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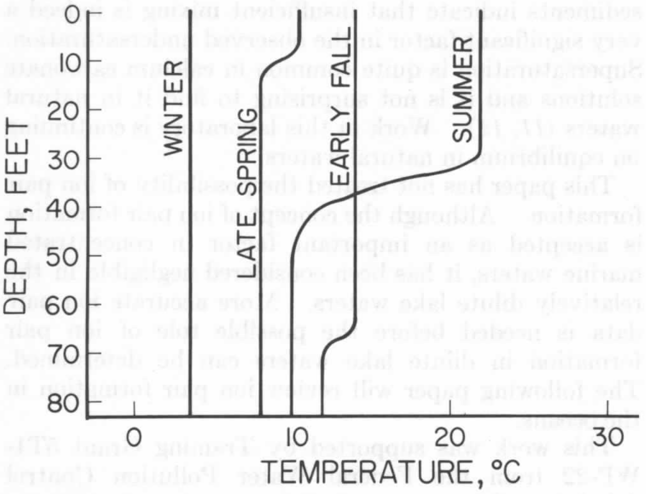
Calcium Carbonate Equilibria in Lakes

The chemistry of the aquatic environment under natural conditions may be quite different from that predicted by idealized laboratory experiments. This article and the following one (*1*) will discuss some of the problems of the chemistry of lakes and oceans.

The calcium carbonate chemistry of lakes and oceans is significant for a variety of reasons. In some lakes and oceans, calcium carbonate is a large part of the sediments. It is precipitated both by biological processes, such as in clams and many other organisms, and by inorganic processes. The limestone formations of today were formed by calcium carbonate precipitation in the seas of past geologic time. Scale formation in pipes and boilers is governed by the calcium carbonate chemistry of water supplies. Analysis of clamshells, for what is coprecipitated with calcium carbonate, may prove to be a fruitful method of determining past climatological cycles (*2*).

Many lakes and oceans are thermally stratified with a warmer, well mixed layer of water near the surface and a colder, poorly mixed layer near the bottom. This thermal stratification hinders complete mixing of the water as contrasted with the easily mixed solutions in reaction vessels in the laboratory. Many lakes lose their stratification in fall, regaining it in spring; the deep water oceans are continually stratified. The figure shows temperature versus depth for Lake Mendota, Madison, Wisconsin. It can be seen that the thermocline, the region of maximum change of temperature with depth, is nearer the surface in summer than in fall. In late fall, winter, and early spring, the lake is isothermal from top to bottom.

Because of photosynthesis in the upper layers where light can penetrate, carbon dioxide is consumed and the *p*H is higher than near the bottom where carbon dioxide is produced by decomposition of decaying organic matter. However, after fall overturn (disappearance of stratification), the *p*H is nearly constant from top to bottom (see the table).



Representative temperature versus depth for Lake Mendota.

Calculation of Calcium Carbonate Solubility

For a nonhydrolyzing substance such as $BaSO_4$, the solubility is given by $\sqrt{K_{sp}}$, and $(Ba^{2+}) = (SO_4^{2-})$ in a $BaSO_4$-H_2O system. For a nonhydrolyzing substance of the form A_2B_3 which dissociates into two A ions and three B ions, the solubility $= \sqrt[5]{K_{sp}/108}$.[1] Calcium carbonate is much more complicated and (Ca^{2+}) is not generally equal to (CO_3^{2-}) in a $CaCO_3$-H_2O system. The usual equations are given below with the equilibrium constants for 25°C. It should be emphasized that *K* values are temperature dependent and that values for the appropriate temperature must be used (*4*–*7*) in any calculations involving these equations.

$$(Ca^{2+})(CO_3^{2-}) = K_{sp} = 10^{-8.34} \qquad (1)$$

$$(H^+)(HCO_3^-)/(H_2CO_3) = K_1 = 10^{-6.35} \qquad (2)$$

$$(H^+)(CO_3^{2-})/(HCO_3^-) = K_2 = 10^{-10.33} \qquad (3)$$

Note that by convention (H_2CO_3) means $(CO_2 + H_2CO_3)$. The amount of H_2CO_3 species is about 400 times less than the amount of dissolved CO_2 species. Indeed, H_2CO_3 is actually a medium strength acid with a pK_1 of about 3.7 if (H_2CO_3) in eqn. (2) is taken to be only the H_2CO_3 species (*8*, *9*). Some texts do not make this very clear.

