Part 2. The Hydrosphere

Chapter 11. Gases in Water

Chapter 11. Gases in Water

11.1 Simple gases

- Henry's Law:

$P_g = KX_1$, P_g=partial pressure of the gas in the bulk atmosphere/Pa, K is the Henry's law constant/Pa, X_1 is the equil. mole fraction of the solute in the bulk liquid (aqueous) phase

- Practical form: (at low conc.) reciprocal of Henry's law

$[G]_l = K_H P_g$, $[G]_l$ is the equil. conc. of the solute in the bulk liquid (aqueous) phase/mol L^{-1}, K_H is the Henry's law constant/mol L^{-1} P_a^{-1}, P_g=partial pressure of the gas in the bulk atmosphere/Pa.

Table 11.1 Henry's law constants for selected gases dissolved in water at 25℃

Gas	K_H/mol L^{-1} Pa^{-1}
O_2	1.3×10^{-8}
N_2	6.4×10^{-9}
CH_4	1.3×10^{-8}
CO_2	3.3×10^{-7}
SO_2	1.2×10^{-5}
NH_3	5.7×10^{-4}
Hg	8.6×10^{-7}
CCl_4	3.7×10^{-7}
CH_3COCH_3	3.9×10^{-3}

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11.1 Simple gases

- E.g. Equil. conc. of oxygen in water at 25 ^{0}C

$$\mathrm{P}_{\mathrm{O}_2} = (P^\circ - P_{H_2O})X_{O_2}$$

where $\mathrm{P}^\circ =$ atmospheric pressure at 25℃ is 3.2×10^3 Pa.

$$P_{O_2} = (1.01\times10^5 - 3.2\times10^3)Pa\times0.209 \quad \text{Mixing ratio of } \mathrm{O}_2 \text{ in air}$$

$$= 2.04\times10^4\,Pa.$$

Using eqn 11.2:

$$[O_2]_{aq} = 1.3\times10^{-8}\,molL^{-1}Pa^{-1}\times2.04\times10^4\,Pa$$

$$= 2.7\times10^{-4}\,molL^{-1}$$

$$= 8.5\mathrm{mgL}^{-1}$$

- Solubility of oxygen:

5 ^{0}C	12.4 mg/L
30 ^{0}C	7.5 mg/L

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11.2 Gases reacting with water

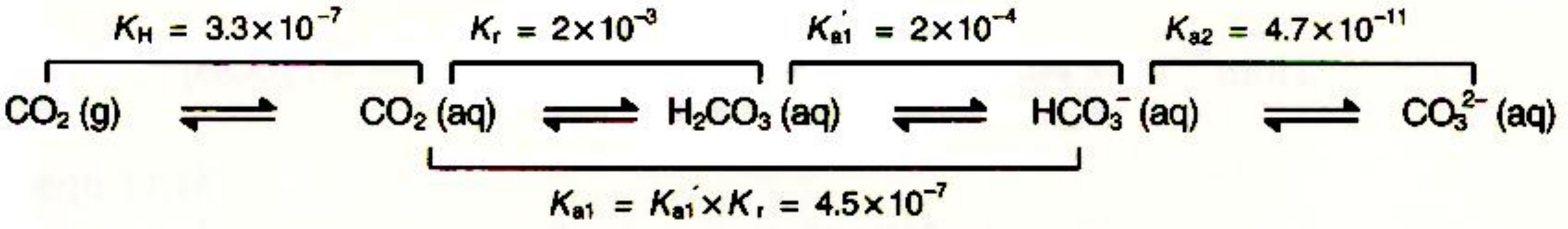
- E.g. CO_2, SO_2 and NH_3
- Dissolution of CO_2 in water

