Part 2. The Hydrosphere

Chapter 9. The Hydrosphere

Chapter 9. The hydrosphere

9.0 The hydrosphere: generals

- Distribution of Hydrosphere

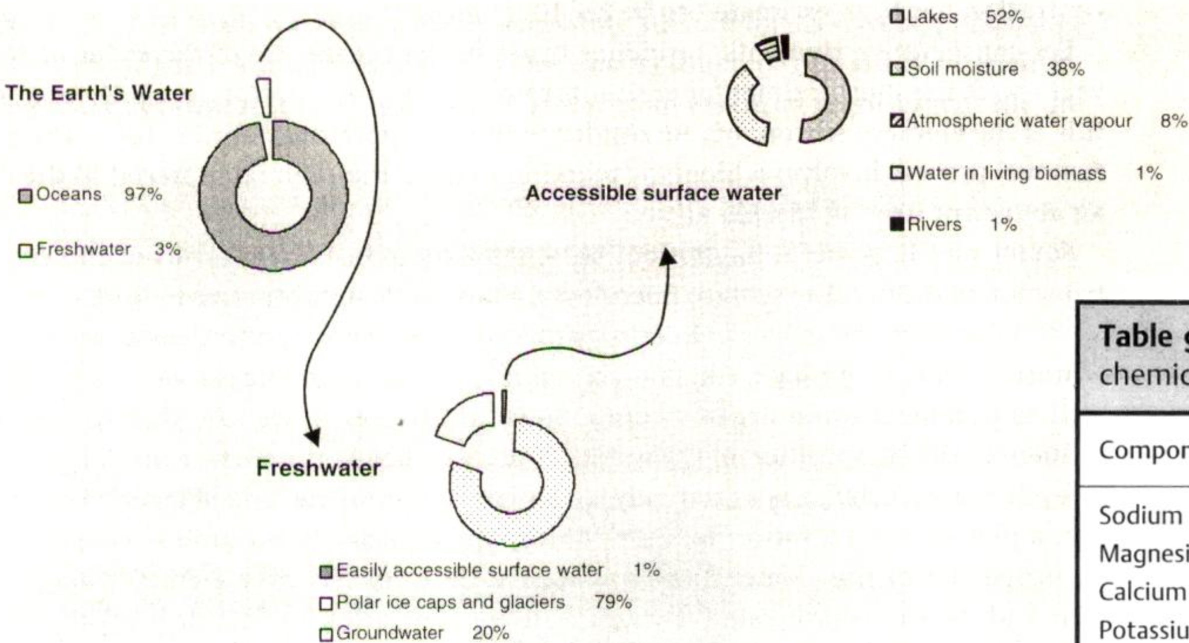

Fig. 9.1 Distribution of global water resources. (G. Lean, D. Hinrichsen, and A. Markham, *Atlas of the Environment*, Prentice Hall, New York; 1990.)

Table 9.1 Composition of sea water—major inorganic chemical constituents

Component	Concentration
Sodium	10 760 mg kg^{-1}
Magnesium	1294
Calcium	413
Potassium	387
Strontium	8
Chloride	19 353
Sulfate	2712
Hydrogen carbonate	142
Bromide	67
Boron	4
Fluoride	1

Data from Martin, D., *Marine Chemistry, Vol. 1 Analytical Methods*, Marcel Dekker, New York; 1968.

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- Fresh water Distribution in the ground

