

↗ 1 Sv is a large dose
 1 Sv ... risk of cancer later in life. (5%)
 10 Sv ... risk of death within days or weeks.

(99)

Hazards from radiation

Stochastic effects \equiv random with no threshold; depend on **total dose**, not on the dose rate

Fatal Cancers (all):	0.05 Sv^{-1} (no "signature" cancers)
Non-fatal cancers:	0.01 Sv^{-1}
Hereditary effects:	0.01 Sv^{-1}

- background radiation for a 75 year life span @ 0.001 Sv/yr
 $\sim 75 \text{ yr} \times 0.001 \text{ Sv/yr} \rightarrow 0.075 \text{ Sv}$
 \rightarrow fatal cancer probability ~ 0.004

This is 0.4% of all mortalities; total cancer death rate = 0.25

Radiation workers: ICRP recommendation for maximum lifetime exposure = $1 \text{ Sv} \rightarrow 20 \text{ mSv yr}^{-1}$ for a 50 year maximum working life for the maximally-exposed individual.

lifetime fatal cancer risk:

$$= 0.02 \text{ Sv yr}^{-1} \times 50 \text{ yr} \times 0.05 \text{ Sv}^{-1} = 0.05$$

annual fatal cancer risk:

$$= 0.02 \text{ Sv yr}^{-1} \times 0.05 \text{ Sv}^{-1} = 0.001 \text{ yr}^{-1}$$

Compare these values:

- total fatal cancer risk of ~ 0.25 in North America
- manufacturing industry: risk of accidental death = 1 in 40,000 per year (Vennart, 1991); 0.001 over 50 yr.

General Public: maximum additional exposure $< 1 \text{ mSv yr}^{-1}$, adding another 0.004 (maximum) to the lifetime fatal cancer risk (not distinguishable epidemiologically)

50 mSv - TLV for annual dose for radiation workers in any one year
 20 mSv - TLV for annual average dose for radiation workers averaged over 5 years.
 1 mSv - ICRP recommended annual dose limit for general public

International Commission on Radiological Protection

100

Dilemmas implicit in the ICRP approach (all worst case scenarios)

- The standard to protect radiation workers adds an excess fatal cancer rate of 0.05, which is ^{risk ratio} ~ 20% of the prevailing rate for the population at large ($RR = 1.2$). It is much higher than the risk of accidental death in industry (estimated ~ 1 in 40,000 in North American manufacturing).
- These standards are very different from those used to regulate chemical toxicants (e.g., the arbitrary standard of 10^{-6} extra fatal cancers per lifetime).

