at 25 °C. $K_{SP} = 3.0 \times 10^{-29}$.

$\text{HgI}_2(s) \rightleftharpoons \text{Hg}^{2+}(aq) + 2\text{I}^-(aq)$

What would happen to the solubility of this compound if iodide ion were added (from a soluble compound like sodium iodide)? *Hint: consider LeChatelier’s Principle.*

- **common ion effect**: addition of an ion already present in a solution at equilibrium results in the equilibrium position shifting away from producing more of that ion.

Consider chromium(III) hydroxide in otherwise pure water at 25 °C.

$\text{Cr(OH)}_3(s) \rightleftharpoons \text{Cr}^{3+}(aq) + 3\text{OH}^-(aq)$

What would happen to the solubility of this compound if a base (OH$^-$) were added? *Hint: consider LeChatelier’s Principle.*

Conversely, what would happen to the solubility if an acid (H$_3$O$^+$) were added? *Hint: again, consider LeChatelier’s Principle.*

For insoluble compounds with like stoichiometry (e.g., AgI, AgBr, AgCl or Ca$_3$(PO$_4$)$_2$, Sr$_3$(PO$_4$)$_2$, Ba$_3$(PO$_4$)$_2$), the value of $K_{SP}$ corresponds to the relative solubility. The smaller the value of $K_{SP}$, the less soluble the compound. Thus compounds can be separated by differences in their $K_{SP}$ values as an ion common to the compounds is changed in concentration.
Acids, Bases, & Acid-Base Equilibria

Many models have been proposed over hundreds of years to describe acids and bases.

Observations about acids:
- taste sour (DO NOT taste lab chemicals!)
- tend to react with metals to produce $\text{H}_2$ gas
- turn blue litmus red
- tend to react with bases to produce water and a salt

Observations about bases:
- feel slippery and often taste bitter (DO NOT touch or taste lab chemicals!)
- turn red litmus blue
- tend to react with acids to produce water and a salt

Common household acids include aspirin, the juices of citrus fruits, vinegar
Common household bases include milk of magnesia, ammonia, lye

Brønsted-Lowry Definition/Model of Acids and Bases
(early 20$^{th}$ C., two scientists working separately who got the same results)

- **Brønsted acid**: a substance that donates $\text{H}^+$ to another substance, i.e., a proton donor.
  All Arrhenius acids are also Brønsted acids, but not vice versa.

  \[
  \text{HCl} + \text{H}_2\text{O} \rightarrow \text{Cl}^- + \text{H}_3\text{O}^+
  \]

- **Brønsted base**: a substance that accepts $\text{H}^+$ from another substance, i.e., a proton acceptor.
  Arrhenius bases contain the Brønsted base $\text{OH}^-$.

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

Note that water can react as an acid or a base—this behavior is referred to as *amphotерism* (adjective: *amphoteric*).

Most acid-base equilibria we discuss will be modeled using the Brønsted definition.
**Conjugate Acid-Base Pairs**

Consider the forward and reverse reactions:

\[
\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(l) \leftrightarrow \text{NH}_4^+(\text{aq}) + \text{OH}^- (\text{aq}) \quad \text{(forward)}
\]

\[
\text{NH}_4^+(\text{aq}) + \text{OH}^- (\text{aq}) \leftrightarrow \text{NH}_3(\text{aq}) + \text{H}_2\text{O}(l) \quad \text{(reverse)}
\]

Members of a conjugate acid-base pair differ by a proton (H\(^+\)). e.g., A conjugate acid has one more H atom and one more positive charge (or one fewer negative charge) than the base it came from.

Acid-base reactions involve a competition between the bases for the proton (H\(^+\)): where the proton ends up depends on the relative strengths of the acids and bases, i.e., on \(K\) for the equilibrium process. (Recall “strong” vs. “weak” acids and bases in Chapter 4; we will revisit this concept in much greater depth shortly.)

