

# MARINE AND OCEAN CHEMISTRY

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Read the details of the information provided below from the sources recommended as a reference.

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# PLAN – CONTENT – REFERENCES

1. Introduction
2. The water in seawater
3. Salinity, chlorinity, conductivity, and density
4. Major constituents of seawater
5. Simple gases
6. Salts in solution
7. Carbon dioxide
8. Nutrients
9. Trace metals and other minor elements
10. Chemical extraction of useful substances from the sea

## **References:**

1. An Introduction to the Chemistry of the Sea, Michael E. Q. Pilson
2. Marine Chemistry & Geochemistry, John H. Steele et al.
3. Chemistry in the Marine Environment, R. E. Hester and R. M. Harrison
4. Marine Chemistry, P. J. Wangersky

# CARBON DIOXIDE

1. Reservoirs of carbon dioxide
2. Relationships in solution
3. Calcium carbonate
4. Anthropogenic carbon dioxide
5. Longer-term issues

- The carbon dioxide system is responsible for about 95% of the **acid–base buffering** over the normal range of pH in ordinary seawater.
- Short-term changes in the concentration of total CO<sub>2</sub> in seawater are due largely to the **photosynthetic and respiratory activities** of organisms

- The questions associated with the problems of precipitation and solution of calcium carbonate in the oceans can only be approached on the basis of a thorough understanding of the  $\text{CO}_2$  system itself.
- The climate of the Earth is strongly affected by the concentration of  $\text{CO}_2$  in the atmosphere.

- The reservoir of  $\text{CO}_2$  in the oceans is much greater than that in the atmosphere, so small changes in processes affecting the oceanic reservoir could have comparatively large effects on the concentration in the atmosphere.
- Humans are significantly increasing the atmospheric concentration of  $\text{CO}_2$ , and the oceans play an important role in modulating this increase.

# RESERVOIRS OF CARBON DIOXIDE

- The largest reservoirs of carbon accessible on the surface of the Earth are in the rocks, and most of this is in the form of **limestone**. This rock type is composed largely of **calcium carbonate** and calcium–magnesium carbonate (**dolomite**). In addition, some carbon is found in beds of coal.



## RELATIONSHIPS IN SOLUTION



- The rate of reaction is pseudo first order, which means that the rate of the reaction may be calculated using the concentration of only one reacting substance.

$$\frac{d[\text{CO}_2]}{dt} = -k_{\text{CO}_2}[\text{CO}_2]$$

- It is observed that, at 25 °C,  $k_{\text{CO}_2} = 0.03 \text{ s}^{-1}$
- The direct hydration reaction is remarkably slow.

- The back reaction:



$$\frac{d[\text{H}_2\text{CO}_3]}{dt} = -k_{\text{H}_2\text{CO}_3}[\text{H}_2\text{CO}_3]$$

- Where  $k_{\text{H}_2\text{CO}_3} = 26 \text{ s}^{-1}$
- Reactions are perfectly reversible, and are commonly represented this way:

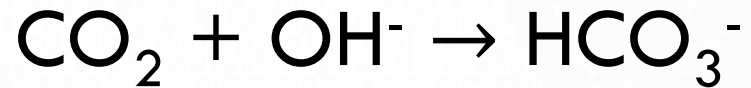


- When the rates of the forward and back reactions are the same, the reactants are at equilibrium, and the equilibrium constant (designated  $K_0$ ) is thus the ratio of the two rate constants:

$$K_0 = \frac{[H_2CO_3]}{[CO_2]} = \frac{-k_{CO_2}}{-k_{H_2CO_3}} = \frac{0.03}{26} = \frac{1}{870}$$

- It shows that, of the two forms considered here, by far the greatest proportion is present in the form of  $CO_2(f)$ , rather than  $H_2CO_3$ .

- If the solution is alkaline, the following reaction also becomes significant:



- The rate constant,  $k_{\text{OH}}$   $8500 \text{ s}^{-1}$
- The various rates of reactions are either directly or indirectly dependent on the pH. Since the overall rates of reactions are pH-dependent, so is the rate of approach to equilibrium, and it happens that there is a minimum in this rate at intermediate values of pH.

# Equilibria In Solution

- The carbon dioxide that has combined with water is called **carbonic acid**.

The dissociation constants are formulated as follows:

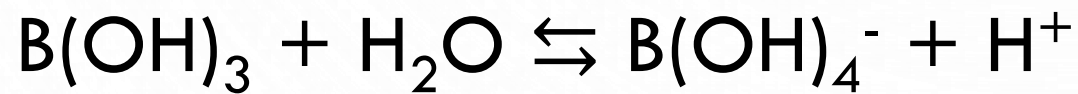
$$K_0 = \frac{\{\text{H}_2\text{CO}_3\}}{\{\text{H}_2\text{O}\} \times \{\text{CO}_2(\text{f})\}}$$

$$K_1 = \frac{\{\text{H}^+\} \times \{\text{HCO}_3^-\}}{\{\text{H}_2\text{CO}_3\}}$$

$$K_2 = \frac{\{\text{H}^+\} \times \{\text{CO}_3^{2-}\}}{\{\text{HCO}_3^-\}}$$

## Boric Acid Equilibria

- The second most important buffer in seawater after the  $\text{CO}_2$  system is composed of the couple, **boric acid and borate ion**.
- The boric acid dissociation is given by:



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

and

$$K_{\text{B}}^* = \frac{\{\text{H}^+\} \times [\text{B(OH)}_4^-]}{[\text{B(OH)}_3]}$$