Solubility of gases in water: Henry’s Law

concentration dissolved / 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
  - everyday example = can of pop:
    \[ p(\text{CO}_2)_{\text{atm}} = 3 \times 10^{-4} \text{ atm} \]
    \[ p(\text{CO}_2)_{\text{inside can}} = 2 \text{ atm} \]
- \( K_H \) always decreases with T
  - gases less soluble at higher T (all gases, all solvents)
  - from gas to solution is a process for which \( H^\circ \) and \( S^\circ \) are both -ve
  - solution (dissolved state) is more ordered but enthalpy increases with dissolution
  - temperature increases favour the gaseous state because \( TS^\circ \) for dissolution becomes more +ve
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>
</tr>
</thead>
<tbody>
<tr>
<td>O$_2$</td>
<td>$1.3 \times 10^{-3}$</td>
</tr>
<tr>
<td>NO</td>
<td>$1.9 \times 10^{-3}$</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>$1.2 \times 10^{-2}$</td>
</tr>
<tr>
<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>
</tr>
<tr>
<td>CO$_2$</td>
<td>$3.4 \times 10^{-2}$</td>
</tr>
<tr>
<td>H$_2$S</td>
<td>0.12</td>
</tr>
<tr>
<td>CH$_3$ONO$_2$</td>
<td>2.6</td>
</tr>
<tr>
<td>OH</td>
<td>25</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>62</td>
</tr>
<tr>
<td>CH$_3$OOH</td>
<td>230</td>
</tr>
<tr>
<td>HO$_2$</td>
<td>2000</td>
</tr>
<tr>
<td>H$_2$O$_2$</td>
<td>75,000</td>
</tr>
<tr>
<td>HCl</td>
<td>730</td>
</tr>
<tr>
<td>CH$_3$COOH</td>
<td>8800</td>
</tr>
<tr>
<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$_2$ in water** – context is whether water will support aquatic life

$K_H = 1.3 \times 10^{-3}$ mol L$^{-1}$ atm$^{-1}$ at equilibrium, at 25°C

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

$\rightarrow$ 8.7 mg/L (8.7 ppm)

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

- $c(O_2) < 8.7$ ppm:
  - at higher temperatures (thermal pollution)
  - if decaying or oxidizable material consumes O$_2$
  $\rightarrow$ concept of *biochemical oxygen demand* (BOD)
  - water is stagnant (reduced air exchange)
Measures of dissolved oxygen

• Titration - Winkler's method
  \[ \text{Mn}^{2+} + 2\text{OH}^- + \frac{1}{2}\text{O}_2 \rightarrow \text{MnO}_2(s) + \text{H}_2\text{O} \]
  \[ \text{MnO}_2 + 4\text{H}^+ + 2\text{I}^- \rightarrow \text{I}_2 + \text{Mn}^{2+} + 2\text{H}_2\text{O} \]
  \[ \text{I}_2 + \text{Na}_2\text{S}_2\text{O}_3 \rightarrow \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaI} \]

• Spectrophotometry - dyes that change colour upon oxidation (methylene blue, indigo carmine)

• Electrochemically - Makareth oxygen electrode: oxygen diffuses through a thin polyethylene membrane. Ultimately a lead anode is oxidized by hydroxide ions produced at the silver cathode by reaction of \text{O}_2(g) with water.

Measurement of total oxidizable substance
- indirect means to determining the oxygen "status" of the water via the demand for oxygen

• Biological Oxygen Demand (BOD)
  - incubate with microorganisms for 5 days in closed contained, measure \(c(\text{O}_2)\) before and after
  - different organisms used by different labs, oxygen cannot be the limiting reactant (i.e. you can't run out of oxygen or you don't know how much more the water would have used up)

• Chemical Oxygen Demand (COD)
  - titrate the sample vs excess \(\text{Na}_2\text{Cr}_2\text{O}_7/\text{H}^+\)
  - easily oxidized substances consume \(\text{Na}_2\text{Cr}_2\text{O}_7\)
  - determine the amount of \(\text{Na}_2\text{Cr}_2\text{O}_7\) left over
    - unreacted chromate is reduced using \(\text{Fe}^{2+}\)
    - \(1 \text{ mol Na}_2\text{Cr}_2\text{O}_7 / 1.5 \text{ mol O}_2\)