**Acid-Base Properties of Water**

\[
2\text{H}_2\text{O}(l) \leftrightarrow \text{H}_3\text{O}^+(\text{aq}) + \text{OH}^-(\text{aq})
\]

\[
K_W = [\text{H}_3\text{O}^+][\text{OH}^-]
\]

Measurements of “pure” water show that

\[
[\text{H}_3\text{O}^+]_W = [\text{OH}^-]_W = 1.0 \times 10^{-7} \text{ M at } 25 \, ^\circ\text{C}
\]

\[
\therefore \quad K_W = 1.0 \times 10^{-14} \text{ at } 25 \, ^\circ\text{C}.
\]

In any aqueous solution,

\[
K_W = [\text{H}_3\text{O}^+]_{\text{TOT}}[\text{OH}^-]_{\text{TOT}}
\]

Auto-ionization of water is always already happening in water. When an acid or base is added, another equilibrium joins in. Then there are two or more equilibria!

Since the product \([\text{H}_3\text{O}^+]_{\text{TOT}}[\text{OH}^-]_{\text{TOT}}\) is constant (= \(K_W\)), the larger \([\text{H}_3\text{O}^+]\) is, the smaller \([\text{OH}^-]\) is (and vice versa). In general:

<table>
<thead>
<tr>
<th>Condition</th>
<th>Solution Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{H}_3\text{O}^+] = [\text{OH}^-])</td>
<td>NEUTRAL</td>
</tr>
<tr>
<td>([\text{H}_3\text{O}^+] &gt; [\text{OH}^-])</td>
<td>ACIDIC</td>
</tr>
<tr>
<td>([\text{H}_3\text{O}^+] &lt; [\text{OH}^-])</td>
<td>BASIC</td>
</tr>
</tbody>
</table>

**PROTIP**

You may know of a definition of “neutral” that involves the number 7. That is correct only at 25 °C. The definition above is general to all temperatures.
**pH scale**

[H$_3$O$^+$] varies over a very wide range. The pH scale simplifies expressing acidity/basicity.

\[
\text{pH} = -\log[H_3O^+] = \log\left(\frac{1}{[H_3O^+]}\right)
\]

(really an approximation; just as we did for $K$ expressions we will use molar concentrations instead of activities. The true definition uses the activity of H$_3$O$^+$, not molarity.)

pH frequently ranges between 0 and 14, but can be negative (a very acidic solution) or greater than 14 (a very basic solution).

**Regarding sig figs and logs:** the number of sig figs appears after the decimal point in the log.

- e.g., a solution that has [H$_3$O$^+$] = 0.013 M has pH = –log(0.013) = 1.89

“p function” = negative log$_{10}$.

\[
pOH = -\log[OH^-]_{TOT}
\]

So, using the properties of logs,

\[
\log([H_3O^+][OH^-]) = \log K_W
\]

\[
\log[H_3O^+] + \log[OH^-] = \log K_W
\]

\[
-\log[H_3O^+] - \log[OH^-] = -\log K_W
\]

\[
\text{pH} + \text{pOH} = 14.00 \text{ (at 25 °C)}
\]

**Strength of Acids and Bases**

For any acid HA in water, an equilibrium is established:

\[
\text{HA(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{A}^-(aq) \quad K_a = \frac{[H_3O^+][A^-]}{[HA]}
\]

- By convention, the acids considered “strong” have $K_a > 1$ while “weak” acids have $K_a < 1$. Recall that a strong acid is 100% dissociated in solution (Chapter 4).
- For very strong acids, the equilibrium position lies far enough to the right that the reaction is essentially “complete” and the equation is usually written with a single arrow ($\rightarrow$).

- e.g., HCl (a “selected” strong acid in Table 4.3), $K_a \approx 1 \times 10^6$

\[
\text{HCl(aq)} + \text{H}_2\text{O(l)} \rightarrow \text{H}_3\text{O}^+(aq) + \text{Cl}^-(aq)
\]

\[
K_a = \frac{[H_3O^+][Cl^-]}{[HCl]} \approx 1 \times 10^6. \text{ Ratio of products to reactants is very large.}
\]

Therefore, we usually write \( \text{HCl(aq)} + \text{H}_2\text{O(l)} \rightarrow \text{H}_3\text{O}^+(aq) + \text{Cl}^-(aq) \) with a single arrow.

Similarly for bases, an equilibrium is established:

\[
\text{B(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{BH}^+(aq) + \text{OH}^-(aq) \quad K_b = \frac{[BH^+][OH^-]}{[B]}
\]

- same arguments as above for acids (strong vs. weak, single vs. equilibrium arrows)
Molecular Properties and Acid Strength (Big Question #3 Alert!)