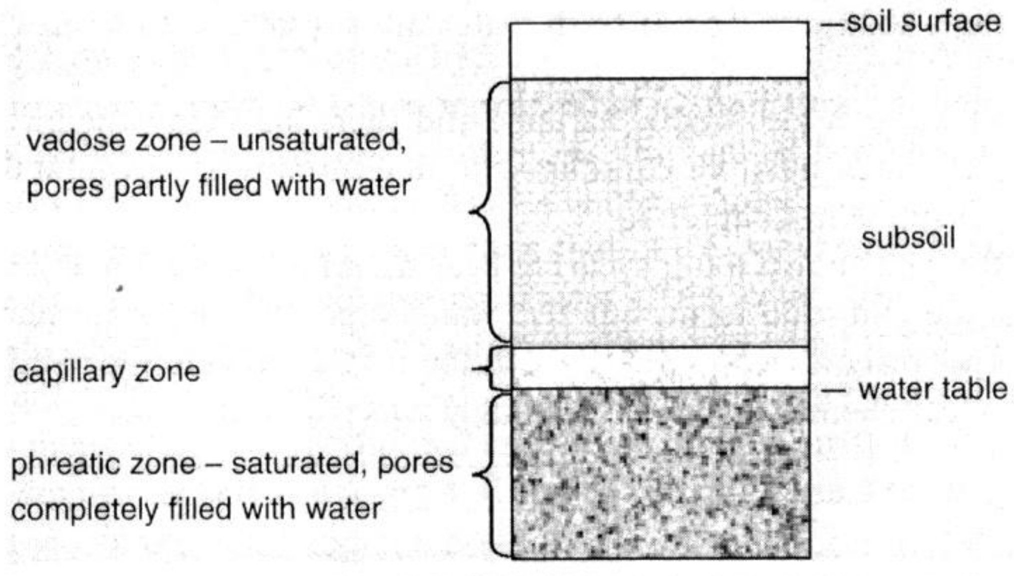

Fig. 9.2 Nomenclature for zones in soil/permeable rock depth profiles.

Only 1% of all fresh water (=0.03% of Earth's total water supply): dominates studies in environmental chemistry, because it is readily available and essential requirement for the survival and growth of many forms of animal and plant life on the planet.

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9.1 Physical and chemical properties of water: Ice and liquid water

- Structure of Ice

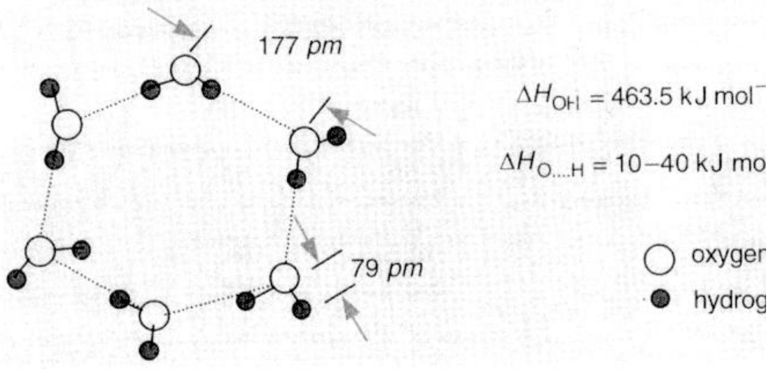

Fig. 9.4 Structure of ice.

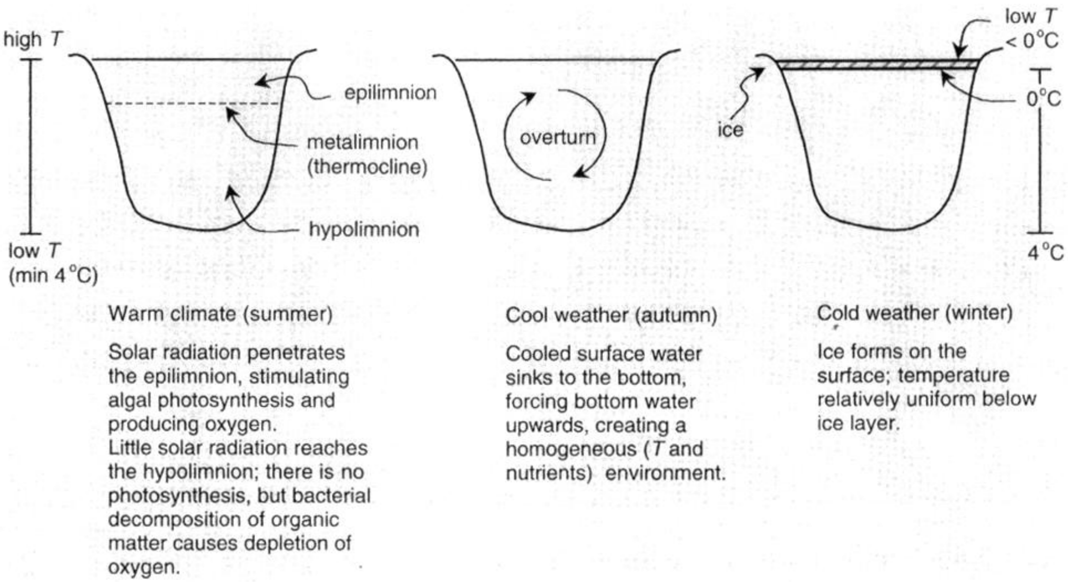

Fig. 9.5 Seasonal changes in the vertical profile of a water body in parts of the world with temperate climate.

