Solubility of gases in water: Henry’s Law

- concentration dissolved \(\alpha\) partial pressure of the gas

\[
K_H \text{ (units mol } L^{-1} \text{ atm}^{-1}) = \frac{c_X}{p_X}
\]

Large \(K_H\) means high solubility; \(K_H\) always decreases with \(T\); gases less soluble at higher \(T\) (all gases, all solvents)

**Henry’s law constants at 298 K:** \(K_H\) in mol \(L^{-1}\) atm\(^{-1}\) from Seinfeld and Pandis, *Atmospheric Chemistry and Physics*, Wiley, 1998 p. 341; values do not include subsequent reactions of the dissolved species, such as acid dissociation.

<table>
<thead>
<tr>
<th>Substance</th>
<th>(K_H)</th>
<th>Substance</th>
<th>(K_H)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(_2)</td>
<td>(1.3 \times 10^{-3})</td>
<td>NO</td>
<td>(1.9 \times 10^{-3})</td>
</tr>
<tr>
<td>NO(_2)</td>
<td>(1.2 \times 10^{-2})</td>
<td>O(_3)</td>
<td>(1.13 \times 10^{-2})</td>
</tr>
<tr>
<td>N(_2)O</td>
<td>(2.5 \times 10^{-2})</td>
<td>CO(_2)</td>
<td>(3.4 \times 10^{-2})</td>
</tr>
<tr>
<td>H(_2)S</td>
<td>0.12</td>
<td>SO(_2)</td>
<td>1.23</td>
</tr>
<tr>
<td>CH(_3)ONO(_2)</td>
<td>2.6</td>
<td>CH(_3)O(_2)</td>
<td>6</td>
</tr>
<tr>
<td>OH</td>
<td>25</td>
<td>HNO(_2)</td>
<td>49</td>
</tr>
<tr>
<td>NH(_3)</td>
<td>62</td>
<td>CH(_3)OH</td>
<td>220</td>
</tr>
<tr>
<td>CH(_3)OOH</td>
<td>230</td>
<td>HCl</td>
<td>730</td>
</tr>
<tr>
<td>HO(_2)</td>
<td>2000</td>
<td>CH(_3)COOH</td>
<td>8800</td>
</tr>
<tr>
<td>H(_2)O(_2)</td>
<td>75,000</td>
<td>HNO(_3)</td>
<td>200,000</td>
</tr>
</tbody>
</table>

**Note:** Environment Canada quotes \(K_H\) in the reverse direction (escape from water): units Pa m\(^3\) mol\(^{-1}\), hence large \(K_H\) \(\rightarrow\) low water solubility.
Solubility of O\textsubscript{2} in water – context is whether water will support aquatic life

\[ K_H = 1.3 \times 10^{-3} \text{ mol L}^{-1} \text{ atm}^{-1} \text{ at equilibrium, at } 25^\circ C \]

\[ \rightarrow c(O_2) = 2.7 \times 10^{-4} \text{ mol } / \text{L} \]

\[ \rightarrow 8.7 \text{ mg/L} \text{ (8.7 ppm)} \]

Note definition of ppm for solids and solutions (by mass)

- \( c(O_2) < 8.7 \text{ ppm} \):
  - at higher temperatures (thermal pollution)
  - if decaying or oxidizable material consumes O\textsubscript{2} –> concept of biochemical oxygen demand (BOD)
  - water is stagnant (reduced air exchange)

Measures of the oxygen status of water

- BOD; incubate with microorganisms for 5 days in closed container, measure \( c(O_2) \) before and after
- Chemical Oxygen Demand (COD) – titrate the sample vs excess Na\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7}/H\textsuperscript{+}; easily oxidized substances consume Na\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7}; determine the amount of Na\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7} left over; 1 mol Na\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7} \( \approx 1.5 \text{ mol } O_2 \)
- Total Organic Carbon (TOC) – oxidize the organic compounds to CO\textsubscript{2} by combustion; analyze CO\textsubscript{2} produced
- Dissolved Oxygen (DO) – often done by titration:

\[
\begin{align*}
\text{Mn}^{2+} + 2\text{OH}^- + \frac{1}{2}\text{O}_2 & \rightarrow \text{MnO}_2(s) + \text{H}_2\text{O} \\
\text{MnO}_2 + 4\text{H}^+ + 2\text{I}^- & \rightarrow \text{I}_2 + \text{Mn}^{2+} + 2\text{H}_2\text{O} \\
\text{I}_2 + \text{Na}_2\text{S}_2\text{O}_3 & \rightarrow \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaI}
\end{align*}
\]
CO₂ solubility in water

