Example. What are the pH and composition of a solution made of $10^{-2.7}$ NaAc + $10^{-3.7}$ NaHCO$_3$, which then equilibrates with atmospheric CO$_2$?

Initial solution (prior to contact with gas), using HCO$_3^-$ and Ac$^-$ as components:

<table>
<thead>
<tr>
<th></th>
<th>H$_2$O</th>
<th>H$^+$</th>
<th>HCO$_3^-$</th>
<th>Ac$^-$</th>
<th>Na$^+$</th>
<th>log K</th>
<th>Conc'n</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.00</td>
<td>0</td>
</tr>
<tr>
<td>H$^+$</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.00</td>
<td>0</td>
</tr>
<tr>
<td>HCO$_3^-$</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>Ac$^-$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>Na$^+$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>OH$^-$</td>
<td>1</td>
<td>-1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-14.00</td>
<td></td>
</tr>
<tr>
<td>HAc</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>4.74</td>
<td></td>
</tr>
<tr>
<td>H$_2$CO$_3$</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>6.35</td>
<td></td>
</tr>
<tr>
<td>CO$_3^{2-}$</td>
<td>-1</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-10.33</td>
<td></td>
</tr>
</tbody>
</table>

Inputs:
- NaAc: $10^{-2.7}$
- NaHCO$_3$: $10^{-3.7}$

Initial Solution Composition:

\[
0 + 0 = (H^+)_{eq} + (HAc)_{eq} + (H_2CO_3)_{eq} - (OH^-)_{eq} - (CO_3^{2-})_{eq}
\]

\[
(H^+) + (HAc) + (H_2CO_3) = (OH^-) + (CO_3^{2-})
\]

Gas-Liquid Equilibrium:

Log c – pH Diagram After Equilibration with Atmosphere:

\[
0 + 0 + 1(??) = (H^+)_{eq} + (HAc)_{eq} + (H_2CO_3)_{eq} - (OH^-)_{eq} - (CO_3^{2-})_{eq}
\]

\[
(H^+)_{eq} + (HAc)_{eq} + (H_2CO_3)_{eq} = (OH^-)_{eq} + (CO_3^{2-})_{eq} + ??
\]
Same system, but using $\text{H}_2\text{CO}_3$ and $\text{Ac}^-$ as components

<table>
<thead>
<tr>
<th></th>
<th>$\text{H}_2\text{O}$</th>
<th>$\text{H}^+$</th>
<th>$\text{H}_2\text{CO}_3$</th>
<th>$\text{Ac}^-$</th>
<th>$\text{Na}^+$</th>
<th>log $K$</th>
<th>Conc'n</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{O}$</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>$\text{H}^+$</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>$\text{H}_2\text{CO}_3$</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0.00</td>
<td>1.29x10^{-5}</td>
</tr>
<tr>
<td>$\text{Ac}^-$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>$\text{Na}^+$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>$\text{OH}^-$</td>
<td>1</td>
<td>-1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-14.00</td>
<td></td>
</tr>
<tr>
<td>$\text{HAc}$</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>4.74</td>
<td></td>
</tr>
<tr>
<td>$\text{HCO}_3^-$</td>
<td>0</td>
<td>-1</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>-6.35</td>
<td></td>
</tr>
<tr>
<td>$\text{CO}_3^{2-}$</td>
<td>0</td>
<td>-2</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>-16.68</td>
<td></td>
</tr>
</tbody>
</table>

Inputs
- NaAc: $0$ $0$ $0$ $1$ $1$ $10^{-2.7}$
- NaHCO$_3$: $0$ $-1$ $1$ $0$ $1$ $10^{-3.7}$
- $\text{H}_2\text{CO}_3$: $0$ $0$ $1$ $0$ $0$ $?$

0 + (-1)10^{-3.7} + 0 = (\text{H}^+) + (\text{HAc}) - (\text{OH}^-) - (\text{HCO}_3^-) - 2(\text{CO}_3^{2-})

$(\text{H}^+) + (\text{HAc}) + 10^{-3.7} = (\text{OH}^-) + (\text{HCO}_3^-) + 2(\text{CO}_3^{2-})$

**Gas-Liquid Equilibrium**

- At initial condition, $(\text{H}_2\text{CO}_3) = 10^{-5.4}$, so solution was undersaturated, and CO$_2$ dissolved when the solution equilibrated with the atmosphere.
- Final composition could have been found directly; determination of initial composition was informative, but not necessary.
- Amount of CO$_2$ that dissolved can be computed as $\text{TOTCO}_3_{\text{fin}} - \text{TOTCO}_3_{\text{init}} = 6.0 \times 10^{-4}$ mol/L.
- If the amount of a species that enters or leaves solution is unknown, that uncertainty can be circumvented by choosing the species as a component in the TOTH equation.

**Gas-Liquid Equilibrium**

- Buffering by acidic or basic gases
  - When an acid is added to a solution containing an acidic neutral volatile species (e.g., CO$_2$), the conjugate base (HCO$_3^-$) is converted to the acid, causing the acid to become supersaturated and evolve out of solution. If a base is added, the opposite reaction occurs, and the gaseous acid dissolves. If the dissolved neutral volatile species is a base (e.g., NH$_3$), the reverse occurs.
  - In any of the above scenarios (acid or base added, acidic or basic volatile species), the net effect is that gas transfer partially counteracts acid or base addition. Therefore, the dissolved volatile species acts as a buffer.
  - The buffer intensity depends on the details of H and pH, which establish how much gas transfer occurs for a given change in pH.
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 \( \text{CO}_2 \) 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.)