

Solubility of gases in water: Henry's Law

- concentration dissolved \propto partial pressure of the gas

$$K_H \text{ (units mol L}^{-1} \text{ atm}^{-1}\text{)} = c_X/p_X$$

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.

substance	K_H	substance	K_H
O ₂	1.3×10^{-3}	NO	1.9×10^{-3}
NO ₂	1.2×10^{-2}	O ₃	1.13×10^{-2}
N ₂ O	2.5×10^{-2}	CO ₂	3.4×10^{-2}
H ₂ S	0.12	SO ₂	1.23
CH ₃ ONO ₂	2.6	CH ₃ O ₂	6
OH	25	HNO ₂	49
NH ₃	62	CH ₃ OH	220
CH ₃ OOH	230	HCl	730
HO ₂	2000	CH ₃ COOH	8800
H ₂ O ₂	75,000	HNO ₃	200,000

Note: Environment Canada quotes K_H in the reverse direction (escape from water): units Pa m³ mol⁻¹, hence large $K_H \rightarrow$ low water solubility.

Solubility of O₂ in water – context is whether water will support aquatic life

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

$$\longrightarrow c(\text{O}_2) = 2.7 \times 10^{-4} \text{ mol /L}$$

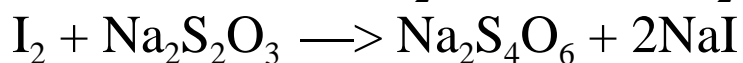
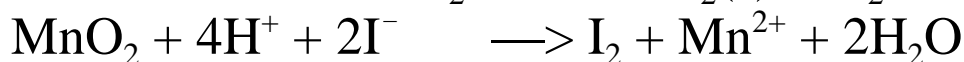
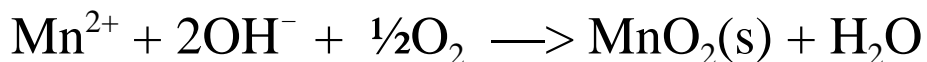
$$\longrightarrow 8.7 \text{ mg/L (8.7 ppm)}$$

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

- $c(\text{O}_2) < 8.7 \text{ ppm}$:
 - at higher temperatures (thermal pollution)
 - if decaying or oxidizable material consumes O₂ \longrightarrow 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 $c(\text{O}_2)$ before and after
- Chemical Oxygen Demand (COD) – titrate the sample vs excess Na₂Cr₂O₇/H⁺; easily oxidized substances consume Na₂Cr₂O₇; determine the amount of Na₂Cr₂O₇ left over; 1 mol Na₂Cr₂O₇ \equiv 1.5 mol O₂
- Total Organic Carbon (TOC) – oxidize the organic compounds to CO₂ by combustion; analyze CO₂ produced
- Dissolved Oxygen (DO) – often done by titration:



CO₂ solubility in water

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



$$K_{\text{H}} = 3.4 \times 10^{-2} \text{ mol L}^{-1} \text{ atm}^{-1}$$



$$K_{\text{a}} = 4.2 \times 10^{-7} \text{ mol L}^{-1}$$

- 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

- $p(\text{CO}_2, \text{g}) = 375 \text{ ppmv} \longrightarrow c(\text{CO}_2, \text{aq}) = 1.3 \times 10^{-5} \text{ mol/L}$
- for $K_{\text{a}} = [\text{H}^+][\text{HCO}_3^-]/[\text{H}_2\text{CO}_3] = 4.2 \times 10^{-7} \text{ mol/L (25}^\circ\text{C)}$

$$\begin{aligned} [\text{H}^+][\text{HCO}_3^-] &= x^2 = K_{\text{a}} [\text{H}_2\text{CO}_3] \\ &= (1.3 \times 10^{-5} \text{ mol/L})(4.2 \times 10^{-7} \text{ mol/L}) \\ x &= 2.3 \times 10^{-6} \text{ mol/L} \end{aligned}$$