- More complex than O₂ because CO₂(aq) ≡ H₂CO₃(aq), which can dissociate through acid-base equilibria
  \[ \text{CO}_2(g) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{CO}_3(aq) \]
  \[ K_H = 3.4 \times 10^{-2} \text{ mol L}^{-1} \text{ atm}^{-1} \]
  \[ \text{H}_2\text{CO}_3(aq) \rightleftharpoons \text{H}^+(aq) + \text{HCO}_3^-(aq) \]
  \[ K_a = 4.2 \times 10^{-7} \text{ mol L}^{-1} \]

- Note that in carrying out calculations, the concentrations of CO₂(g) and H₂CO₃(aq) do not change, because the atmosphere is an inexhaustible reservoir

- Total “dissolved carbonate” = \{H₂CO₃(aq) + HCO₃⁻(aq) + CO₃²⁻(aq)\}: increases with increasing pH

Calculation of the solubility of CO₂ in pure water

- \( p(\text{CO}_2, \text{g}) = 375 \text{ ppmv} \rightarrow c(\text{CO}_2, \text{aq}) = 1.3 \times 10^{-5} \ \text{mol/L} \)

- for \( K_a = [\text{H}^+][\text{HCO}_3^-]/[\text{H}_2\text{CO}_3] = 4.2 \times 10^{-7} \ \text{mol/L} \ (25°C) \)

\[ [\text{H}^+][\text{HCO}_3^-] = x^2 = K_a [\text{H}_2\text{CO}_3] \]
\[ = (1.3 \times 10^{-5} \ \text{mol/L})(4.2 \times 10^{-7} \ \text{mol/L}) \]
\[ \ x = 2.3 \times 10^{-6} \ \text{mol/L} \]

\( \text{pH} = 5.63; \)
\( \text{total “carbonate”} = \{1.3 \times 10^{-5} + 2.3 \times 10^{-6} \ \text{mol/L}\} \)
\[ = 1.5 \times 10^{-5} \ \text{mol/L} \]

- Even completely clean water in equilibrium with atmospheric CO₂ does not have pH = 7!! Keep this thought for discussion of acid rain.
When the pH of the water is fixed by the presence of other solutes:
- total dissolved carbonate increases as pH rises

- Note the speciation of carbonate
**Alkalinity** of water is a measure of the concentration of all bases in the water, **not** its pH, which is determined largely by the strongest base present: text pp. 140-142

- Alkalinity is measured by titrating the water against standard acid = moles/concentration of H⁺ needed to neutralize the bases
- Phenolphthalein alkalinity is the amount of acid needed to reach the phenolphthalein endpoint (pH 8.5) **remembering that titration is from high to low pH**
- Total alkalinity is the amount of acid needed to reach the methyl orange endpoint (pH 4)
- If there are no other bases present (as in *e.g.*, industrial waste water), the phenolphthalein endpoint measures mostly CO₃²⁻; the methyl orange endpoint measures CO₃²⁻ + HCO₃⁻

- Two measurements to determine both CO₃²⁻ and HCO₃⁻:
  - both total and phenolphthalein alkalinity **or**
  - one of the above plus pH —> ratio [CO₃²⁻]/[HCO₃⁻]
**Hardness** of water is a measure of the concentration of “hardness ions” (mainly Ca$^{2+}$ and Mg$^{2+}$) that form insoluble salts, especially carbonates: text, pp. 142-146.