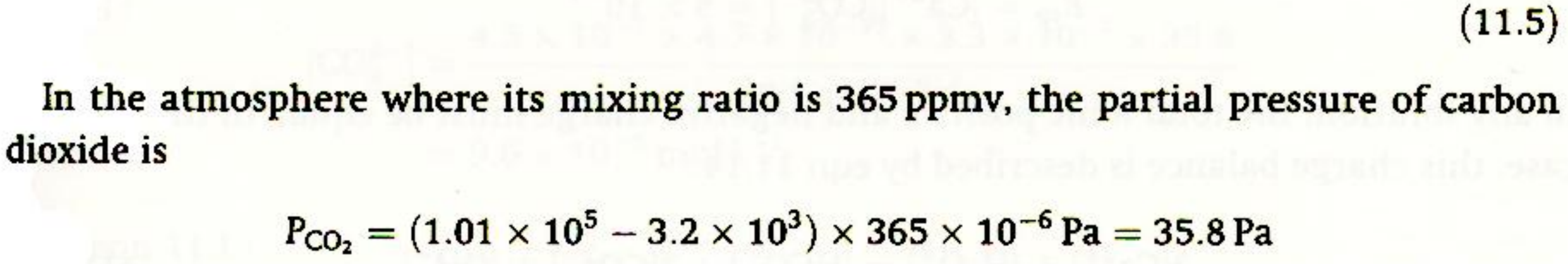
$CO_2(aq) + H_2O \rightarrow H_2CO_3(aq)$ $K_r=[H_2CO_3]/[CO_2(aq)]= 2 \times 10^{-3}$

$H_2CO_3(aq) \rightarrow HCO_3^-(aq) + H^+$ $K_{a1}' = 2 \times 10^{-4}$

$HCO_3^- (aq) \rightarrow CO_3^{2-}(aq) + H^+$ $K_{a2} = 4.7 \times 10^{-11}$

$HCO_3^-(aq) + H^+ \rightarrow CO_2(aq) + H_2O$ $K_{a1} = K_{a1}' \times K_r = 4.5 \times 10^{-7}$




(11.5)

In the atmosphere where its mixing ratio is 365 ppmv, the partial pressure of carbon dioxide is

$$P_{CO_2} = (1.01 \times 10^5 - 3.2 \times 10^3) \times 365 \times 10^{-6}\,\mathrm{Pa} = 35.8\,\mathrm{Pa}$$

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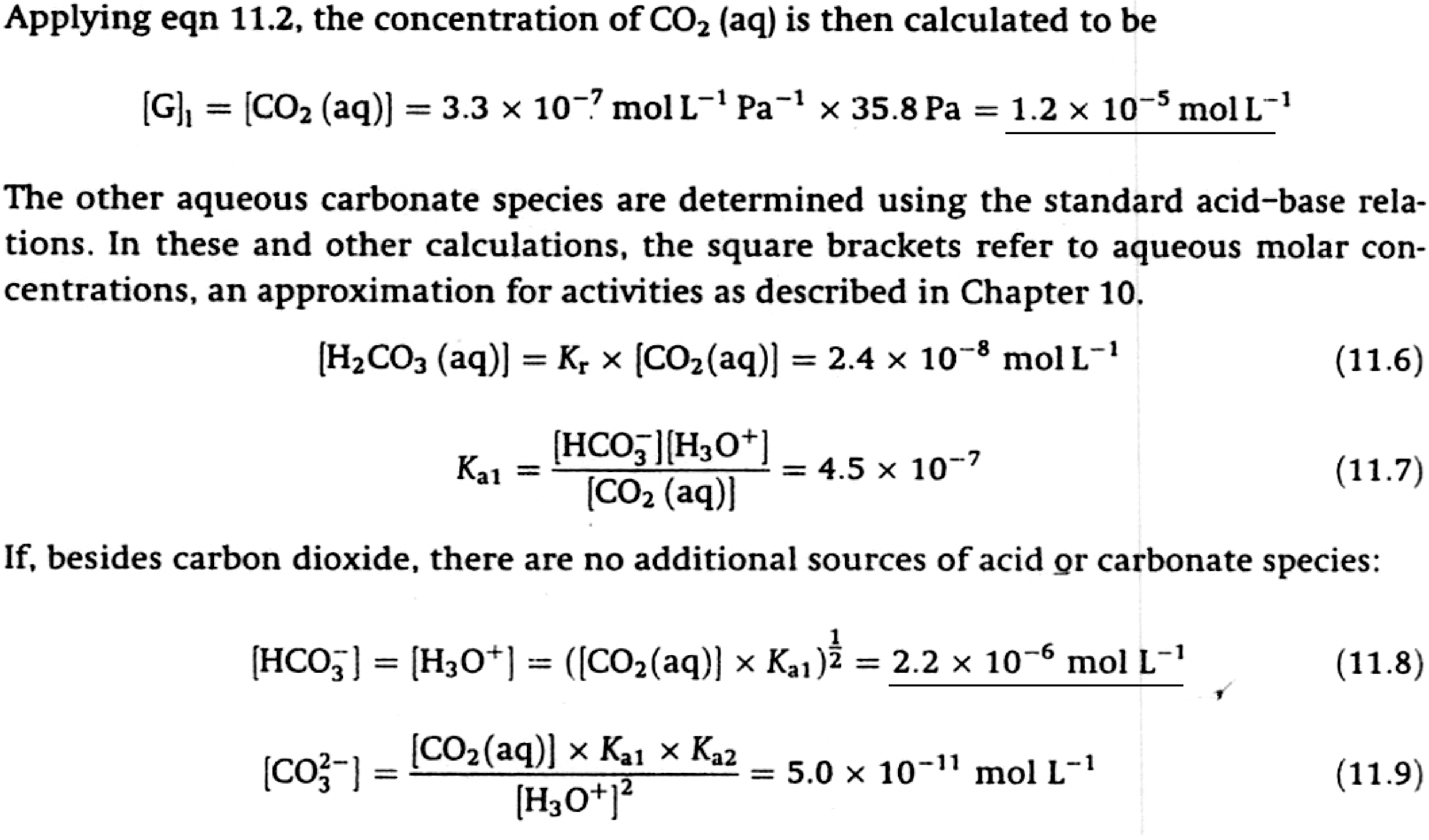
11.2 Gases reacting with water