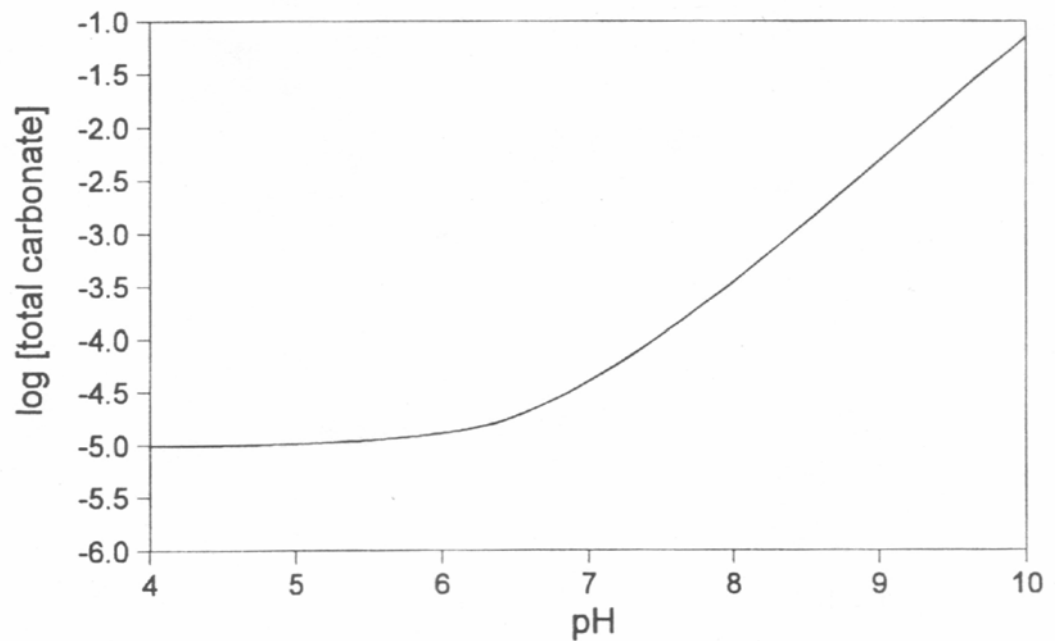
$$\text{pH} = 5.63;$$

$$\begin{aligned} \text{total “carbonate”} &= \{1.3 \times 10^{-5} + 2.3 \times 10^{-6} \text{ mol/L}\} \\ &= 1.5 \times 10^{-5} \text{ mol/L} \end{aligned}$$

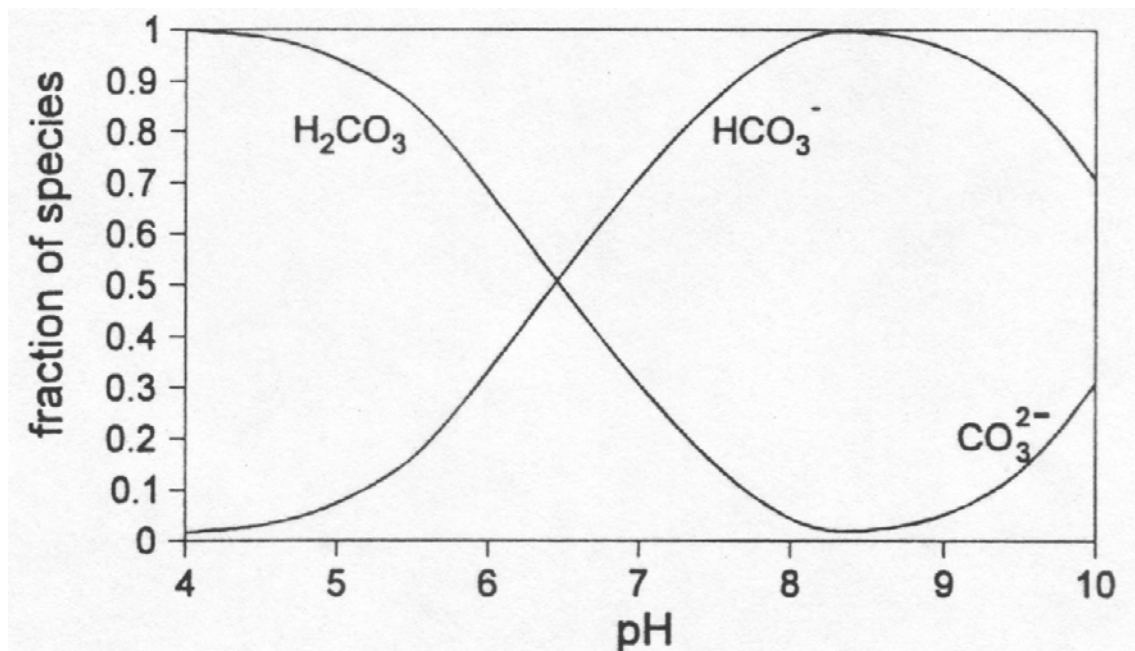
- Even completely clean water in equilibrium with atmospheric CO₂ does not have pH = 7!! Keep this thought for discussion of acid rain.