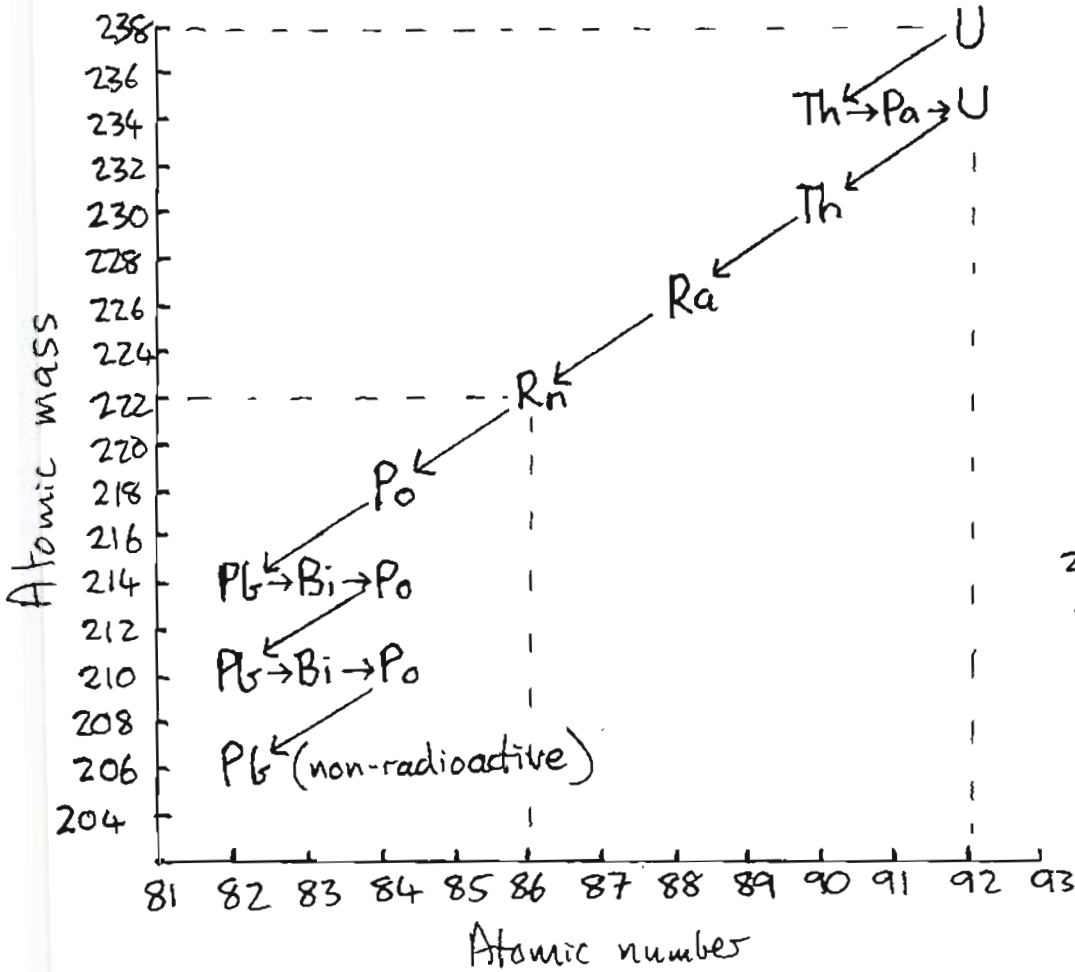
So: Is the standard for regulating chemical carcinogens too strict?

Or: Is the standard for regulating ionizing radiation too lax?

Radon - a bit of a problem

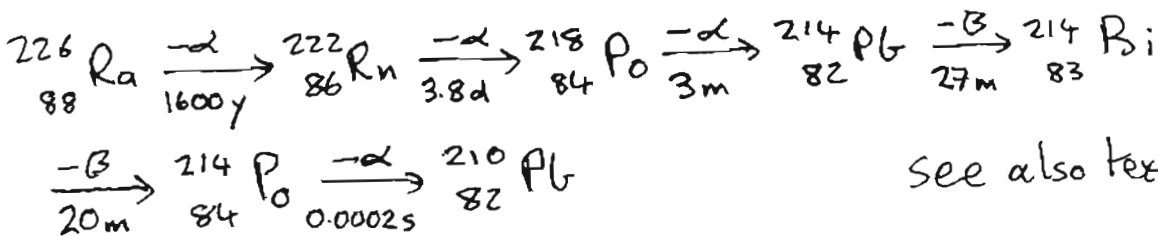
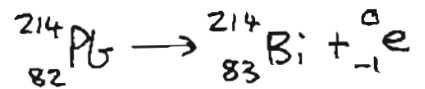
Rocks, granitic soils etc. contain uranium, so radioactive decay occurs all around us - ... there are 14 sequential decay processes, along the way producing radon (Rn) - ... a gas which can leak into our environment

Accounts for over 1/2 the natural radioactivity we are exposed to.



Note: β particle is an electron (formed when a neutron splits into a proton and an e^- in the nucleus). Hence the atomic # increases by 1 unit

e.g.



see also text-p 118.

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${}^{226}_{88}\text{Rn}$ has a half-life of 3.8 days, long enough to diffuse through the rock in which it is formed. Although relatively short lived, it is constantly replaced by the decay of radium (Ra).

The hazards are not only radon, but also the disintegration products - - - radon daughters.

Most radon escapes into the atmosphere ... but it, and the daughters can hang around in buildings, especially basements.

The metallic daughters can form oxides which can get into the lungs - - - disintegration near the bronchial tissue can occur. - - - α particles are short range in tissue ($\sim 60 \mu\text{m}$), but can damage stem cells leading to cancer.

US Environmental protection agency (EPA) reckons about 7000 \rightarrow 30,000 lung cancer deaths per year.

The other main source of radon is ground water - - - equilibrates with underground rocks.