- Dissolution of CO_2 in water (cont'd)



Applying eqn 11.2, the concentration of CO_2 (aq) is then calculated to be

$$[G]_l = [CO_2\,(aq)] = 3.3 \times 10^{-7}\,\text{mol}\,L^{-1}\,Pa^{-1} \times 35.8\,Pa = \underline{1.2 \times 10^{-5}\,\text{mol}\,L^{-1}}$$

The other aqueous carbonate species are determined using the standard acid–base relations. In these and other calculations, the square brackets refer to aqueous molar concentrations, an approximation for activities as described in Chapter 10.

$$[H_2CO_3\,(aq)] = K_r \times [CO_2(aq)] = 2.4 \times 10^{-8}\ \text{mol}\,L^{-1} \tag{11.6}$$

$$K_{a1} = \frac{[HCO_3^-][H_3O^+]}{[CO_2\,(aq)]} = 4.5 \times 10^{-7} \tag{11.7}$$

If, besides carbon dioxide, there are no additional sources of acid or carbonate species:

$$[HCO_3^-] = [H_3O^+] = ([CO_2(aq)] \times K_{a1})^{\frac{1}{2}} = \underline{2.2 \times 10^{-6}\ \text{mol}\ L^{-1}} \tag{11.8}$$

$$[CO_3^{2-}] = \frac{[CO_2(aq)] \times K_{a1} \times K_{a2}}{[H_3O^+]^2} = 5.0 \times 10^{-11}\ \text{mol}\ L^{-1} \tag{11.9}$$

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11.2 Gases reacting with water

- Dissolution of CO_2 in water (cont'd)

In many environmental situations, water is exposed to atmospheric CO_2 and also in contact with limestone ($CaCO_3$). So, if the system is at equil.,

K_H=

$$K_{a1} = \frac{[HCO_3^-][H_3O^+]}{[CO_2]} = 4.5 \times 10^{-7} \quad (11.11)$$

$$K_{a2} = \frac{[CO_3^{2-}][H_3O^+]}{[HCO_3^-]} = 4.7 \times 10^{-11} \quad (11.12)$$

$$K_{sp} = [Ca^{2+}][CO_3^{2-}] = 5 \times 10^{-9} \quad (11.13)$$

In any solution, the total ionic positive and negative charge must be equal. In the present case, this charge balance is described by eqn 11.14.

