Gas-Liquid Equilibrium

- Alkalinity contributions by acidic or basic gases
  - Adding a weak base via gas dissolution is no different from adding it in some other way
  - $\text{H}_2\text{CO}_3$ addition or removal from solution has no effect on Alk, so dissolution or evolution of CO$_2$ also has no effect on Alk. Note that this result is independent of the solution pH. (The contribution of a species to pH always depends on the composition of what is added and the composition at the Alk endpoint, not on the speciation at intermediate times.)

Example: Waters A (pH 9.50) and B (pH 7.30) are both in equilibrium with the atmosphere and are then mixed 1:1 without gas exchange. CO$_2$ species control pH.

(a) What are TOTCO$_3$, Alk, and TOTH of each solution and of the mixture? Use CO$_3^{2-}$ as a component for computing TOTH.

(b) What are the pH and the composition of the mixture?

(c) How much and in what direction is CO$_2$ exchange as the mixture equilibrates with the atmosphere?

<table>
<thead>
<tr>
<th>(H$^+$)</th>
<th>(OH$^-$)</th>
<th>(H$_2$CO$_3$)</th>
<th>(HCO$_3^-$)</th>
<th>(CO$_3^{2-}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>10$^{-9.50}$</td>
<td>10$^{-4.50}$</td>
<td>1.29x10$^{-4}$</td>
<td>1.82x10$^{-2}$</td>
</tr>
<tr>
<td>B</td>
<td>10$^{-7.30}$</td>
<td>10$^{-6.70}$</td>
<td>1.29x10$^{-4}$</td>
<td>1.15x10$^{-4}$</td>
</tr>
</tbody>
</table>

TOTCO$_3$, Alk, and TOTH are all conservative quantities, so their values in the mixture are just weighted averages of their values in the two solutions.

<table>
<thead>
<tr>
<th></th>
<th>TOTCO$_3$ (meq/L)</th>
<th>Alk (meq/L)</th>
<th>TOTH</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2.09x10$^{-2}$</td>
<td>23.6</td>
<td>1.82x10$^{-2}$</td>
</tr>
<tr>
<td>B</td>
<td>1.28x10$^{-4}$</td>
<td>0.115</td>
<td>1.40x10$^{-4}$</td>
</tr>
<tr>
<td>Mix</td>
<td>1.05x10$^{-2}$</td>
<td>1.19x10$^{-2}$</td>
<td>9.16x10$^{-3}$</td>
</tr>
</tbody>
</table>
Value of TOTCO₃ is embedded in the log c – pH diagram. Satisfying the Alk equation is an alternative (to satisfying the CB, TOTH, or PC equation) for finding the equilibrium pH of a solution, e.g., for the mixture of A and B:

Equilibrium composition of the original solutions and the mixture before any CO₂ exchange

<table>
<thead>
<tr>
<th></th>
<th>TOTCO₃ (meq/L)</th>
<th>Alk (meq/L)</th>
<th>TOTH (meq/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2.09x10⁻²</td>
<td>23.6</td>
<td>1.82x10⁻²</td>
</tr>
<tr>
<td>B</td>
<td>1.28x10⁻⁴</td>
<td>0.115</td>
<td>1.40x10⁻⁴</td>
</tr>
<tr>
<td>Mix</td>
<td>1.05x10⁻²</td>
<td>1.19x10⁻²</td>
<td>9.16x10⁻³</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>(H⁺)</th>
<th>(OH⁻)</th>
<th>(H₂CO₃⁻)</th>
<th>(HCO₃⁻)</th>
<th>(CO₃²⁻)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>10⁻⁵.28</td>
<td>10⁻⁴.51</td>
<td>1.29x10⁻⁵</td>
<td>1.82x10⁻³</td>
<td>2.70x10⁻³</td>
</tr>
<tr>
<td>B</td>
<td>10⁻⁷.38</td>
<td>10⁻⁶.70</td>
<td>1.29x10⁻⁵</td>
<td>1.15x10⁻⁴</td>
<td>1.07x10⁻⁷</td>
</tr>
<tr>
<td>Mix</td>
<td>10⁻⁹.49</td>
<td>10⁻⁸.11</td>
<td>6.71x10⁻⁶</td>
<td>9.18x10⁻³</td>
<td>1.32x10⁻³</td>
</tr>
</tbody>
</table>

(c) How much and in what direction is CO₂ exchange as the mixture equilibrates with the atmosphere?

We know the ‘initial’ solution composition (after mixing, but before equilibration with the atmosphere).