Recall (again) that in Chapter 4 you learned several selected strong/weak acids/bases. Now we can consider these general trends:

**Strong Acids**
- HCl, HBr, HI
- Oxoacids where the number of O atoms exceeds the number of ionizable H atoms by 2 or more, e.g., …
  - HNO₃
  - H₂SO₄
  - HClO₄

**Weak Acids**
- HF
- Oxoacids where the number of O atoms exceeds the number of ionizable H atoms by 1 or fewer, e.g., …
  - HNO₂
  - H₂SO₃
  - HOCl
- Acids with H not bonded to O or halogen (group 7A), e.g., …
  - H₂S
  - HCN
- Carboxylic acids (R–COOH), e.g., …
  - CH₃COOH

**Strong Bases**
- Soluble metal oxides & hydroxides (consider solubility rules, Chapter 4), e.g., …
  - Na₂O
  - Ba(OH)₂
  - CsOH
  - SrO

**Weak Bases**
- NH₃
- Amines (R₃N, R₂NH, RNH₂), e.g., …
  - (CH₃)₃N
  - CH₃CH₂NH₂

Explanations for a couple of the above

**Nonmetal Hydrides**
- Electronegativity increases, acidity increases
- Bond strength decreases, acidity increases
- Nonmetal hydride acid strength increases with increasing AEN across a period and decreasing bond strength down a group.

**Oxoacids**
- Same number of O atoms, different central atom
  - Acid strength increases with increasing electronegativity of central atom (O–H bond polarized)
    - HOI: $K_a = 2.3 \times 10^{-11}$
    - HOBr: $K_a = 2.3 \times 10^{-9}$
    - HOCl: $K_a = 2.9 \times 10^{-8}$
- Different number of O atoms, same central atom
  - Acid strength increases with increasing number of O atoms (more electronegative O atoms pull electron density to themselves, polarizing O–H bond)
    - HOCl: $K_a = 2.9 \times 10^{-8}$
    - HOClO₂: $K_a = 1.1 \times 10^{-2}$ (aka “HClO₂”)
    - HOClO₂: $K_a = 5.0 \times 10^2$
    - HOClO₃: $K_a = 1 \times 10^8$

**Presence of Electron-Withdrawing Groups/Atoms**
- Electron-withdrawing groups/atoms frequently increase acidity for the same reason as additional O atoms increase acidity of oxoacids with the same central atom—increased polarization of the O–H bond.
  - CH₃COOH: $K_a = 1.8 \times 10^{-5}$
  - CCl₃COOH: $K_a = 2.2 \times 10^{-1}$
**Leveling Effect**

Acids stronger than $\text{H}_3\text{O}^+$ react completely with water to produce a stoichiometric amount of $\text{H}_3\text{O}^+$. Bases stronger than $\text{OH}^-$ react completely with water to produce a stoichiometric amount of $\text{OH}^-$. It’s not possible to compare the strengths of strong acids in aqueous solution. A non-aqueous solution must be used.

**Equilibria of Acids and Bases in Water!!**

We will discuss several (four to be exact) different cases of equilibria of acids and bases.

1. **Strong, monoprotic acids in water**

   (1) $\text{HA}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_3\text{O}^+(\text{aq}) + \text{A}^-(\text{aq})$ \hspace{1cm} $K_a$ big

   (2) $2\text{H}_2\text{O}(\text{l}) \leftrightarrow \text{H}_3\text{O}^+(\text{aq}) + \text{OH}^-(\text{aq})$ \hspace{1cm} $K_W$ small

   $[\text{H}_3\text{O}^+]_{\text{TOT}} = [\text{H}_3\text{O}^+]_{\text{HA}} + [\text{H}_3\text{O}^+]_W$

   $[\text{H}_3\text{O}^+]_W$ small compared to $[\text{H}_3\text{O}^+]_{\text{HA}}$. Can we neglect $[\text{H}_3\text{O}^+]_W$? Perhaps…

   **If** $[\text{H}_3\text{O}^+]_W \leq 0.05[\text{H}_3\text{O}^+]_{\text{TOT}}$, **then we can neglect** $[\text{H}_3\text{O}^+]_W$.