The case of radon

Radon: naturally-occurring noble gas formed through decay of natural uranium and thorium. Chief isotope of concern is ^{222}Rn , $t_{1/2}$ 3.8 days, α emitter, 5.587 MeV.

$$\begin{aligned} \therefore \text{Energy per disintegration:} \\ &= 5.587 \text{ MeV} \times (1.6 \times 10^{-13} \text{ J MeV}^{-1}) \\ &= 8.9 \times 10^{-13} \text{ J Bq}^{-1} \end{aligned}$$

$$\sim 6.7 \times 10^5 \text{ Bq}$$

U.S. data indicate a quarterly limit of 18 μCi of radon breathed (72 $\mu\text{Ci}/\text{yr}$): CRC Handbook of Chem. and Physics, 1993 ed.

Different countries have set "action levels" for radon (ICRP Publication 60, para 217).

Estimated volume of air breathed: $2 \times 10^4 \text{ L day}^{-1} = 7 \times 10^6 \text{ L yr}^{-1}$

U.S. action level:

$$4 \text{ pCi L}^{-1} \equiv 0.15 \text{ Bq L}^{-1} \equiv 1 \times 10^6 \text{ Bq yr}^{-1} \equiv 30 \mu\text{Ci yr}^{-1}$$

Canadian action level:

$$20 \text{ pCi L}^{-1} \equiv 0.74 \text{ Bq L}^{-1} \equiv 5 \times 10^6 \text{ Bq yr}^{-1} \equiv 150 \mu\text{Ci yr}^{-1}$$

Canadian effective dose rate: (α radiation has $W_R = 20$):

$$\begin{aligned} E &= \frac{(5 \times 10^6 \text{ Bq})}{1 \text{ yr}} \times \frac{(8.9 \times 10^{-13} \text{ J})}{1 \text{ Bq}} \times 20 \\ &= 4 \times 10^{-6} \text{ J yr}^{-1} \end{aligned}$$

Assume 2 kg of lung tissue $\rightarrow 2 \times 10^{-6} \text{ Sv yr}^{-1} \rightarrow 2 \times 10^{-4} \text{ Sv}$ for a 75 year lifetime \rightarrow fatal cancer risk of 1×10^{-5}

"EPA statistics suggest that the risk of lung cancer over 70 years for people spending 75% of their time in the home is equivalent to having 200 chest X-rays yr^{-1} at the 4 pCi L^{-1} action level, and equivalent to smoking 2 packs of cigarettes daily at the 20 pCi L^{-1} level (Canadian level).

Dissolved Gases in Natural Water
Dissolved Solids in Natural Water } Chapt 5. (104)

Solubility of gases in water: Henry's Law

- concentration dissolved \propto partial pressure of the gas
 i.e. $[gas, aq] = K_H \cdot p_{gas}$ (= gas, solvent)
 K_H (units mol L⁻¹ atm⁻¹) = c_x/p_x ↖ more general case, but here we focus on H₂O
 i.e. for $X(g) \rightleftharpoons X(aq)$

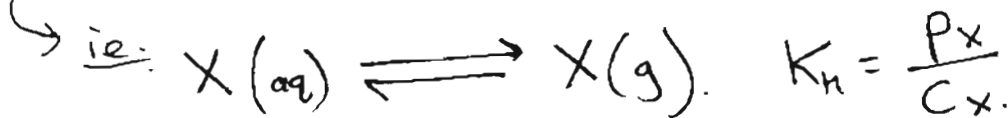
Large K_H means high solubility; K_H always decreases with T;
 gases less soluble at higher T (all gases, all solvents)

Note: gas \rightarrow ~~soln~~ ΔH°_{soln} both -ve (so enthalpy driven). But if T \uparrow the T ΔS° term can dominate.

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. } gases in water

<u>substance</u>	<u>K_H (mol L⁻¹ atm⁻¹)</u>	<u>substance</u>	<u>K_H</u>
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.



often units are L atm mol⁻¹

Real life examples of Henry's Law ??