If pure $CaCO_3$ in excess is added to CO_2-free distilled water, the following equilibrium values are obtained (*4*).

$$\begin{aligned} (Ca^{2+}) &= 10^{-3.9} \text{ molal} \\ (CO_3^{2-}) &= 10^{-4.4} \\ (HCO_3^-) &= 10^{-4.05} \\ (H_2CO_3) &= 10^{-7.6} \\ p\text{H} &= 10.0 \end{aligned}$$

If the system is now allowed to equilibrate with the atmosphere containing carbon dioxide ($p_{CO_2} = 10^{-3.5}$ atm = 0.032% by volume) the new equilibrium values are (*4*)

$$\begin{aligned} (Ca^{2+}) &= 10^{-3.4} \\ (CO_3^{2-}) &= 10^{-4.9} \\ (HCO_3^-) &= 10^{-3.0} \\ (H_2CO_3) &= 10^{-5.0} \\ p\text{H} &= 8.4 \end{aligned}$$

In this case, the *p*H is lower and there is 3.2 times more $CaCO_3$ in solution. However, as it is less basic, there is less CO_3^{2-} and more HCO_3^- and H_2CO_3, i.e., more $(H_2CO_3 + CO_2)$. It can be seen that $CaCO_3$ is more

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[1] The reader is referred to a paper by MEITES, *et al.* (*3*) for a discussion of the ion pair concept and its effect on solubility.

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soluble at low pH than at high pH. It should be mentioned that in large bodies of water, the carbon dioxide in the water is not generally in equilibrium with the carbon dioxide in the air. This is particularly true near the bottom.

Determination of Calcium Carbonate Saturation in Natural Waters

To calculate whether a given water is undersaturated, at equilibrium, or supersaturated with respect to calcium carbonate, certain experimental data is needed. The calcium ion concentration can be determined by conventional means such as EDTA titration or atomic absorption spectrophotometry; the pH with a pH meter. The $(HCO_3^- + CO_3^{2-})$ is commonly determined by acid titration. In the pH range of most natural waters, 6.5–8.5, the (CO_3^{2-}) is negligible compared to the (HCO_3^-) so that $(HCO_3^- + CO_3^{2-}) = (HCO_3^-)$. If other bases such as $H_2BO_3^-$ (which is found in the oceans in large quantities) are present, or if there is much industrial pollution, modifications would have to be made. The ionic strength must be known for the calculation of activity coefficients.

Two approaches are commonly used, both are fundamentally the same as they depend on eqns. (1)–(3). One is the Langelier Saturation Index method (*10*) where the pH (pH$_s$) that the water would have *if saturated* is calculated from $(HCO_3^- + CO_3^{2-})$, (Ca^{2+}), temperature and ionic strength. If pH$_s$ is less than the experimental pH, the water is supersaturated; if greater, it is undersaturated. This approach is useful in water treatment processes. The following approach may be more familiar to the chemistry student.

Example: Chemical analysis of Lake Mendota, September 24, 1966, at a depth of 18 meters; major species only; molal concentration scale.

$$\begin{aligned} T &= 15.0°\text{C} \\ p\text{H} &= 7.10 \\ (Ca^{2+}) &= 8.4 \times 10^{-4} \\ (HCO_3^-) &= 3.2 \times 10^{-3} \\ (Mg^{2+}) &= 1.0 \times 10^{-3} \\ (SO_4^{2-}) &= 2.1 \times 10^{-4} \\ (Cl^-) &= 1.4 \times 10^{-4} \end{aligned}$$

The ionic strength is calculated to be 0.0045 and from the Debye-Huckel equation the activity coefficients, γ, are calculated.