**Strong Acid Rules**

1. If $F_{\text{acid}} \geq 4.5 \times 10^{-7}$ M, then
   a. water dissociation unimportant
   b. $[\text{H}_3\text{O}^+]_{\text{TOT}} \approx F_{\text{acid}}$

2. If $F_{\text{acid}} < 4.5 \times 10^{-7}$ M, then
   a. water dissociation important
   b. solve using: $[\text{H}_3\text{O}^+]_{\text{TOT}}^2 - F_{\text{acid}}[\text{H}_3\text{O}^+]_{\text{TOT}} - K_W = 0$

Similar analysis applies for strong “monobasic” bases in water (e.g., NaOH):

**Strong Base Rules**

1. If $F_{\text{base}} \geq 4.5 \times 10^{-7}$ M, then
   a. water dissociation unimportant
   b. $[\text{OH}^-]_{\text{TOT}} \approx F_{\text{base}}$

2. If $F_{\text{base}} < 4.5 \times 10^{-7}$ M, then
   a. water dissociation important
   b. solve using: $[\text{OH}^-]_{\text{TOT}}^2 - F_{\text{base}}[\text{OH}^-]_{\text{TOT}} - K_W = 0$

2. **Weak, monoprotic acids in water**

   (1) $\text{HA}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \leftrightarrow \text{H}_3\text{O}^+(\text{aq}) + \text{A}^-(\text{aq})$ \hspace{1cm} $K_a$

   (2) $2\text{H}_2\text{O}(\text{l}) \leftrightarrow \text{H}_3\text{O}^+(\text{aq}) + \text{OH}^-(\text{aq})$ \hspace{1cm} $K_W$

   $[\text{H}_3\text{O}^+]_{\text{TOT}} = [\text{H}_3\text{O}^+]_{\text{HA}} + [\text{H}_3\text{O}^+]_W$

**Both** equations involve equilibria that favor reactants. Will $[\text{H}_3\text{O}^+]_W$ be small compared to $[\text{H}_3\text{O}^+]_{\text{HA}}$? i.e., can we neglect $[\text{H}_3\text{O}^+]_W$? Just as for strong acids, it depends on the relative amounts produced by the two reactions…
**Weak Acid Rules**

1. If $K_{a_{acid}} \geq 1.0 \times 10^{-13}$, then
   a. water dissociation unimportant
   b. solve equilibrium problem

2. If $K_{a_{acid}} < 1.0 \times 10^{-13}$, then
   a. water dissociation important
   b. solve using: $[H_3O^+]_{TOT} = \sqrt{K_{a_{acid}} + K_W}$

The treatment is analogous for weak bases: $B(aq) + H_2O(l) \leftrightharpoons BH^+(aq) + OH^-(aq)$ $K_b$

**Weak Base Rules**

1. If $K_{b_{base}} \geq 1.0 \times 10^{-13}$, then
   a. water dissociation unimportant
   b. solve equilibrium problem

2. If $K_{b_{base}} < 1.0 \times 10^{-13}$, then
   a. water dissociation important
   b. solve using: $[OH^-]_{TOT} = \sqrt{K_{b_{base}} + K_W}$

---

**Solving the equilibrium problem of a weak acid/base in water may be more complicated than it first looks. The exact solution involves a system of four (nonlinear) equations in four unknowns!**

To simplify life, we can use a couple of chemically reasonable and mathematically convenient approximations.

**Example:** Calculate the pH of a solution prepared by dissolving 0.10 mol of acetic acid in enough water to make 1.0 L of solution. $K_a(CH_3COOH) = 1.8 \times 10^{-5}$.

**STEP 0. Check rules. Must water dissociation be included?**

**STEP 1. Write balanced chemical equation and $K$ expression; evaluate $Q$.**

**STEP 2. Evaluate magnitude of $K$.**
STEP 3. Add initial concentrations and changes in concentration (Δc) to get equilibrium concentrations.

STEP 4. Substitute into $K$ expression.

STEP 5. Solve.

STEP 6. Check assumptions. If % change is 5% or less, assumption is OK.