We don’t know how much CO₂ exchange occurs, so we analyze the system using H₂CO₃ as a component. In that case, CO₂ exchange does not affect TOTH. We can therefore compute TOTHₐₙ and assign that value to TOTHₑₐₚ.
**Input Parameters for Gases in Visual Minteq**

- Like other species, input parameters for gaseous species are stoichiometry and log K for forming the species from components

\[
\begin{align*}
2 \text{H}^+ + \text{CO}_3^{2-} & \rightleftharpoons \text{CO}_2(g) + \text{H}_2\text{O} \\
K &= \text{??}
\end{align*}
\]

\[
\begin{align*}
2 \text{H}^+ + \text{CO}_3^{2-} & \rightleftharpoons \text{H}_2\text{CO}_3 \\
\text{H}_2\text{CO}_3 & \rightleftharpoons \text{CO}_2(g) + \text{H}_2\text{O} \\
2 \text{H}^+ + \text{CO}_3^{2-} & \rightleftharpoons \text{CO}_2(g) + \text{H}_2\text{O} \\
K &= 10^{16.68} \\
K &= 10^{14.47} \\
K &= 10^{14.47} = 10^{18.11}
\end{align*}
\]

**Using Visual Minteq to Determine Composition of Solutions Equilibrated with Gases**

Example: Waters A (pH 9.5) and B (pH 7.3) are both in equilibrium with the atmosphere and are then mixed 1:1 without gas exchange. CO\(_3\) species control pH.

(a) What are TOT\(_{CO_3}\) and Alk of each solution and of the mixture?

(b) What are the pH and the composition of the mixture?

(c) How much and in what direction is CO\(_2\) exchange as the mixture equilibrates with the atmosphere?

- pH specified by user (7.3 or 9.5)
- Gases/ Specify fixed CO\(_2\) partial pressure (0.00038 atm x 1.0)
Output: Equilibrium Species at pH 7.3 (all calculations at I = 0)

Visual Minteq Input and Output for Mixture Prior to Equilibration with Atmospheric CO₂

**Input**
- pH calculated by mass balance, no Fixed species
- TOTAL CO₃(2-) = (1.278e-4 + 2.090e-2)/2 = 1.0511e-2
- TOTAL H(+) = (1.4048e-4 + 1.8182e-2)/2 = 9.1612e-3

**Output**
- pH = 9.495
- H₂CO₃ = 6.71e-6 (undersaturated, CO₂ will dissolve)

Output: Equilibrium Species at pH 9.5 (all calculations at I = 0)

Visual Minteq Input and Output for Mixture after Equilibration with Atmosphere

**Input**
- pH calculated by mass balance
- CO₂ as Fixed species, log P(CO₂) = -3.48
- TOTAL CO₃ = 1.0511e-2
- TOTAL H(+) = 9.1612e-3

**Output**
- pH = 9.247
- TOTAL CO₃: 1.0511e-2
- TOTAL H(+): 9.1612e-3

**Offline calculations**
- pH = 9.247
- ΔTOTAL CO₃: +5.00e-4
- ΔTOTAL H(+): +1.07e-3
Aqueous Chemistry of Metals

What are metals?
When considering the solid state, metals are defined by the presence of highly mobile electrons, which make the metals electrically conductive.

In aqueous systems, metals are cations that have a significant attraction for unshared electrons (e.g., those at two of the corners of the water tetrahedron).

Oxidation number or state
("di-, tri-, hexa-valent," etc.)

How do metal ions interact with water?
Inner and outer hydration spheres
Free metal ions
Hydrolysis, acidity, etc.
Ligands
Coordination number
Complexation
Stability constant
Chelate
Aqueous Chemistry of Metals

**How do metal ions interact with water and/or OH⁻?**

**Stability constants for Hydrolysis**

- \( \text{Cd}^{2+} + \text{OH}^- \leftrightarrow \text{CdOH}^+ \quad K_1 \)
- \( \text{Cd}^{2+} + \text{H}_2\text{O} \leftrightarrow \text{CdOH}^+ + \text{H}^+ \quad *K_1 (=K_J) \)
- \( \text{Cd}^{2+} + 2 \text{OH}^- \leftrightarrow \text{Cd(OH)}_2^0 \quad \beta_2 \)

**How do metal ions interact with other solutes?**

**Stability constants for complexation with Chloride**

- \( \text{Cd}^{2+} + \text{Cl}^- \leftrightarrow \text{CdCl}^+ \quad K_1 \)
- \( \text{Cd}^{2+} + 2 \text{Cl}^- \leftrightarrow \text{CdCl}_2^0 \quad \beta_2 \)