Solubility of O_2 in water ... will water support aquatic life? (105)

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

$$\begin{aligned} [O_{2,aq}] &= (1.3 \times 10^{-3} \text{ mol L}^{-1} \text{ atm}) (0.21 \text{ atm}) \\ &= 2.7 \times 10^{-4} \text{ mol L}^{-1} \end{aligned}$$

In mg/L

$$\begin{aligned} [O_{2,aq}] &= (2.7 \times 10^{-4} \text{ mol/L}) (32 \text{ g/mol}) (1000 \text{ mg/g}) \\ &= 8.7 \text{ mg/L} \Rightarrow 8.7 \text{ ppm} \end{aligned}$$

Note

1 ppm for liquids & solids defined by mass,
i.e. 1 g in 10^6 g, 1 mg per kg, etc.

Since 1 kg of H_2O is 1 L, then (for H_2O as solvent),
1 ppm \equiv 1 mg L^{-1}

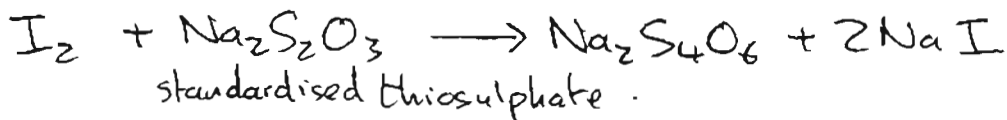
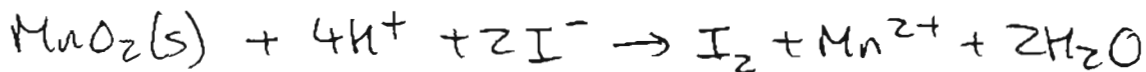
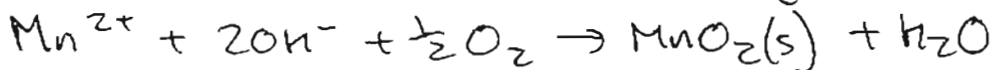
Most fish require 5-6 ppm dissolved O_2 .

Oxygen levels can be < 8.7 ppm, for example:

- thermal pollution e.g. power plant returning warm water ($T \uparrow$).
- decaying or oxidisable material consumes O_2
e.g. sewage, agricultural run-off, industry etc.
- stagnant water (reduced air exchange)

Measurement of dissolved oxygen (actual concn)

- Titration --- Winkler's method (all aq. unless specified).

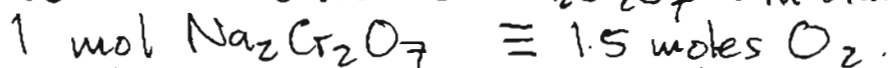


- Spectrophotometry --- dyes that change colour upon oxidation (methylene blue, indigo carmine)
- Electrochemically --- potential of the cell can be related to the concn of O_2 (via Nernst equn.)

Measures of oxygen status: --- refer to the amount of oxidisable substances in water, and so relate indirectly to the oxygen status through the amount of O_2 needed to oxidise them (see text p134 et seq.)

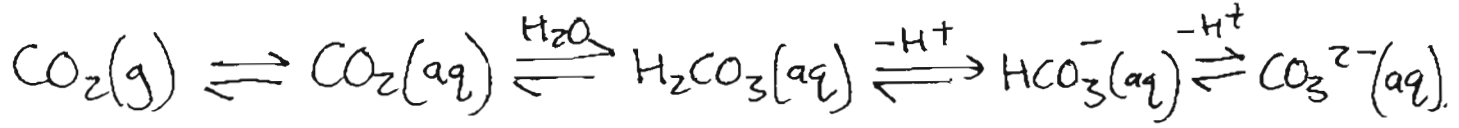
- Biological Oxygen Demand (BOD). --- incubate sealed water sample for 5 days. Measure $c(\text{O}_2)$ before and after. (with aerobic microorganisms)
The BOD equals the amount of O_2 consumed as a result of oxidn. of the dissolved organic matter.
BOD unpolluted water ≈ 0.7 ppm (well < 8.7 ppm)
BOD sewage water \approx few hundred ppm

- Chemical Oxygen Demand (COD) - use dichromate (powerful oxidiser); oxidisable substances consume $\text{Na}_2\text{Cr}_2\text{O}_7$. Determine unreacted $\text{Na}_2\text{Cr}_2\text{O}_7$ with standard Fe^{2+} .