$$2[Ca^{2+}] + [H_3O^+] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] \quad (11.14)$$

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11.2 Gases reacting with water

- Dissolution of CO_2 in water (cont'd)

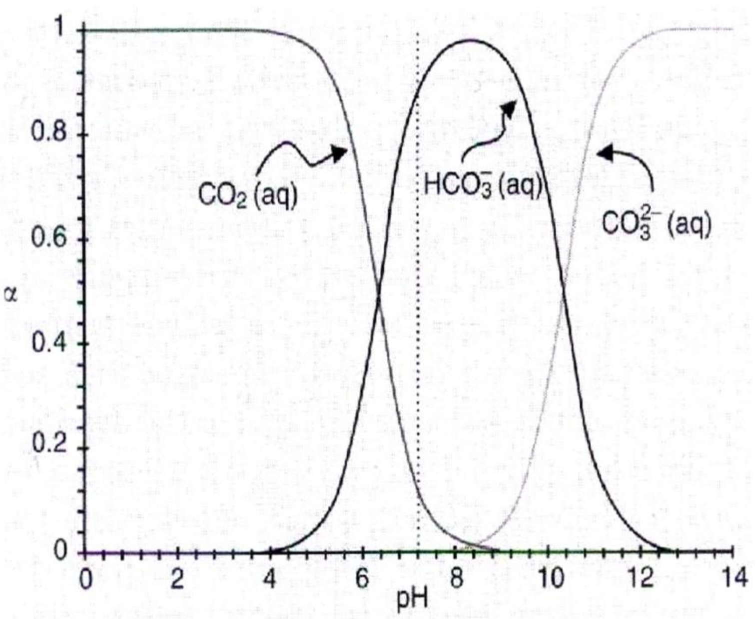

Fig. 1.2 Distribution of carbonate species as a function of pH. The α value is the fraction of a particular species: α = [individual species]/[all species].

From Fig. 1.2, in the pH range 6–9:

$$[H_3O^+] \ll [Ca^{2+}]$$
$$[CO_3^{2-}] \quad \text{and} \quad [OH^-] \ll [HCO_3^-].$$

therefore

$$2 \times [Ca^{2+}] = [HCO_3^-] \tag{11.15}$$

From eqns. 11.10, 11.11, and 11.12

$$[CO_3^{2-}] = \frac{K_{a1} \times K_{a2} \times K_H \times P_{CO_2}}{[H_3O^+]^2} \tag{11.16}$$

From eqns. 11.13 and 11.16

$$[Ca^{2+}] = \frac{K_{sp}[H_3O^+]^2}{K_{a1} \times K_{a2} \times K_H \times P_{CO_2}} \tag{11.17}$$

From eqns. 11.10, 11.11, 11.15, and 11.17

$$[HCO_3^-] = \frac{P_{CO_2} K_H K_{a1}}{[H_3O^+]} = \frac{2K_{sp}[H_3O^+]^2}{K_{a1} \times K_{a2} \times K_H \times P_{CO_2}} \tag{11.18}$$

From eqn 11.18

$$[H_3O^+]^3 = \tag{11.19}$$

We showed above that the atmospheric partial pressure of carbon dioxide is 35.8 Pa and the equilibrium aqueous concentration is 1.2×10^{-5} mol L^{-1}. From eqn 11.19

$$[H_3O^+] = \left(\frac{(3.3 \times 10^{-7})^2 \times (4.5 \times 10^{-7})^2 \times 4.7 \times 10^{-11} \times (35.8)^2}{2 \times 5 \times 10^{-9}}\right)^{\frac{1}{3}}$$
$$= 5.1 \times 10^{-9} \text{ mol L}^{-1}$$
$$\text{pH} = -\log[H_3O^+] = 8.3$$

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11.2 Gases reacting with water

- Dissolution of CO_2 in water (cont'd)

From eqn 11.18

$$[HCO_3^-] = \frac{3.3 \times 10^{-7} \times 4.5 \times 10^{-7} \times 35.8}{5.1 \times 10^{-9}} = 1.04 \times 10^{-3}\ \text{mol L}^{-1}$$