When the pH of the water is fixed by the presence of other solutes:

- total dissolved carbonate increases as pH rises

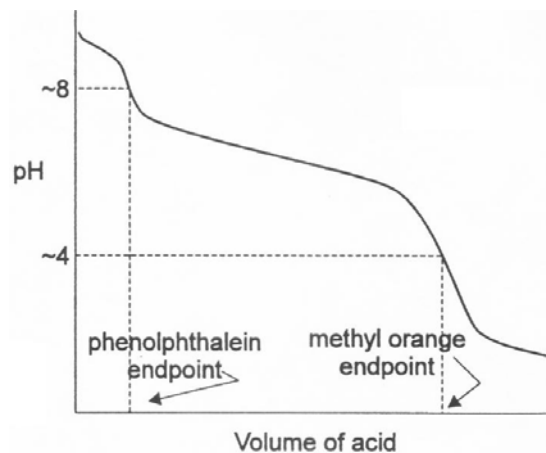
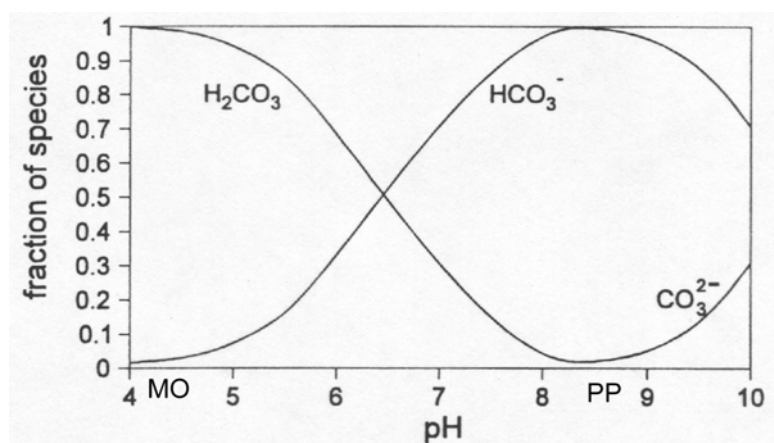


- Note the speciation of carbonate



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 \equiv 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 **or**
 - one of the above plus pH \rightarrow ratio $[CO_3^{2-}]/[HCO_3^-]$

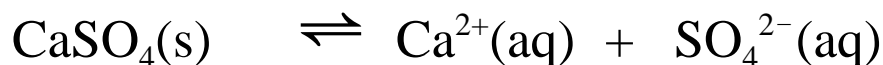
Hardness of water is a measure of the concentration of “hardness ions” (mainly Ca^{2+} and Mg^{2+}) that form insoluble salts, especially carbonates: text, pp. 142-146.

Analysis of hardness ions:

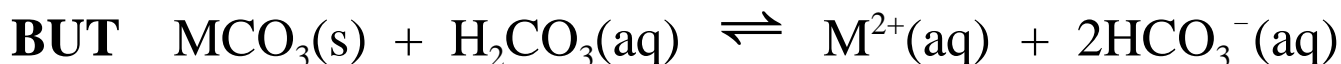
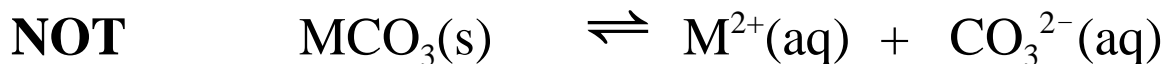
- titration vs EDTA^{4-} using Eriochrome Black T indicator (Ca only)
- atomic absorption spectroscopy

Origin of hardness ions:

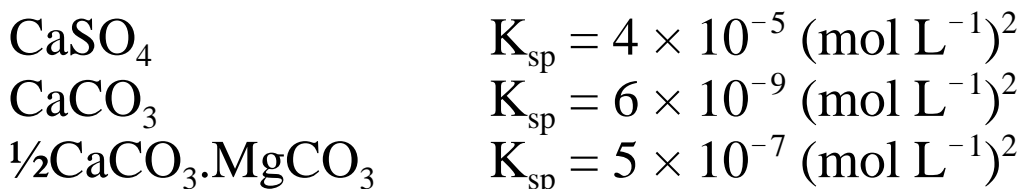
- dissolution of gypsum



- dissolution of limestone rocks: CaCO_3 (limestone); $\text{CaCO}_3 \cdot \text{MgCO}_3$ (dolomite)

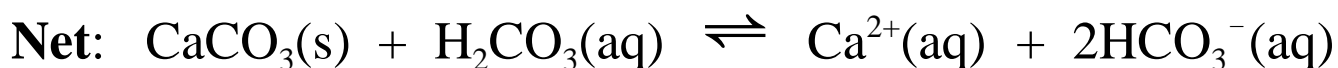
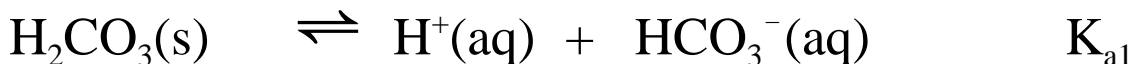
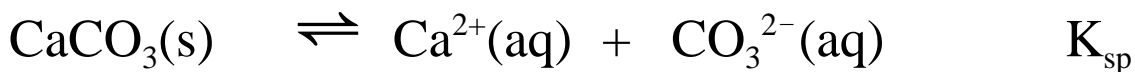


- Note that underground, $p(\text{CO}_2)$ is often much greater than 370 ppmv
- In what follows, note the text, footnote 8, p. 143 about K_{sp} calculations!!



Dissolution of CaCO_3

K =



- K for net reaction = $K_{\text{sp}} \times K_{\text{a1}}/K_{\text{a2}} = 5 \times 10^{-5} (\text{mol L}^{-1})^2$
- when expressed as “ppm of CaCO_3 ”, values up to 300 ppm are obtained in hard water areas

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

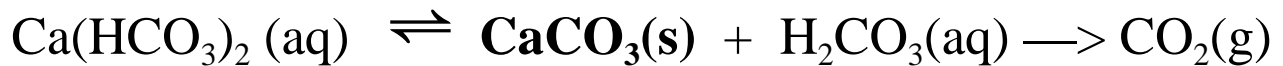
Soft water: low concentrations of hardness ions: sandstone and granite areas *e.g.*, northern and eastern Ontario

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

Thus alkalinity is a measure of buffering capacity; high alkalinity usually correlates with high hardness

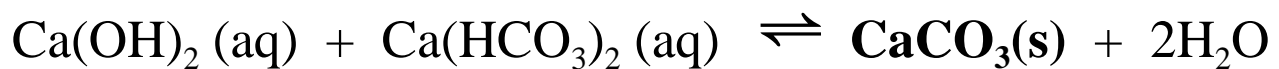
Water Softening: critical application for steam boilers due to deposition of salts

When hard water is heated:

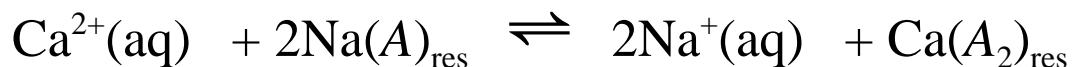


Water softening is the process of removing hardness ions

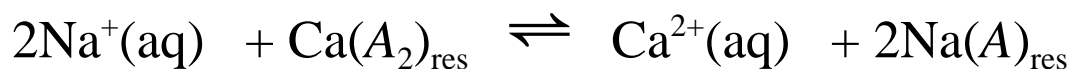
1. Lime Softening (industrial use only): neutralize HCO_3^- with OH^-



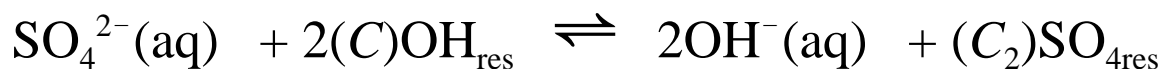
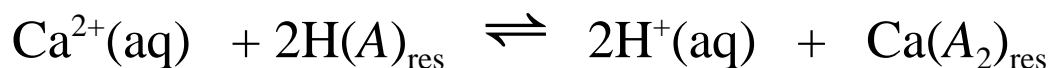
2. Ion exchange resins, *e.g.*, $\text{Na}(\text{A})$ where (A) = polymeric anion – example of Ca^{2+} removal through cation exchange



Resin regeneration with concentrated brine:



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



Hence:



- 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.