STEP 7. Check.
What if the 5% Rule assumption fails?
- Use quadratic formula
- Use successive approximations

e.g., What is the pH of a 0.10 F solution of chlorous acid? \( K_a(\text{HClO}_2) = 1.1 \times 10^{-2} \).

\[
K_a = \frac{[\text{H}_3\text{O}^+][\text{ClO}^-]}{[\text{HClO}_2]} \begin{array}{c|ccc|c}
(I) & \text{0.10} & "0" & 0 & \\
C & -\Delta c & +\Delta c & +\Delta c & \\
[E] & 0.10-\Delta c & \Delta c & \Delta c & \\
\end{array}
\]

\[K_a = 1.1 \times 10^{-2} = \frac{(\Delta c)(\Delta c)}{0.10-\Delta c} \approx \frac{(\Delta c)(\Delta c)}{0.10} \Rightarrow \Delta c = \sqrt{0.10(1.1 \times 10^{-2})} = 0.033 \text{ M} \rightarrow \% \text{ change} = 33%!!!\]

Using successive approximations: \( K_a = 1.1 \times 10^{-2} = \frac{(\Delta c')(\Delta c')}{0.10-\Delta c} = \frac{(\Delta c')^2}{0.10-0.033} \Rightarrow \Delta c' = 0.027 \text{ M} \)

Then another round: \( 1.1 \times 10^{-2} = \frac{(\Delta c'')(\Delta c'')}{0.10-\Delta c'} = \frac{(\Delta c'')^2}{0.10-0.027} \Rightarrow \Delta c'' = 0.028 \text{ M} \rightarrow \)

Further cycles give \( \Delta c = 0.028 \text{ M} \).

\[
\therefore [\text{H}_3\text{O}^+] = 0.028 \text{ M} \text{ and pH} = 1.55
\]

**Percent Dissociation**

\[
\% \text{ dissociation} = \frac{\text{amount dissociated}}{\text{initial concentration}} \times 100%
\]

e.g., from calculations above, 0.10 F acetic acid is 1.3% dissociated, and 0.10 F chlorous acid is 28% dissociated. (by contrast, a 0.10 F strong acid is 100% dissociated.)

Out of 1000 acetic acid molecules in a 0.10 F solution, 13 are dissociated and 987 of them are undissociated at any time. (1.3% or 0.013 \times 1000 = 13)

**Recap: Weak Monoprotic Acid Alone in Water**

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

\[
(I) \quad \text{F}_{\text{acid}} \quad 0 \quad 0 \quad 0
\]

\[
[C] \quad \text{F}_{\text{acid}}-\Delta c \quad \Delta c \quad \Delta c
\]

\[
K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = \frac{(\Delta c)(\Delta c)}{\text{F}_{\text{acid}}-\Delta c} \approx \frac{(\Delta c)(\Delta c)}{\text{F}_{\text{acid}}} \Rightarrow \Delta c = [\text{H}_3\text{O}^+] = \sqrt{K_aF_{\text{acid}}}
\]

\[
\therefore [\text{H}_3\text{O}^+] = [\text{A}^-] = \Delta c, \text{ and } [\text{HA}] = \text{F}_{\text{acid}} - \Delta c
\]

\[
pH = -\log[\text{H}_3\text{O}^+] \text{ (for a solution of an acid, should be <7 no matter how weak or dilute)}
\]

**Assumptions:**
- Water dissociation unimportant (i.e., \( [\text{H}_3\text{O}^+]_0 = "0" \))
- 5% Rule satisfied (i.e., \( \text{F}_{\text{acid}} - \Delta c \approx \text{F}_{\text{acid}} \))

**PROTIP**

Occasionally someone argues that they and their calculator can solve a weak acid equilibrium problem exactly without the simplifying assumptions/approximations. Good for them—they should still be able to do it the way above though.

Consider the equation from above for a solution of either a very weak acid or a very dilute solution: \( [\text{H}_3\text{O}^+]_{\text{TOT}} = \sqrt{K_aF_{\text{acid}} + K_w} \)

- Pure water: \( \text{F}_{\text{acid}} = 0 \) so \( [\text{H}_3\text{O}^+]_{\text{TOT}} = \sqrt{K_w} (1.0 \times 10^{-7} \text{ M} @ 25 \text{ °C}) \)
- Concentrated enough or strong enough acid to neglect water dissociation: drop \( K_w \) so \( [\text{H}_3\text{O}^+] = \sqrt{K_aF_{\text{acid}}} \) (as in box above)

Both bullets above are special cases of the first equation really.
**Diprotic Acids**

Diprotic acids have two ionizable protons that undergo successive ionization.