**Analysis of hardness ions:**
- titration vs EDTA$^{4-}$ using Eriochrome Black T indicator (Ca only)
- atomic absorption spectroscopy

**Origin of hardness ions:**
- dissolution of gypsum
  \[
  \text{CaSO}_4(s) \rightleftharpoons \text{Ca}^{2+}(aq) + \text{SO}_4^{2-}(aq)
  \]
- dissolution of limestone rocks: \text{CaCO}_3 \text{ (limestone)}; \text{CaCO}_3\cdot\text{MgCO}_3 \text{ (dolomite)}

**NOT** \text{MCO}_3(s) \rightleftharpoons \text{M}^{2+}(aq) + \text{CO}_3^{2-}(aq)

**BUT** \text{MCO}_3(s) + \text{H}_2\text{CO}_3(aq) \rightleftharpoons \text{M}^{2+}(aq) + 2\text{HCO}_3^-(aq)

- Note that underground, $p(\text{CO}_2)$ is often much greater than 370 ppmv
- In what follows, note the text, footnote 8, p. 143 about $K_{sp}$ calculations!!

\[
\begin{align*}
\text{CaSO}_4 & \quad K_{sp} = 4 \times 10^{-5} \text{ (mol L}^{-1})^2 \\
\text{CaCO}_3 & \quad K_{sp} = 6 \times 10^{-9} \text{ (mol L}^{-1})^2 \\
\frac{1}{2}\text{CaCO}_3\cdot\text{MgCO}_3 & \quad K_{sp} = 5 \times 10^{-7} \text{ (mol L}^{-1})^2
\end{align*}
\]
Dissolution of CaCO₃

\[
\begin{align*}
\text{CaCO}_3(s) & \rightleftharpoons \text{Ca}^{2+}(aq) + \text{CO}_3^{2-}(aq) & K_{sp} \\
\text{H}_2\text{CO}_3(s) & \rightleftharpoons \text{H}^+(aq) + \text{HCO}_3^-(aq) & K_{a1} \\
\text{H}^+(aq) + \text{CO}_3^{2-}(aq) & \rightleftharpoons \text{HCO}_3^-(aq) & \frac{1}{K_{a2}}
\end{align*}
\]

Net: \( \text{CaCO}_3(s) + \text{H}_2\text{CO}_3(aq) \rightleftharpoons \text{Ca}^{2+}(aq) + 2\text{HCO}_3^-(aq) \)

or: \( \text{CaCO}_3(s) + \text{H}_2\text{CO}_3(aq) \rightleftharpoons \text{Ca(HCO}_3^2)(aq) \)

- \( K \) for net reaction = \( K_{sp} \times \frac{K_{a1}}{K_{a2}} = 5 \times 10^{-5} \) (mol L⁻¹)²
- when expressed as “ppm of CaCO₃”, values up to 300 ppm are obtained in hard water areas

**Hard water**: contains hardness ions: usually limestone areas e.g., southern Ontario

**Soft water**: low concentrations of hardness ions: sandstone and granite areas e.g., northern and eastern Ontario

All water must have a **balance of cations and anions**; ∴ hard water is usually well buffered against acidification —→ relatively high concentrations of weak bases

*Thus alkalinity is a measure of buffering capacity; high alkalinity usually correlates with high hardness*
**Water Softening:** critical application for steam boilers due to deposition of salts

When hard water is heated:

$$\text{Ca(HCO}_3\text{)}_2 \text{(aq)} \rightleftharpoons \text{CaCO}_3\text{(s)} + \text{H}_2\text{CO}_3\text{(aq)} \rightarrow \text{CO}_2\text{(g)}$$

Water softening is the process of removing hardness ions

1. **Lime Softening** (industrial use only): neutralize $\text{HCO}_3^-\text{ with OH}^-$

   $$\text{Ca(OH)}_2\text{(aq)} + \text{Ca(HCO}_3\text{)}_2\text{(aq)} \rightleftharpoons \text{CaCO}_3\text{(s)} + 2\text{H}_2\text{O}$$

2. **Ion exchange resins**, *e.g.*, $\text{Na(}A\text{)}$ where $(A) =$ polymeric anion – example of $\text{Ca}^{2+}\text{ removal through cation exchange}$

   $$\text{Ca}^{2+}\text{(aq)} + 2\text{Na}(A)_{\text{res}} \rightleftharpoons 2\text{Na}^+\text{(aq)} + \text{Ca}(A_2)_{\text{res}}$$