Ion	conc, mol/L	input, Tmol/yr	τ , Myr
Na ⁺	0.46	9.0	70
K ⁺	0.010	1.9	7
Mg ²⁺	0.054	5.5	10
Ca ²⁺	0.010	12.2	1
Cl ⁻	0.55	7.2	100
SO ₄ ²⁻	0.028	3.8	10
HCO ₃ ⁻	0.0023	32	0.1
CO ₃ ²⁻	0.0003	included with HCO ₃ ⁻	

- Ocean water **approximately** in equilibrium with CaCO₃, but $Q_{sp} = [\text{Ca}^{2+}][\text{CO}_3^{2-}] \gg K_{sp}$: text, p. 150
- First reason: $a(\text{Ca}^{2+})$ and $a(\text{CO}_3^{2-}) < [\text{Ca}^{2+}][\text{CO}_3^{2-}]$, *i.e.*, $\gamma(\text{Ca}^{2+}) \sim 0.26$; $\gamma(\text{CO}_3^{2-}) \sim 0.20$
- 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

Irrigation and water quality

- Read text pp. 147-149
- Read article from *The Economist*, link to internet =

http://www.economist.com/displaystory.cfm?story_id=1906914

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

$$\Delta T = K_f \times m$$

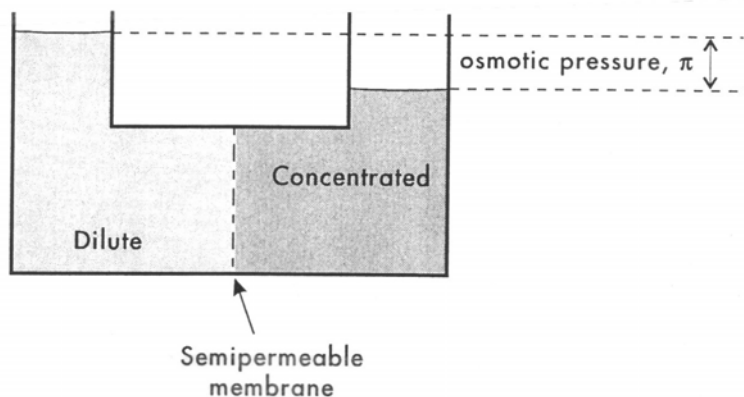
K_f = molal freezing point depression constant,
units K kg mol^{-1}

m = molal concentration of solute, mol kg^{-1}

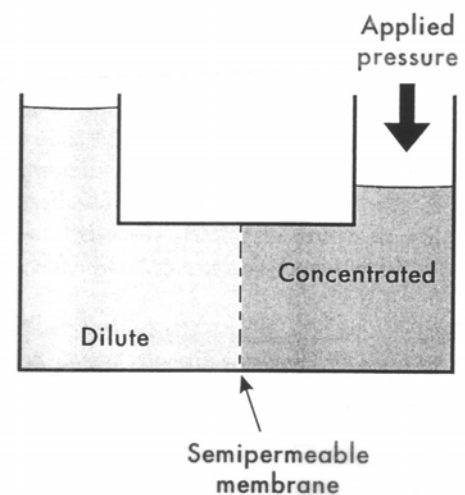
- The freezing point depression is *independent* of the identity of the solute. For ionic solutes consider all the ions separately, *e.g.*, for NaCl there are *two* solutes to consider, Na^+ and Cl^-
- Applications:
road salt
trees in winter, fish in polar oceans
(laboratory): determining molar mass

Osmosis and Reverse Osmosis

- osmotic pressure $\pi = c \times RT$ c in mol L^{-1}
 R in $\text{L atm mol}^{-1} \text{K}^{-1}$
 π 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



Osmosis



Reverse Osmosis