\[
\begin{align*}
\text{H}_2\text{A} + \text{H}_2\text{O} & \rightleftharpoons \text{H}_3\text{O}^+ + \text{HA}^- \\
\text{HA}^- + \text{H}_2\text{O} & \rightleftharpoons \text{H}_3\text{O}^+ + \text{A}^{2-}
\end{align*}
\]

\[
K_{a_1} = \frac{[\text{H}_3\text{O}^+][\text{HA}^-]}{[\text{H}_2\text{A}]} \\
K_{a_2} = \frac{[\text{H}_3\text{O}^+][\text{A}^{2-}]}{[\text{HA}^-]}
\]

In general, \( K_{a_1} \gg K_{a_2} \). (Harder to remove \( \text{H}^+ \) from something already negatively charged.) In this case, the two ionization reactions can be treated as occurring stepwise and we can proceed as follows:

- The calculation of \([\text{H}_3\text{O}^+], [\text{HA}^-], \) and \([\text{H}_2\text{A}]\) start exactly the same way as for monoprotic acids.
- From the first dissociation \( (K_{a_1}) \),
  - \([\text{H}_3\text{O}^+]_1 = [\text{HA}^-]_1 = \Delta c \) (solved using assumptions, successive approximations, or quadratic formula as needed) and
  - \([\text{H}_2\text{A}] = F_{\text{acid}} - [\text{H}_3\text{O}^+] \) (i.e., \( F_{\text{acid}} - \Delta c \) as above).
- Then, the second ionization step can be considered:
  \[
  \begin{align*}
  \text{HA}^- (aq) + \text{H}_2\text{O}(l) & \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{A}^{2-}(aq) \\
  \text{C} & \rightleftharpoons [\text{HA}^-]_1 + \Delta c \\
  [\text{E}] & \rightleftharpoons \frac{[\text{H}_3\text{O}^+]_1 + \Delta c}{[\text{HA}^-]_1 + \Delta c} = \frac{[\text{HA}^-]_1}{[\text{H}_2\text{A}]_1} = K_{a_2}
  \end{align*}
  \]

So, \([\text{H}_3\text{O}^+]_{\text{TOT}} \approx [\text{H}_3\text{O}^+]_1\)

\([\text{HA}^-]_{\text{TOT}} \approx [\text{HA}^-]_1\)

\([\text{H}_2\text{A}] = F_{\text{acid}} - [\text{H}_3\text{O}^+]\)

\([\text{A}^{2-}] = K_{a_2}\)

Same \([\text{H}_3\text{O}^+], [\text{HA}^-], \) and \([\text{H}_2\text{A}]\) as if only the first ionization were considered. The second ionization...

(1) uses up so little \( \text{HA}^- \) and (2) produces so little additional \( \text{H}_3\text{O}^+ \) ...that it doesn’t contribute significantly to those quantities.

### 3. Salts of weak, monoprotic acids in water

**conjugate pair**

- **HA(aq) + H₂O(l) ⇌ H₃O⁺(aq) + A⁻(aq)**
  \( K_a \) (acid)
- **A⁻(aq) + H₂O(l) ⇌ HA(aq) + OH⁻(aq)**
  \( K_b \) (conj. base)

For any conjugate acid-base pair, \( K_aK_b = K_W \)

As an acid gets stronger, its conjugate base gets weaker (and vice versa)

**Salts containing ions that hydrolyze (i.e., ionize in water)**

e.g., CH₃COONa contains CH₃COO⁻, the conjugate base of CH₃COOH (a weak acid), and Na⁺, the cation of NaOH (a strong base).

CH₃COO⁻ is basic. Na⁺ is not acidic. ∴ CH₃COONa solution is basic.

e.g., NH₄Cl contains NH₄⁺, the conjugate acid of NH₃ (a weak base), and Cl⁻, the conjugate base of HCl (a strong acid).

NH₄⁺ is acidic. Cl⁻ is not basic. ∴ NH₄Cl solution is acidic.
Quantitative treatment: Salt of a Weak, Monoprotic Acid in Water

(1) \( A^- (aq) + H_2O(l) \rightleftharpoons HA(aq) + OH^- (aq) \)
\[ K_b(A^-) = \frac{[HA][OH^-]}{[A^-]} \]

(2) \( 2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^- (aq) \)
\[ K_w \]

Salt of Weak Acid Rules
1. If \( K_{b_{salt}} \geq 1.0 \times 10^{-13} \), then
   a. water dissociation unimportant
   b. solve equilibrium problem
2. If \( K_{b_{salt}} < 1.0 \times 10^{-13} \), then
   a. water dissociation important
   b. solve using: \( [OH^-]_{TOT} = \sqrt{K_{b_{salt}} + K_w} \)

e.g., what is the pH of a 0.10 M solution of sodium acetate? (\( K_a \) of acetic acid = \( 1.8 \times 10^{-5} \).)