• Total Organic Carbon (TOC)
  - oxidize the organic compounds to \(\text{CO}_2\) by combustion
  - analyze \(\text{CO}_2\) produced by GC

Note Problems With These Techniques:
• not all organics oxidize with equal ease, carhs go fast, alkanes are slow (no functional gp), therefore, TOC is an arbitrary measure, can be used to compare samples
• COD compensates somewhat for differences between organic
compounds since acidic dichromate reacts readily with alcohols, alkenes, not as fast with alkanes, carboxylic acids and aromatic rings

• BOD best choice? time, temperature, organism all arbitrary choices of parameters for the test

Factors affecting the above measures:
• rate of oxidation of compound (text - problem 9)
• rate of addition of compound to the water
• temperature (affects rate of oxidation)
• distance from source of contaminant
**CO₂ solubility in water**

- More complex than O₂ because CO₂(aq) / H₂CO₃(aq), which can dissociate through acid-base equilibria

\[ \text{CO}_2(g) + \text{H}_2\text{O}(l) \leftrightarrow \text{H}_2\text{CO}_3(aq) \]

\[ K_h = 3.4 \times 10^{-2} \text{ mol L}^{-1} \text{ atm}^{-1} \]

\[ \text{H}_2\text{CO}_3(aq) \leftrightarrow \text{H}^+(aq) + \text{HCO}_3^-(aq) \]

\[ K_a = 4.2 \times 10^{-7} \text{ mol L}^{-1} \]

- 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”

\[ = \{\text{H}_2\text{CO}_3(aq) + \text{HCO}_3^-(aq) + \text{CO}_3^{2-}(aq)\} \]

– increases with increasing pH

Calculation of the solubility of CO₂ in pure water

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

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

\[ [\text{H}^+][\text{HCO}_3^-] = x^2 = K_a \ [\text{H}_2\text{CO}_3] \]

\[ = (1.3 \times 10^{-5} \text{ mol/L})(4.2 \times 10^{-7} \text{ mol/L}) \]

\[ x = 2.3 \times 10^{-6} \text{ mol/L} \quad \text{pH} = 5.63 \]

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 CO\(_3^{2-}\)

- the methyl orange endpoint measures CO\(_3^{2-}\) + HCO\(_3^{-}\)

Two measurements to determine both CO\(_3^{2-}\) and HCO\(_3^{-}\)
- both total and phenolphthalein alkalinity
  - one of the above plus pH
  - $\rightarrow$ ratio $[\text{CO}_3^{2-}]/[\text{HCO}_3^-]$
**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
  \[
  \text{CaSO}_4(s) \rightarrow \text{Ca}^{2+}(aq) + \text{SO}_4^{2-}(aq)
  \]
- dissolution of limestone rocks: CaCO$_3$ (limestone); CaCO$_3$•MgCO$_3$ (dolomite)
  \[
  \text{MCO}_3(s) + \text{H}_2\text{CO}_3(aq) \rightarrow \text{M}^{2+}(aq) + 2\text{HCO}_3^-(aq)
  \]

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

*BUT*

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!!

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

$\text{CaCO}_3(s) \rightarrow \text{Ca}^{2+}(aq) + \text{CO}_3^{2-}(aq)$  \hspace{1cm} \text{Ksp}$

$\text{H}_2\text{CO}_3(s) \rightarrow \text{H}^+(aq) + \text{HCO}_3^-(aq)$  \hspace{1cm} \text{K}_{a1}$

$\text{H}^+(aq) + \text{CO}_3^{2-}(aq) \rightarrow \text{HCO}_3^-(aq)$  \hspace{1cm} 1/\text{K}_{a2}$

