→ i.e. cations (unlike the discussion of alkalinity ↓ (anions))

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.

these guys, Ca^{2+}, Mg^{2+} etc. cause precipitation with soaps

ethylenediaminetetraacetic acid

Analysis of hardness ions:

- titration vs $EDTA^{4-}$ using Eriochrome Black T indicator (Ca^{2+} only)
- atomic absorption spectroscopy

Origin of hardness ions:

- dissolution of gypsum

$$CaSO_4(s) \rightleftharpoons Ca^{2+}(aq) + SO_4^{2-}(aq)$$

- dissolution of limestone rocks: $CaCO_3$ (limestone); $CaCO_3.MgCO_3$ (dolomite)

NOT $$MCO_3(s) \rightleftharpoons M^{2+}(aq) + CO_3^{2-}(aq)$$

BUT $$MCO_3(s) + H_2CO_3(aq) \rightleftharpoons M^{2+}(aq) + 2HCO_3^-(aq)$$

- Note that underground, $p(CO_2)$ is often much greater than 370 ppmv and the water is cold, e.g. 5°C (more $CO_2(aq)$)

- In what follows, note the text, footnote 8, p. 143 about K_{sp} calculations!!

$CaSO_4$	$K_{sp} = 4 \times 10^{-5}$ (mol L^{-1})^2
$CaCO_3$	$K_{sp} = 6 \times 10^{-9}$ (mol L^{-1})^2 ← intrinsically less soluble than $CaSO_4$ but ↗ as pH drops
½$CaCO_3.MgCO_3$	$K_{sp} = 5 \times 10^{-7}$ (mol L^{-1})^2

Dissolution of $CaCO_3$

	K =
$CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$	K_{sp}
$H_2CO_3(s) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$	K_{a1}
$H^+(aq) + CO_3^{2-}(aq) \rightleftharpoons HCO_3^-(aq)$	$1/K_{a2}$

Net: $CaCO_3(s) + H_2CO_3(aq) \rightleftharpoons Ca^{2+}(aq) + 2HCO_3^-(aq)$

or: $CaCO_3(s) + H_2CO_3(aq) \rightleftharpoons Ca(HCO_3)_2\ (aq)$ ← so CO_2 laden water can (slowly) dissolve rock ---- good for "spelunkers"

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

Soft water areas pH 6-7
Hard water areas pH 7-8.5 (typical $[HCO_3^-]$ above 10^{-3} mol/L)
(order of magnitude less for soft water).

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

When hard water is heated:

$$Ca(HCO_3)_2\,(aq) \rightleftharpoons \mathbf{CaCO_3(s)} + H_2CO_3(aq) \longrightarrow CO_2(g)$$

Water softening is the process of removing hardness ions

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

$$Ca(OH)_2\,(aq) + Ca(HCO_3)_2\,(aq) \rightleftharpoons 2\mathbf{CaCO_3(s)} + 2H_2O$$

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

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

Resin regeneration with concentrated brine:

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

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 $CaSO_4$

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

anion exchanger $$SO_4^{2-}(aq) + 2(C)OH_{res} \rightleftharpoons 2OH^-(aq) + (C_2)SO_{4res}$$

Hence:

$$2H^+(aq) + 2OH^-(aq) \longrightarrow 2H_2O$$

- Regeneration of the resin beds????

Cation exch: use HCl
Anion exch.: use NaOH

<u>**Seawater**: a solution of high ionic strength</u>. The main environment we will encounter where activities must be used rather than concentrations.

mainly from rivers. Oceans act as reservoirs for soluble ions

← tera (10^{12})

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 $CaCO_3$, but $Q_{sp} = [Ca^{2+}][CO_3^{2-}] >> K_{sp}$: text, p. 150 implies supersaturated, so $CaCO_3$ should precipitate. But does not
- First reason: $a(Ca^{2+})$ and $a(CO_3^{2-}) < [Ca^{2+}][CO_3^{2-}]$, *i.e.*, $\gamma(Ca^{2+}) \sim 0.26$; $\gamma(CO_3^{2-}) \sim 0.20$ because of ← the high ionic strength.
- Second reason: complexation: formation of species such as:
  ($CaSO_4$): 8% of total Ca; $(CaHCO_3)^+$: 1% of total Ca

  Need to work with "activities"

  ($MgCO_3$): 64% of total CO_3; $(NaCO_3)^-$: 19% of total CO_3; ($CaCO_3$): 7% of total CO_3

Irrigation and water quality high rates of evaporation

- Read text pp. 147-149 — hence high salinity leading to plant growth failure
- Read article from *The Economist*, link to internet =

http://www.economist.com/displaystory.cfm?story_id=1906914
(no longer available – unless you are a subscriber).

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 depresssion contant, 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

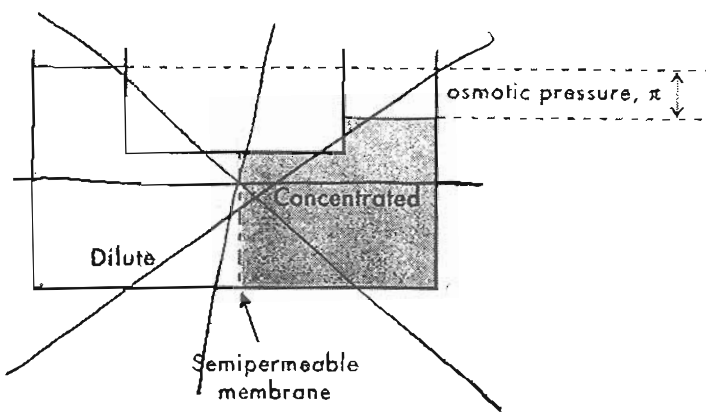
Osmosis and Reverse Osmosis

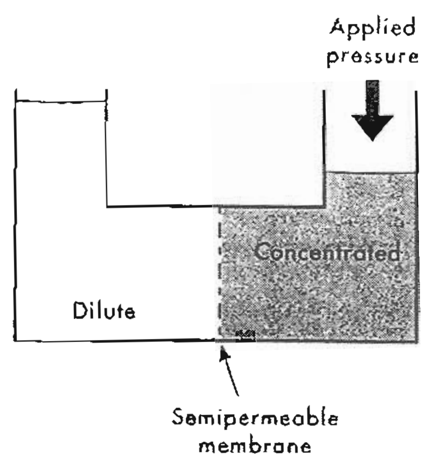
- osmotic pressure $\pi = c \times RT$ — c in mol L^{-1}; R in L atm mol^{-1} K^{-1}; π in atm

- 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

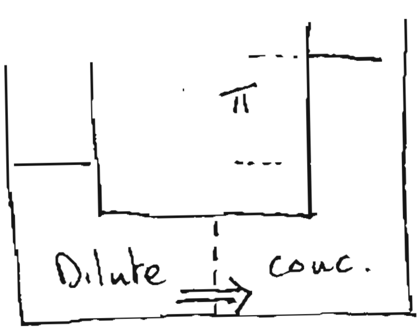
- reverse osmosis: a method of water purification





Osmosis

Reverse Osmosis



Sea water ~0.7 M NaCl
- requires 30 atm to purify