From eqn 11.16

$$[CO_3^{2-}] = \frac{4.5 \times 10^{-7} \times 4.7 \times 10^{-11} \times 3.3 \times 10^{-7} \times 35.8}{(5.1 \times 10^{-9})^2}$$
$$= 9.6 \times 10^{-6}\ \text{mol L}^{-1}$$

From eqn 11.17

$$[Ca^{2+}] = \frac{5 \times 10^{-9} \times (5.1 \times 10^{-9})^2}{4.5 \times 10^{-7} \times 4.7 \times 10^{-11} \times 3.3 \times 10^{-7} \times 35.8}$$
$$= 5.2 \times 10^{-4}\ \text{mol L}^{-1}$$

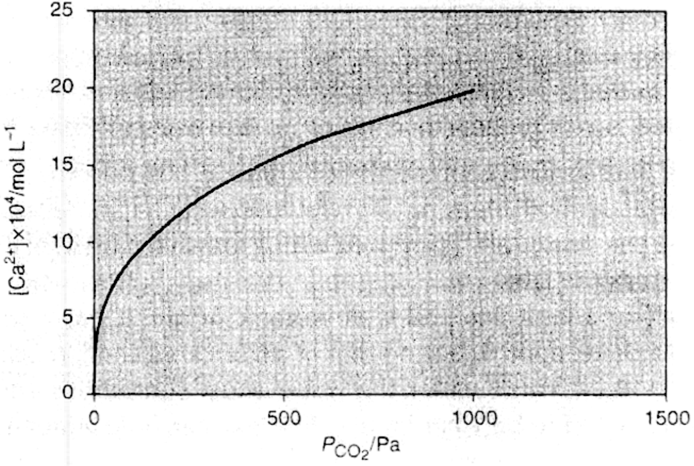

Fig. 11.1 Solubility of calcium carbonate as a function of the partial pressure of carbon dioxide in the atmosphere.

The calculations confirm that the two most important species contributing to mass balance are Ca^{2+} and HCO_3^-. The pH of the solution is 8.30. Undissociated CO_2 and CO_3^{2-} are present only in small concentrations.

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11.2 Gases reacting with water: Alkalinity

- Alkalinity of water with dissolved carbonate species
- Alkalinity: a measure of the ability of a water body to neutralize acids, i.e. proton-accepting ability, and is very important in predicting the extent of acidification of lakes and rivers

$$\text{alkalinity} = \underbrace{[OH^-] + [HCO_3^-] + 2[CO_3^{2-}]}_{} - \underbrace{[H_3O^+]}_{} \tag{11.20}$$

A related but broader concept is the acid neutralizing capacity (ANC):

$$\text{ANC} = \underbrace{[OH^-] + [HCO_3^-] + 2\,[CO_3^{2-}] + [B(OH)_4^-] + [H_3SiO_4^-] + [HPO_4^{2-}] + [HS^-] + [NOM^-] + \ldots}_{} - \underbrace{[H_3O^+] - 3\,[\,Al^{3+}] - \ldots}_{} \tag{11.21}$$

In this definition, NOM refers to

Chapter 11. Gases in Water

11.2 Gases reacting with water: Alkalinity

- Alkalinity of water with dissolved carbonate species (cont'd)

$$B(OH)_4^-(aq) + H_3O^+(aq) \rightarrow H_3BO_3 + 2H_2O \quad pKa=9.14 \qquad (11.22)$$

$$H_3SiO_4^-(aq) + H_3O^+(aq) \rightarrow Si(OH)_4 + H_2O \quad pKa=9.66 \qquad (11.23)$$

$$HPO_4^{2-}(aq) + H_3O^+(aq) \rightarrow H_2PO_4^-(aq) + H_2O \quad pKa=7.20 \qquad (11.24)$$

$$HS^-(aq) + H_3O^+(aq) \rightarrow H_2S + H_2O \quad pKa=7.00 \qquad (11.25)$$

-Above rxns have negligible effects on neutralization

-carbonate species and hydroxyl ions are the most significant species to alkalinity

