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

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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

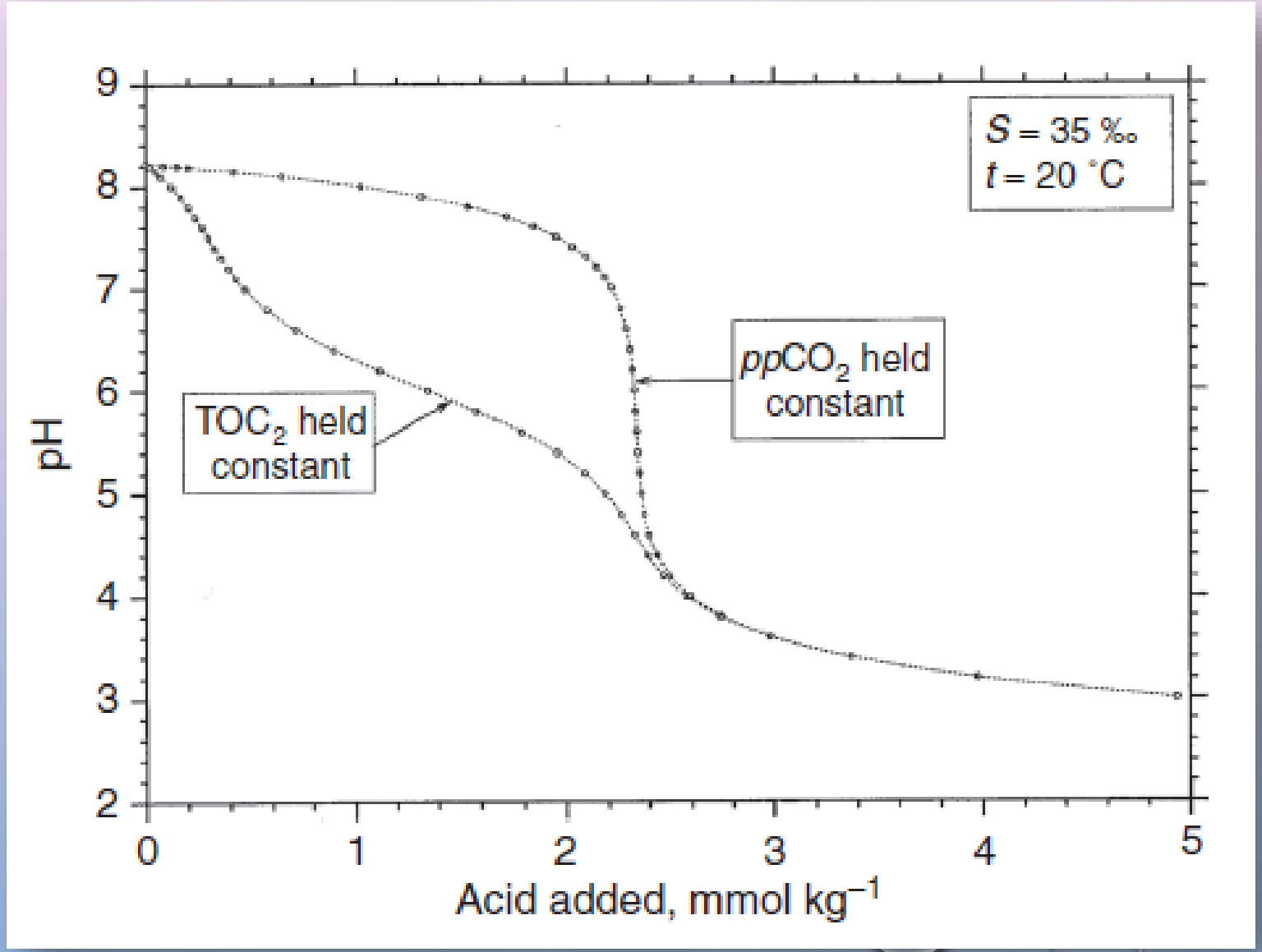
1. Reservoirs of carbon dioxide
2. Relationships in solution
3. Calcium carbonate
4. Anthropogenic carbon dioxide
5. Longer-term issues

Alkalinity 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 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.

Substances contributing to the alkalinity of seawater	
Substance	**µmol kg^{-1} (S=35‰, pH=8.2, t=18 °C)**
HCO_3^-	1861
CO_3^{2-}	182
$B(OH)_4^-$	82
OH^-	4
Organic matter	3 to 8
$HPO_4^{2-} + PO_4^{3-}$	3
$MgOH^+$	2
$H_3SiO_4^-$	Very low in surface waters
NH_3	

What Happens When We Add Acid?



CALCIUM CARBONATE

- The residence time of calcium in the oceans is about 700 000 years. The amount entering the sea today is estimated at about 21×10^{12} moles per year or about 840 million tons of calcium per year.

- The $CaCO_3$ that leaves the ocean does so via some deep-sea sediments and by precipitation on coral reefs and in other shallow areas.
- Calcium carbonate usually precipitates in either of two major crystal forms: aragonite and calcite.
- Aragonite is less stable and more soluble under normal conditions than calcite, so in sediments aragonite is much less abundant than calcite.
- Many kinds of organisms make calcareous shells that eventually sink towards the bottom of the sea.

Among the major agents of calcium carbonate removal are the following:

1. Foraminifera
2. Coccoliths
3. Mollusc shells
4. Coral reefs
5. Green calcareous algae
6. Inorganic precipitation

Solubility Of Calcium Carbonate

- The thermodynamic solubility product constant for calcium carbonate is expressed as follows:

$$CaCO_3 \leftrightarrows Ca^{2+} + CO_3^{2-}, \qquad K_{sp} = \{Ca^{2+}\}\{CO_3^{2-}\}.$$

aragonite $K_{sp} \approx 5 \times 10^{-9}$,

calcite $K_{sp} \approx 3.35 \times 10^{-9}$.

$$[Ca^{2+}][CO_3^{2-}] = (10.28 \times 10^{-3})(2.15 \times 10^{-4})$$

$$IP = 22.2 \times 10^{-7}.$$

$$\frac{IP}{K_{sp}} = \frac{22.2 \times 10^{-7}}{3.35 \times 10^{-9}} = 663.$$

$$\gamma Ca^{2+} = 0.256, \gamma CO_3^{2-} = 0.205.$$

$$\frac{IP}{K_{sp}} = \frac{[Ca^{2+}]\gamma_{Ca^{2+}}[CO_3^{2-}]\gamma_{CO_3^-}}{3.35 \times 10^{-9}} = 35.$$

ANTHROPOGENIC CARBON DIOXIDE

- The effects of carbon dioxide introduced by humans into the atmosphere stems largely from the fact that this causes an increase in the so-called **greenhouse effect**.

- Water vapor, CO_2, and some other less-abundant gases absorb some of the infrared heat rays that otherwise the earth would radiate to outer space, and thus these gases help to keep the temperature of earth considerably warmer than it would be in their absence.
- Only recently has it become generally appreciated that acidification of the ocean caused by increased CO_2 is also a matter of considerable concern.