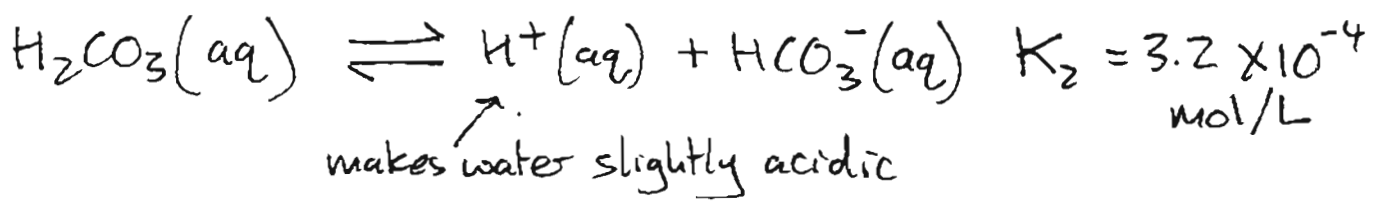
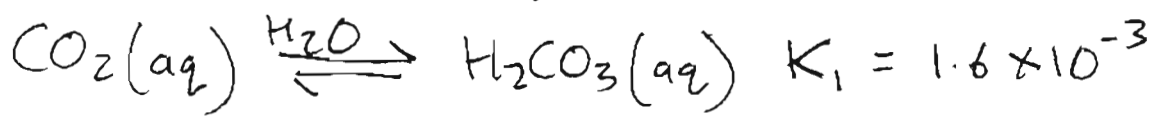
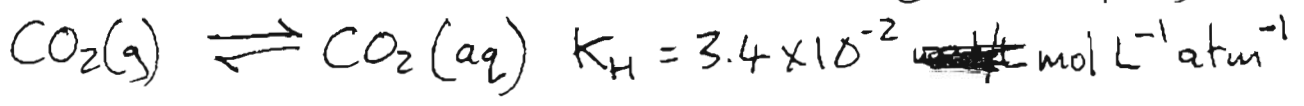


- Total Organic Carbon (TOC) --- oxidise organic compounds $\Rightarrow \text{CO}_2$ by combustion. Analyse CO_2 by GC or IR.

CO₂ solubility in water ... more complicated 'cos CO₂ interacts chemically with water.



We will consider the total of CO₂(aq) and undissociated H₂CO₃ together (txt p137) (aq).



Almost none of the HCO₃⁻(aq) dissociates

CO₂(aq) and H₂CO₃(aq) equilibrate rapidly, so we can write the composite acidity constant K_a as,

$$K_a = K_1 K_2 = 4.2 \times 10^{-7} \text{ mol/L at } 25^\circ\text{C}$$

This is for: H₂CO₃(aq) ⇌ H⁺(aq) + HCO₃⁻(aq).

Note The concns of CO₂(g) and H₂CO₃(aq) do not change; the atmosphere is an inexhaustible reservoir of CO₂ and the concn of CO₂(aq) in equilibrium with the air is given by

$$P(CO_2(g)) = 375 \text{ ppmv} \rightarrow c(CO_2(aq)) = 1.3 \times 10^{-5} \text{ mol/L}$$

↑
note, book (p138) uses 300 ppmv

So, we can figure out the pH and total carbonate

$$K_a = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} = 4.2 \times 10^{-7} \text{ mol/L}$$

$$[H^+][HCO_3^-] = x^2 = K_a [H_2CO_3] = (4.2 \times 10^{-7} \text{ mol/L})(1.3 \times 10^{-5} \text{ mol/L})$$

$$x = [H^+] = [HCO_3^-] = 2.3 \times 10^{-6} \text{ mol/L}$$

pH = 5.63 *i.e.* pure water in equilib. with air is not at pH 7 (see later, "acid rain")

Since CO₂(aq) and HCO₃⁻(aq) are the quantitatively important forms of carbonate.