Resin regeneration with concentrated brine:

   $$2\text{Na}^+\text{(aq)} + \text{Ca}(A_2)_{\text{res}} \rightleftharpoons \text{Ca}^{2+}\text{(aq)} + 2\text{Na}(A)_{\text{res}}$$

3. **Deionized water:** cation and anion exchangers in series, using $\text{H}^+$ form of the cation exchanger and $\text{OH}^-$ form of the anion exchanger – example of $\text{CaSO}_4$

   $$\text{Ca}^{2+}\text{(aq)} + 2\text{H}(A)_{\text{res}} \rightleftharpoons 2\text{H}^+\text{(aq)} + \text{Ca}(A_2)_{\text{res}}$$

   $$\text{SO}_4^{2-}\text{(aq)} + 2(C)\text{OH}_{\text{res}} \rightleftharpoons 2\text{OH}^-\text{(aq)} + (C_2)\text{SO}_4_{\text{res}}$$

Hence:

$$2\text{H}^+\text{(aq)} + 2\text{OH}^-\text{(aq)} \rightarrow 2\text{H}_2\text{O}$$

• Regeneration of the resin beds????
Seawater: a solution of high ionic strength. The main environment we will encounter where activities must be used rather than concentrations.

<table>
<thead>
<tr>
<th>Ion</th>
<th>conc, mol/L</th>
<th>input, Tmol/yr</th>
<th>τ, Myr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>0.46</td>
<td>9.0</td>
<td>70</td>
</tr>
<tr>
<td>K⁺</td>
<td>0.010</td>
<td>1.9</td>
<td>7</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>0.054</td>
<td>5.5</td>
<td>10</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>0.010</td>
<td>12.2</td>
<td>1</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>0.55</td>
<td>7.2</td>
<td>100</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>0.028</td>
<td>3.8</td>
<td>10</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>0.0023</td>
<td>32</td>
<td>0.1</td>
</tr>
<tr>
<td>CO₃²⁻</td>
<td>0.0003</td>
<td>included with HCO₃⁻</td>
<td></td>
</tr>
</tbody>
</table>

• Ocean water approximately in equilibrium with CaCO₃, but $Q_{sp} = [Ca^{2+}][CO_3^{2-}] >> K_{sp}$: text, p. 150

• First reason: $a(Ca^{2+})$ and $a(CO_3^{2-}) < [Ca^{2+}][CO_3^{2-}]$, i.e., $\gamma(Ca^{2+}) \sim 0.26$; $\gamma(CO_3^{2-}) \sim 0.20$

• Second reason: complexation: formation of species such as:
  
  (CaSO₄): 8% of total Ca; (CaHCO₃)⁺: 1% of total Ca

  (MgCO₃): 64% of total CO₃; (NaCO₃)⁻: 19% of total CO₃; (CaCO₃): 7% of total CO₃
Properties of Water

- Amounts on Earth:
  - Oceans, \( \sim 10^{20} \) mol
  - Rivers and lakes, \( \sim 10^{15} \) mol

Freezing point depression

- Solutes depress the freezing point of water

\[
\Delta T = K_f \times m
\]

- \( K_f \) = molal freezing point depression constant, units K kg mol\(^{-1}\)
- \( m \) = molal concentration of solute, mol kg\(^{-1}\)

- The freezing point depression is independent of the identity of the solute. For ionic solutes consider all the ions separately, e.g., for NaCl there are two solutes to consider, Na\(^+\) and Cl\(^-\)

- Applications:
  - road salt
  - trees in winter, fish in polar oceans
  - (laboratory): determining molar mass
Osmosis and Reverse Osmosis

• osmotic pressure \( \pi = c \times RT \)  
  \( c \) in mol L\(^{-1}\)  
  \( R \) in L atm mol\(^{-1}\) K\(^{-1}\)  
  \( \pi \) in atm

• osmotic pressure independent of the solute identity

• applications  
  - water rise in trees  
  - hypertonic and hypotonic solutions; impact on cells  
  - (laboratory): measuring molar mass of polymers and biopolymers

• reverse osmosis: a method of water purification