Boric acid equilibria

The second most important buffer in seawater after the CO_2 system is composed of the couple, boric acid and borate ion. Since our main interest is usually in the carbonate system, a means must be developed to subtract the effects of borate ion from the total titration result.

The boric acid dissociation is given by:

$$\boxed{B(OH)_3 + H_2O \leftrightharpoons B(OH)_4^- + H^+.}$$

(The alternate expression, which is less correct,

$$H_3BO_3 \leftrightharpoons H_2BO_3^- + H^+.$$

The thermodynamic dissociation constant, K_B, is converted to an apparent dissociation constant, in the same manner as for the first and second dissociation constant of carbonic acid:

$$K_B = \frac{\{H^+\} \times \{B(OH)_4^-\}}{\{B(OH)_3\}}$$

and

$$K_B^* = \frac{\{H^+\} \times [B(OH)_4^-]}{[B(OH)_3]}. \tag{7.25}$$

$$K_B \approx \frac{[H^+][B(OH)_4^-]}{[B(OH)_3]}$$

$$B(OH)_3 + H_2O \rightleftharpoons B(OH)_4^- + H^+$$

In order to subtract the contribution made by boric acid to the buffering by seawater, we need to know the concentration of $B(OH)_4^-$, the borate ion. Since boron in seawater is thought to be conservative, i.e. to have a constant ratio to the salinity, the concentration of total boron (TB, in mol kg^{-1}), may be calculated by the relationship:

$$[TB] = 11{,}88 \cdot 10^{-6} \times S \quad (\text{Salinity})$$

$$[TB] = [B(OH)_4^-] + [B(OH)_3]$$

but

$$K_B = \frac{[H^+][B(OH)_4^-]}{[B(OH)_3]}$$

$[TB] = [B(OH)_4^-] + [B(OH)_3]$ but $K_B = \frac{[H^+][B(OH)_4^-]}{[B(OH)_3]}$

$[TB] - [B(OH)_4^-] = [B(OH)_3]$

$$K_B \cdot [B(OH)_3] = [H^+] \cdot [B(OH)_4^-]$$

$$K_B \cdot ([TB] - [B(OH)_4^-]) = [H^+][B(OH)_4^-]$$

$$K_B \cdot [TB] - K_B [B(OH)_4^-] = [H^+][B(OH)_4^-]$$

$$K_B [TB] = [B(OH)_4^-](K_B + [H^+])$$

$$[B(OH)_4^-] = \frac{K_B [TB]}{K_B + [H^+]}$$

We now have expression for the most important constituent of the AlK of seawater

Seawater normally has a pH that ranges between 7.9 and 8.4. For surface water, the average value is near 8.2; it is, therefore, alkaline, because it is on the alkaline side of the pH of a neutral solution.

The term *alkalinity*, as used in referring to seawater, has little to do with the fact that seawater is slightly basic, however. Instead, the term refers to the ability of substances in seawater to combine with hydrogen ions during the titration of seawater with strong acid to the point where essentially all the carbonate species are protonated.

END POINT TITRATION

When seawater is titrated with acid the pH drops, at first slowly and then more rapidly, as the major species that react with hydrogen ions are protonated:

$$CO_3^{2-} + H^+ \rightarrow HCO_3^-$$

$$HCO_3^- + H^+ \rightarrow H_2CO_3$$

$$B(OH)_4^- + H^+ \rightarrow B(OH)_3 + H_2O$$

pH ≃ 4

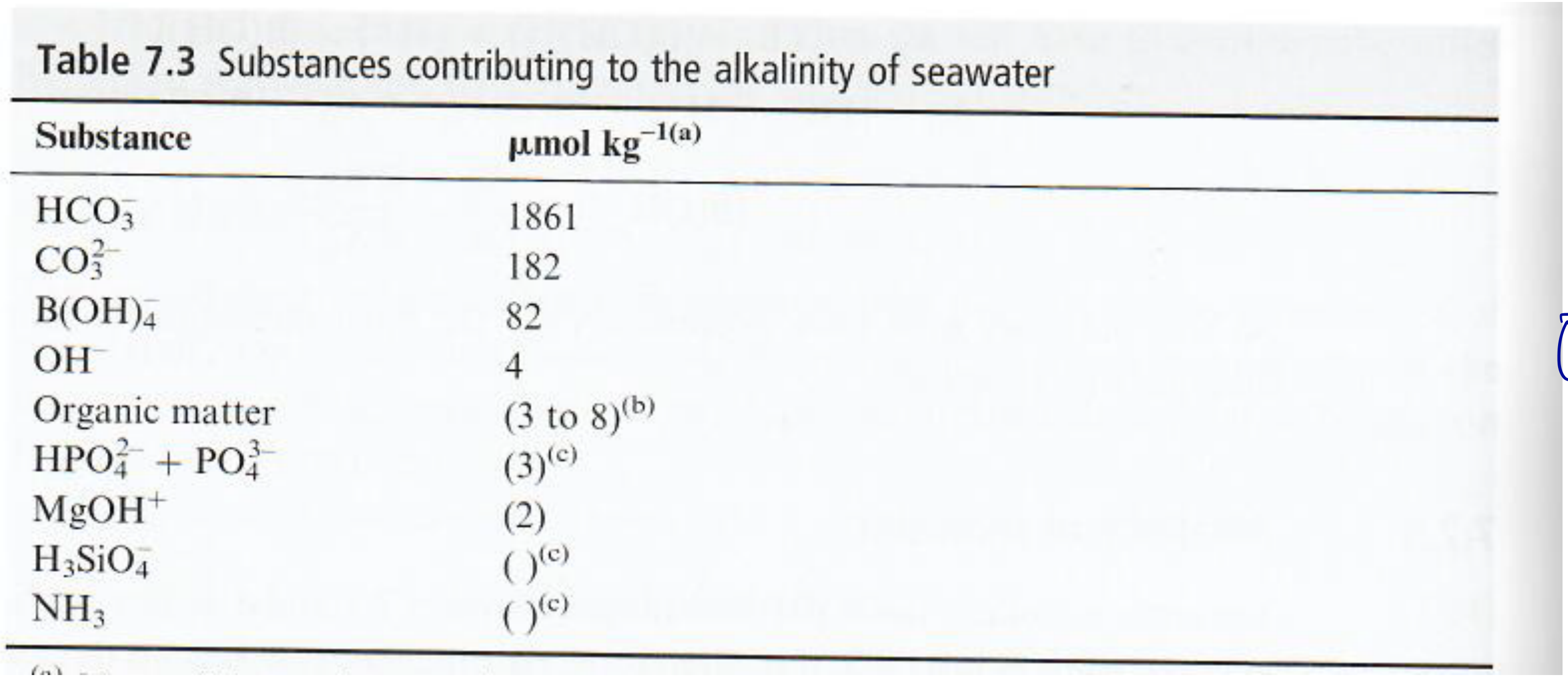


Table 7.3 Substances contributing to the alkalinity of seawater

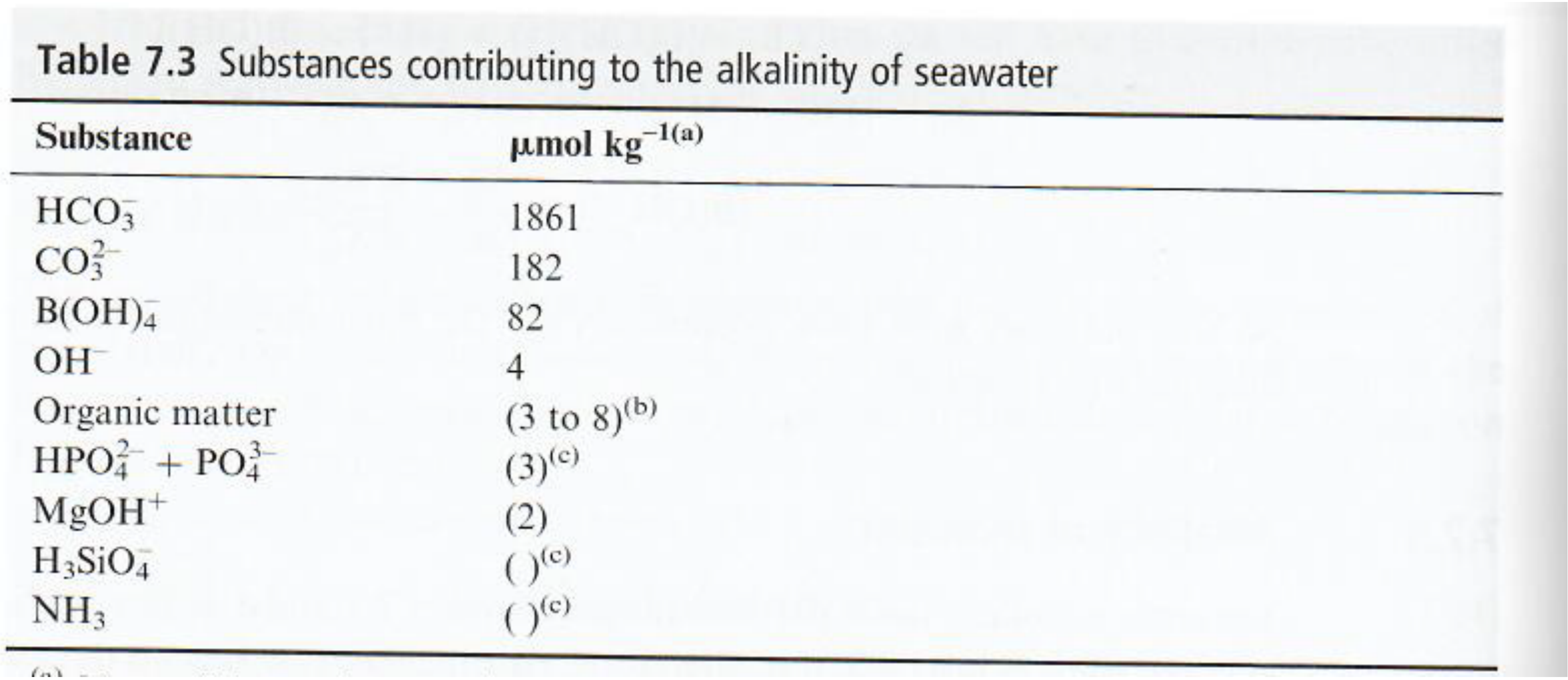
Substance	µmol kg$^{-1(a)}$
HCO_3^-	1861
CO_3^{2-}	182
$B(OH)_4^-$	82
OH^-	4
Organic matter	(3 to 8)$^{(b)}$
$HPO_4^{2-} + PO_4^{3-}$	(3)$^{(c)}$
$MgOH^+$	(2)
$H_3SiO_4^-$	( )$^{(c)}$
NH_3	( )$^{(c)}$

$$[B(OH)_4^-] = \frac{K_B[TB]}{K_B + [H^+]}$$

$$[Alk] = 2[CO_3^{=}] + [HCO_3^-] + [B(OH)_4^-] + [OH^-] - [H^+]$$

$$[Alk_C] = [Alk] - [B(OH)_4^-] - [OH^-] + [H^+]$$

$$= [Alk] - \frac{K_B[TB]}{K_B + [H^+]} - \frac{K_W}{[H^+]} + [H^+] = 2[CO_3^{=}] + [HCO_3^-]$$



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