$$\text{Total carbonate} = [H_2CO_3] + [HCO_3^-]$$

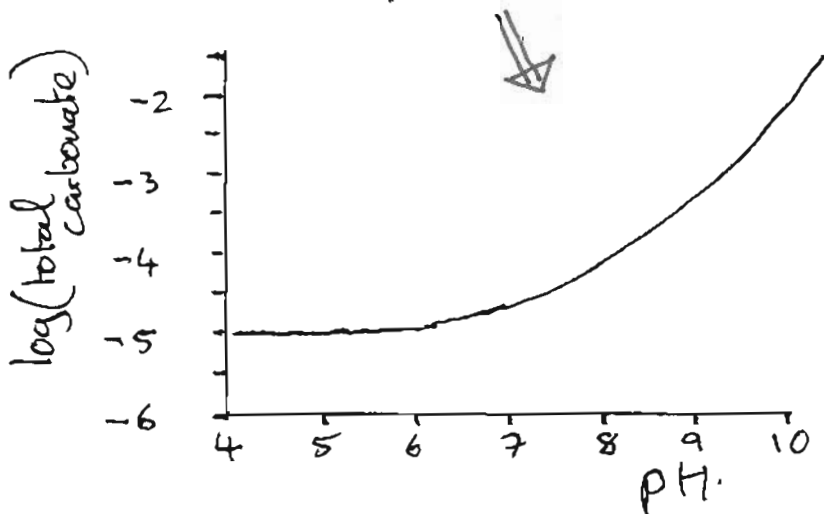
$$= 1.3 \times 10^{-5} \text{ mol/L} + 2.3 \times 10^{-6} \text{ mol/L}$$

$$= 1.5 \times 10^{-5} \text{ mol/L. } ([CO_3^{2-}] \text{ is } \sim 5 \times 10^{-11} \text{ mol/L})$$

much less

In cases where the pH of water is at a higher value due to other bases, the total concn of carbonate (= [CO₂] + [H₂CO₃] + [HCO₃⁻] + [CO₃²⁻]) in equilib.

with the atmosphere increases.



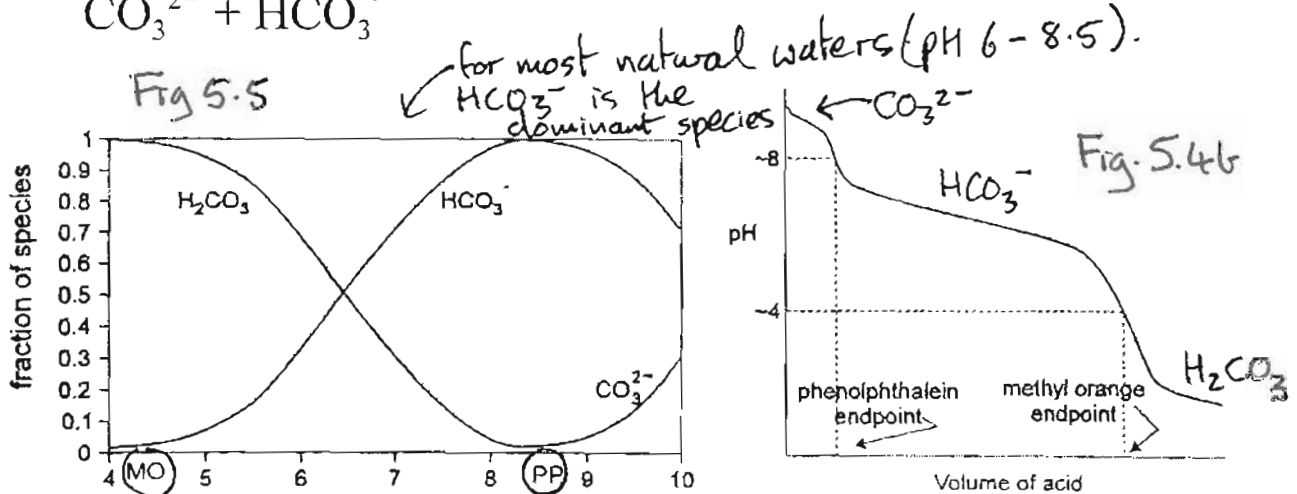
artist's impression of Fig 5.3 (text p 139) which uses 350 ppmv CO₂(g)

includes the important proton-accepting components of natural water, i.e. HCO_3^- and CO_3^{2-} (and OH^-).

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

Note: the weak carbonate bases are more abundant than OH^- . HCO_3^- is the predominant species.

- 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 $\text{CO}_3^{2-} + \text{HCO}_3^-$



Speciation (evolution) of H_2CO_3 , HCO_3^- , CO_3^{2-} with pH

Titration curve of water against HCl

- 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 $[\text{CO}_3^{2-}]/[\text{HCO}_3^-]$