	$\log \gamma$	γ
Ca^{2+}	-0.13	0.74
CO_3^{2-}	-0.13	0.74
HCO_3^-	-0.02	0.96

It can be seen that even for a relatively dilute fresh water lake, such as Mendota, the activity coefficients of divalent ions are appreciably different from unity and cannot be ignored. From eqn. (*3*).

$$\begin{aligned} m_{CO_3^{2-}} &= K_2\gamma_{HCO_3^-} - m_{HCO_3^-}/\gamma_{CO_3^{2-}}a_{H^+} \\ &= 10^{-10.43}10^{-0.02}10^{-2.50}/10^{-0.13}10^{-7.10} = 10^{-5.72} \end{aligned}$$

Now the (Ca^{2+}), theoretically in equilibrium with this carbonate, is calculated from eqn. (1).

$$\begin{aligned} m_{Ca^{2+}} &= K_{sp}/\gamma_{CO_3^{2-}}\gamma_{Ca^{2+}}m_{CO_3^{2-}} \\ &= 10^{-8.22}/10^{-0.13}10^{-0.13}10^{-5.72} = 10^{-2.24} = 5.7 \times 10^{-3}m \end{aligned}$$

If this calculated value is compared with the experimental value of 8.4×10^{-4}, it can be seen that the lake at these conditions is undersaturated by a factor of about seven with respect to calcium ion. However, this assumes that all concentrations are correct except for calcium which is not realistic. If $CaCO_3$ goes into solution at this pH, HCO_3^- (not any appreciable CO_3^{2-}) will also be formed. Therefore, the equations are solved again, changing both calcium ion and bicarbonate ion in the ratio of 1:2. If this is done, it will be found that the water is undersaturated with respect to calcium carbonate by a factor of about three.

Discussion

Representative data for Lake Mendota is presented in the table. Perhaps the most noticeable feature is the insensitivity of the calcium ion concentration to pH.

Representative Data for Lake Mendota[a]

	Summer	Fall	Winter (ice covered)	Spring
Temp. °C.				
Top	22.0	14.3	3.5	10.4
Bottom	10.1	11.8	3.5	8.2
pH				
Top	9.0	8.2	7.9	9.0
Bottom	7.7	7.2	7.7	8.7
$(Ca^{2+}) \times 10^4$ m				
Top	5.4	5.5	7.0	5.4
Bottom	5.6	6.8	6.6	5.4
$(HCO_3^-) \times 10^3$ m				
Top	3.2	3.2	3.1	3.2
Bottom	3.1	3.8	3.2	3.2
Approximate % $CaCO_3$ saturation				
Top	300	100	60	300
Bottom	50	33	40	150

[a] Lake Mendota, Madison, Wisconsin, is a fresh water lake, formed by glacial action about 10,000 years ago, with an area of about 15 square miles, a maximum depth of 84 ft, and an average depth of 40 ft. The sediments are about 30% calcium carbonate.

In summer, for example, the pH decrease of about 1.3 units from top to bottom would be expected to increase the calcium ion concentration by a factor of about six; however, there is practically no change. There is evidence that this same lack of equilibrium is also true for some other lakes and oceans in spite of the great age of these waters. The undersaturation in large bodies of water might be due to inadequate vertical mixing. It should be noted that molecular diffusion is far too slow a process to cause any appreciable mixing in large bodies of water. Experiments currently underway in this laboratory on Lake Mendota water and sediments indicate that insufficient mixing is indeed a very significant factor in the observed undersaturation. Supersaturation is quite common in calcium carbonate solutions and it is not surprising to find it in natural waters (*11, 12*). Work in this laboratory is continuing on equilibrium in natural waters.

This paper has not treated the possibility of ion pair formation. Although the concept of ion pair formation is accepted as an important factor in concentrated marine waters, it has been considered negligible in the relatively dilute lake waters. More accurate ion pair data is needed before the possible role of ion pair formation in dilute lake waters can be determined. The following paper will review ion pair formation in the oceans.

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