-typical alkalinity value = 50~2000 μmol L^{-1}

N.B. acid-base property

In terms of **pH**: intensity factor-measures the conc. of alkali or acid immediately available for reaction

In terms of **alkalinity**: capacity factor-a measure of the ability of a water sample to sustain reaction with added acids or base. Can have negative value, meaning that extensive acidification has already occurred so that there is an excess of proton-donating species

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11.2 Gases reacting with water: Alkalinity

- Alkalinity of water with dissolved carbonate species (cont'd)

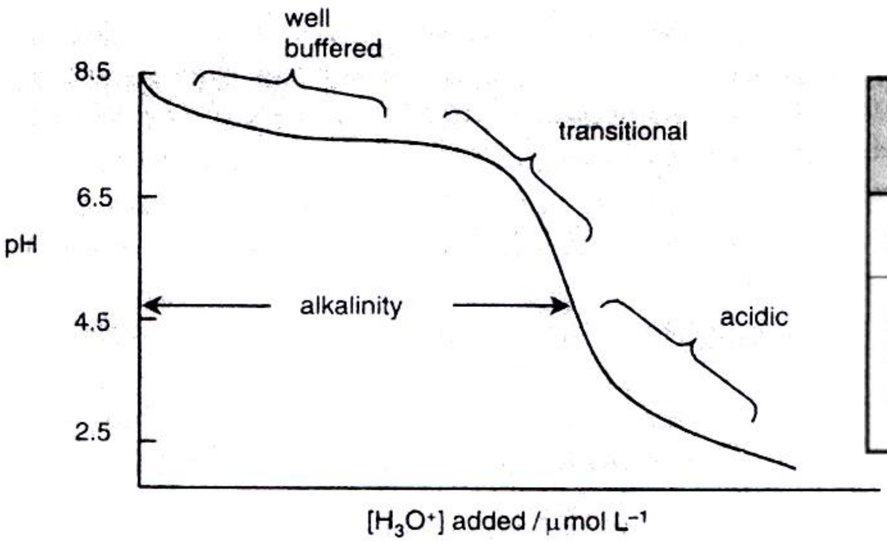

Fig. 11.2 Lake status in terms of acid/base properties.

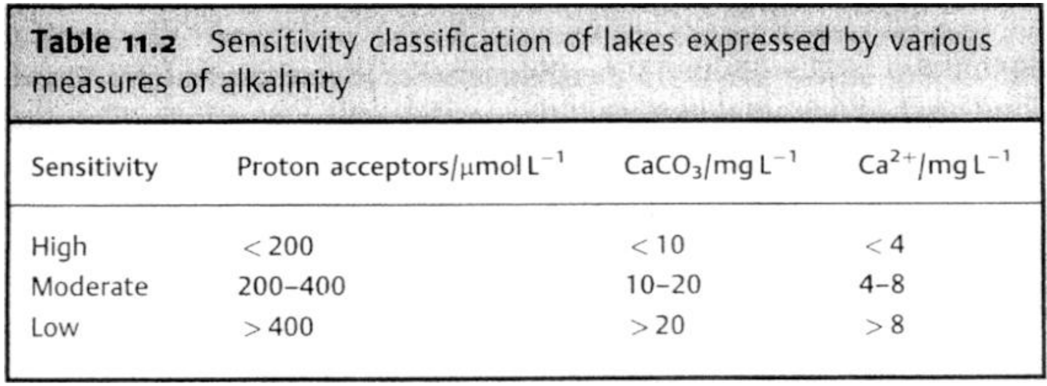

Table 11.2 Sensitivity classification of lakes expressed by various measures of alkalinity

Sensitivity	Proton acceptors/µmol L^{-1}	CaCO$_3$/mg L^{-1}	Ca^{2+}/mg L^{-1}
High	< 200	< 10	< 4
Moderate	200–400	10–20	4–8
Low	> 400	> 20	> 8

N.B. Sensitivity classification can also be in terms of alkalinity using units proton-accepting capacity,

-high value of alkalinity means that a large amount of acid would have to be added to bring the lake into the transitional and acidic ranges