Density of Ice = 0.917 kgL^{-1}

Enthalpy of fusion = 6.02 $kJmol^{-1}$

On melting, , meaning that liq. water at 0 ^{0}C retains a considerable component of the ice structure.

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9.1 Physical and chemical properties of water: Hydration

- Water has one of the largest constants, meaning good solvent for .
- : water molecules orient themselves around ions
- Degree of hydration (Hydration number) depends on:
  -the charge to radius ratio (see Tab. 9.2): most influential factor

Table 9.2 Charge and radius properties of the alkali metals in aqueous solution

	Li^+	Na^+	K^+	Rb^+	Cs^+
Ionic radius/pm	60	95	133	148	169
Charge density/C pm^{-1}	0.0167	0.0105	0.0075	0.0068	0.0059
Hydrated radius/pm	340	276	232	228	228
Hydration number	23.3	16.6	10.5	10	9.9

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9.1 Physical and chemical properties of water: Complexation

- 'Aquo' complexes: hydrated ions
- Stability of complexes: expressed by stability constants (or formation constants)

M + L ⇔ ML $K_{f1} = [\mathrm{ML}]/[\mathrm{M}][\mathrm{L}]$

ML + L ⇔ ML_2 $K_{f2} = [\mathrm{ML_2}]/[\mathrm{ML}][\mathrm{L}]$

ML_2 + L ⇔ ML_3 $K_{f3} = [\mathrm{ML_3}]/[\mathrm{ML_2}][\mathrm{L}]$

ML_3 + L ⇔ ML_4 $K_{f4} = [\mathrm{ML_4}]/[\mathrm{ML_3}][\mathrm{L}]$

Overall rxn M + 4L ⇔ ML_4 $\beta_4 = [\mathrm{ML_4}]/[\mathrm{M}][\mathrm{L}]^4$

$$\beta_4 = K_{f1} \times K_{f2} \times K_{f3} \times K_{f4}$$

If no. of ligands bound to the metal ion=n, then $\beta_n = K_{f1} \times K_{f2} \times K_{f3} \times \cdots \times K_{fn}$

E.g. in the ocean, $Hg(H_2O)_6^{2+}(aq) + 4Cl^-(aq) \leftrightarrow Hg(H_2O)_2Cl_4^{2-}(aq) + 4H_2O$

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9.1 Physical and chemical properties of water: Acid-base properties

- Water: substance, undergoing autoprotolysis to form H_3O^+ and OH^- ions

$$2H_2O \leftrightarrow H_3O^+(aq) + OH^-(aq) \qquad K_w = 1.01\times10^{-14} \text{ at } 25℃$$

- E.g. acidification of water, by e.g. oxalic acid, being the degradation products of natural organic matter (NOM)

$$(COOH)_2 + H_2O \Leftrightarrow COOHCOO^-(aq) + H_3O^+(aq) \qquad K_{a1} = 5.6\times10^{-2}$$

$$COOHCOO^-(aq) = H_2O \Leftrightarrow (COO^-)_2(aq) + H_3O^+(aq) \qquad K_{a2} = 5.2\times10^{-5}$$

9.1 Physical and chemical properties of water: Redox properties

$$6H_2O \rightarrow O_2 + 4H_3O^+(aq) + 4e^- \quad E = 1.23 - 0.051\, pH \text{ at } 25℃$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad E = -0.0591\, pH \text{ at } 25℃$$

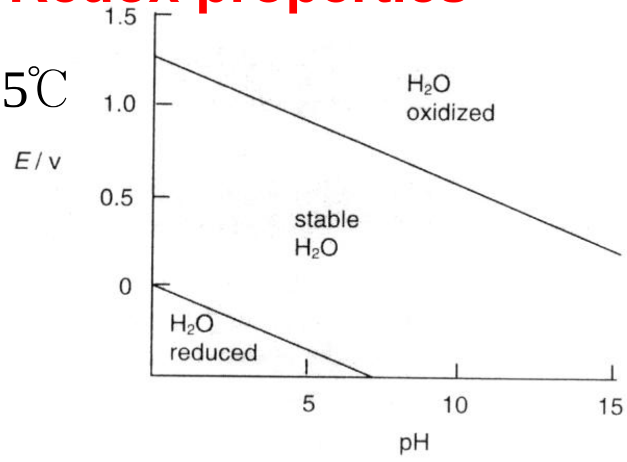

Fig. 9.6 Stability of water as depicted by an *E*/pH diagram.