\[
\begin{align*}
CH_3COO^- : K_b &= \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10} \\
CH_3COO^- + H_2O &\rightleftharpoons CH_3COOH + OH^- \\
(1) &\text{ 0.10 M} \quad - \quad 0 \quad "O" \\
C &\quad -\Delta C \\
[E] &\quad 0.10 - \Delta C \\
\Delta C &\quad \Delta C \\
\Delta C &\quad \Delta C \\
K_b &= \frac{(\Delta C)(\Delta C)}{0.10 - \Delta C} \approx \frac{(\Delta C)^2}{0.10} = 5.6 \times 10^{-10} \\
\Delta C &= \sqrt{5.6 \times 10^{-10}} = 7.5 \times 10^{-6} M \\
[OH^-] &= \frac{5.6 \times 10^{-10}(0.10)}{5.6 \times 10^{-11}} > 10^{-13} \text{ so ignore water dissociation} \\
\text{Assumption OK} \quad \Rightarrow [OH^-] = 7.5 \times 10^{-6} M \\
[OH^-] &= 5.13 \\
pH &= 8.87
\end{align*}
\]

The treatment is analogous for salts of weak bases:

Salt of Weak Base Rules
1. If \( K_{a_{salt}} \geq 1.0 \times 10^{-13} \), then
   a. water dissociation unimportant
   b. solve equilibrium problem
2. If \( K_{a_{salt}} < 1.0 \times 10^{-13} \), then
   a. water dissociation important
   b. solve using: \( [H_3O^+]_{TOT} = \sqrt{K_{a_{salt}} + K_w} \)

Salts containing highly charged metal cations e.g., \( \text{AlCl}_3 \), \( \text{Fe(NO}_3)_3 \), \( \text{CrCl}_3 \)

\[
\begin{align*}
\text{Al(H}_2\text{O)}_6^{3+} + H_2O &\rightleftharpoons H_3O^+ + \text{Al(H}_2\text{O)}_5(OH)^{2+} \\
\text{ }^{3+} &\quad \text{H}_2\text{O} \quad \text{H}_2\text{O} \quad \text{H}_2\text{O} \\
\text{Al} &\quad \text{H}_2\text{O} \quad \text{H}_2\text{O} \quad \text{H}_2\text{O} \\
\text{ }^{2+} &\quad \text{H}_2\text{O} \quad \text{H}_2\text{O} \quad \text{H}_2\text{O}
\end{align*}
\]

\( K_a = 1.0 \times 10^{-5} \) (similar \( K_a \) to acetic acid!)
Reminder about effect of molecular structure on oxoacid strength
More electron-withdrawing character in the rest of the molecule will polarize the O–H bond more greatly, causing the acid strength to increase.

On rest of molecule...
- more oxygen atoms
- more electronegative central atom
- added electron-withdrawing groups
- highly charged aquated metal ion

O–H bond more polarized; 
increase in acid strength

Salts, Conjugate acid-base pairs, and Drugs
Many drugs are formulated as salts since water solubility of a salt is often greater than that of a neutral covalent compound. e.g., “pseudoephedrine HCl” means that the compound is present as the chloride salt of its conjugate acid. Many compounds with amine groups are prepared as “hydrochlorides” this way. Many weakly acidic compounds are prepared as the sodium salts of their conjugate bases (e.g., naproxen sodium).

WARNING! DO NOT do the following acid-base chemistry at home. It is illegal and harmful.

Salt of a Weak Acid and a Weak Base
e.g., Would a solution of methylammonium benzoate, CH₃NH₃C₆H₅COO, be acidic or basic?

contains CH₃NH₃⁺ and C₆H₅COO⁻ ions

CH₃NH₃⁺ = conjugate acid of CH₃NH₂ (Kₗ = 4.4 × 10⁻⁴)

\[
K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{4.4 \times 10^{-4}} = 2.3 \times 10^{-11}
\]

C₆H₅COO⁻ = conjugate base of C₆H₅COOH (Kₗ = 6.3 × 10⁻⁵)