\textbf{Net:}

$\text{CaCO}_3(s) + \text{H}_2\text{CO}_3(aq) \rightarrow \text{Ca}^{2+}(aq) + 2\text{HCO}_3^-(aq)$

\textbf{or:}

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

• K for net reaction = \text{K}_{\text{sp}} \times \text{K}_{a1}/\text{K}_{a2} = 5 \times 10^{-5} \ (\text{mol} \ \text{L}^{-1})^2$

• when expressed as “ppm of CaCO$_3$”, values up to 300 ppm are obtained in hard water areas

\textbf{Hard water:} contains hardness ions: usually limestone areas \textit{e.g.}, southern Ontario

\textbf{Soft water:} low concentrations of hardness ions: sandstone and granite areas \textit{e.g.}, northern and eastern Ontario

All water must have a \textbf{balance of cations and anions}

\therefore hard water is usually well buffered against acidification \rightarrow relatively high concentrations of weak bases

\textit{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:
\[
\text{Ca(HCO}_3\text{)}_2 (\text{aq}) \rightarrow \text{CaCO}_3(\text{s}) + \text{H}_2\text{CO}_3(\text{aq}) \\
\rightarrow \text{CO}_2(\text{g})
\]

Water softening is the process of removing hardness ions

1. **Lime Softening** (industrial use only): neutralize HCO$_3^-$ with OH$^-$
   \[
   \text{Ca(OH)}_2(\text{aq}) + \text{Ca(HCO}_3\text{)}_2(\text{aq}) \rightarrow \text{CaCO}_3(\text{s}) + 2\text{H}_2\text{O}
   \]

2. **Ion exchange resins**, *e.g.*, Na$(A)$ where $(A) =$ polymeric anion
   - example of Ca$^{2+}$ removal through cation exchange
   \[
   \text{Ca}^{2+}(\text{aq}) + 2\text{Na}(A)_{\text{res}} \rightarrow 2\text{Na}^+(\text{aq}) + \text{Ca}(A_2)_{\text{res}}
   \]
   Resin regeneration with concentrated brine:
   \[
   2\text{Na}^+(\text{aq}) + \text{Ca}(A_2)_{\text{res}} \rightarrow \text{Ca}^{2+}(\text{aq}) + 2\text{Na}(A)_{\text{res}}
   \]

3. **Deionized water**: cation and anion exchangers in series, using H$^+$ form of the cation exchanger and OH$^-$ form of the anion exchanger
   - example of CaSO$_4$
   \[
   \text{Ca}^{2+}(\text{aq}) + 2\text{H}(A)_{\text{res}} \rightarrow 2\text{H}^+(\text{aq}) + \text{Ca}(A_2)_{\text{res}} \\
   \text{SO}_4^{2-}(\text{aq}) + 2(\text{C})\text{OH}_{\text{res}} \rightarrow 2\text{OH}^-(\text{aq}) + (\text{C}_2)\text{SO}_4_{\text{res}}
   \]

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>J (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>
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</tr>
<tr>
<td>Cl⁻</td>
<td>0.55</td>
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<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></td>
<td></td>
</tr>
</tbody>
</table>

Ocean water **approximately** in equilibrium with CaCO₃ but

\[ Q_{sp} = [Ca^{2+}][CO_3^{2-}] > K_{sp} \]

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

- Second reason: complexation: formation of species such as:
  - \((CaSO_4)_8\): 8% of total Ca
  - \((CaHCO_3)^+\): 1% of total Ca
  - \((MgCO_3)_6\): 64% of total CO₃
  - \((NaCO_3)^-\): 19% of total CO₃
  - \((CaCO_3)_7\): 7% of total CO₃

**Irrigation and water quality**
- Read text pp. 147-149
- Read article from *The Economist*, December 15, 2001 on web site
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, e.g., 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

\[ B = c \times RT \]
\[ c \text{ in mol L}^{-1} \]
\[ R \text{ in L atm mol}^{-1} K^{-1} \]
\[ B \text{ in atm} \]

- 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

\[ \text{Osmosis} \quad \text{Reverse Osmosis} \]