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

The same principle would apply to determining whether an amphoteric species (such as HCO₃⁻) is acidic or basic in solution. Calculate its Kₐ and Kₗ, and the larger value would rule.
4. Weak, monoprotic acid + salt of the weak acid

- **Buffer solution**: resists change in pH when small amounts of acid or base are added

It’s easy (relatively) to transform the $K_a$ expression to relate pH to the ratio of $A^-$ to $HA$:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

$$\log K_a = \log [H_3O^+] + \log \frac{[A^-]}{[HA]}$$

$$K_a = [H_3O^+] \frac{[A^-]}{[HA]}$$

$$\log K_a = \log \left( \frac{[H_3O^+][A^-]}{[HA]} \right)$$

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

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

**Henderson-Hasselbach Equation**

*Add OH$^-$ to a buffer*: some $H_3O^+$ reacts to consume it.

$$[A^-] \uparrow; [HA] \downarrow; \frac{[A^-]}{[HA]} \text{ increases; pH increases slightly}$$

*Add $H_3O^+$ to a buffer*: some $A^-$ reacts to consume it.

$$[A^-] \downarrow; [HA] \uparrow; \frac{[A^-]}{[HA]} \text{ decreases; pH decreases slightly}$$

¡¡¡Relative amounts of $HA$ and $A^-$ are important!!! Large amounts of $HA$ and $A^-$ will keep relative changes small when small amounts of acid or base are added.

**Buffer capacity**: measure of the ability of a buffer to resist pH change—the amount of acid/base a buffer can “absorb” without “significant” change in pH—usually defined as ±1 pH unit, “buffer range”

**Optimal buffering occurs when $[A^-] = [HA]$.**

- When $[A^-] = [HA]$, solution will buffer equally well against addition of acid or base.
- If not equal, the buffer will be better against either acid or base than the other.

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

so if $[A^-] = [HA]$, then $pH = pK_a$.

e.g., if you want a pH 4 buffer with $[A^-] = [HA]$, you need to find an acid with $pK_a = 4$, i.e., $K_a = 10^{-4}$.

**A Buffer Prepared with a Base and its Conjugate Acid**

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

$$pOH = pK_b + \log \frac{[BH^+]}{[B]}$$

e.g., if you want a pH 10 buffer with $[BH^+] = [B]$, you need to find a base with $pK_b = 4$, i.e., $K_b = 10^{-4}$.

¡¡¡**CAUTION!!!**

It is NOT necessarily true that a “basic buffer” (a buffer solution with pH >7) must be made with a weak base and its conjugate acid. For example, if you used equal concentrations of $HA$ and $A^-$ where $HA$ had $K_a = 1.0 \times 10^{-8}$, then the pH of that buffer would be 8.00.
Titration Curves

- **end point**: where the indicator changes color in a titration
- **equivalence point**: where exactly enough base (acid) has been added to react with the acid (base) originally present in a titration.

Ideally, the end point and equivalence point are reached at the same time in your titration.

**Weak Acid/Strong Base titration**

\[
\begin{align*}
HA(aq) + H_2O(l) &\leftrightarrow H_3O^+(aq) + A^-(aq) \\
H_3O^+(aq) + OH^-(aq) &\rightarrow 2H_2O(l) \\
HA(aq) + OH^-(aq) &\rightarrow H_2O(l) + A^-(aq)
\end{align*}
\]

- **pH at equivalence point > 7.0**
  At equivalence point, solution contains water, the cation of the strong base, and the anion of the weak acid (its conjugate base). The anion of a weak acid is basic, so the pH at the equivalence point is > 7.

- **buffer region**

- **Half-equivalence point**
  at “half-titration” (i.e., \( V_{\text{BASE}} = \frac{1}{2} V_{\text{EP}} \)), half of the original acid has been converted to its conjugate base (i.e., \([A^-] = \frac{1}{2}[HA]_o \)). Thus \([A^-] = [HA] \) here, so at this point, \( pH = pK_a \) of the weak acid.

![Fig. 19.7; “HPr” = CH₃CH₂COOH, propionic acid HPr + OH⁻ → H₂O + Pr⁻ (Na⁺ = spectator)](image)

**Lewis Acid-Base Model**

- **Lewis acid**: a substance that accepts a pair of electrons.
- **Lewis base**: a substance that donates a pair of electrons.

All Arrhenius/Brønsted acids are Lewis acids (ditto for bases) (but not the other way around)