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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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

SALTS IN SOLUTION

1. Solubility of salts
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SOLUBILITY OF SALTS

In complex solutions with many ions present, it is necessary to use the solubility product constant, which is formulated as follows:

$$K_{sp} = [M^{+}]^{\nu+}[A^{-}]^{\nu-}$$

K_{sp} = The solubility product constant

$[M^+]$ and $[A^-]$ = The concentrations of cations and anions

ν^+ And ν^- = The numbers of cations and anions

- If the ion product (IP) calculated as above is less than the solubility product constant, the solution is undersaturated, and if it is greater the solution is supersaturated.

S = 35‰	mg kg^{-1} S^{-1}	g kg^{-1}	mmol kg^{-1}	mM
Ca^{2+}	11.76	0.4115	10.27	10.52
CO_3^{2-}	0.317	0.0111	0.184	0.189

$$IP = [Ca^{2+}] \times [CO_3^{2-}] = (10.52 \times 10^{-3})(189 \times 10^{-6}) \approx 2104 \times 10^{-9}$$

$$\Omega = \frac{IP}{K_{sp}} \approx \frac{2104 \times 10^{-9}}{3.35 \times 10^{-9}} \approx 628$$

Ω = The degree of saturation

- In typical surface seawater, a simple-minded calculation would show $CaCO_3$ to be supersaturated by a factor of about 630.
- Obviously, the oceans are not now instantaneously turning milky-white with a precipitate of calcium carbonate.

Is the ocean really this supersaturated, or
is the calculation too simplistic and somehow in error?

These are the properties of solutions which are called "**colligative properties**", because they act together; that is, there is a generally constant proportionality between them.

- Depression of the freezing point;
- Depression of the vapor pressure;
- Elevation of the boiling point; and
- Elevation of osmotic pressure.

- The magnitudes of these effects appear to be proportional to the ratio of the number of moles of solute to the number of moles of solvent.

- In 1885, the Dutch scientist Jacobus Henricus van’t Hoff discovered that in dilute solutions the osmotic pressure follows the relationship:

$$\Pi = c\,R\,T$$

Π = The pressure

c = The concentration in moles per liter

R = Gas constant

T = The absolute temperature in Kelvin

ACTIVITY COEFFICIENTS

- **The activity** of each ion was reduced by the presence of the other ions, and this effect was sufficient to account for the other effects on colligative properties.

- The activity of a salt is expressed in concentration units and the ratio of the activity to the actual concentration is the activity coefficient. Thus:

$$\{NaCl\} = [NaCl] \times \gamma_{NaCl}$$

[ ] = The chemical concentration of a substance

{ } = The activity of that substance

- As the concentration of all ions in the solution approaches zero, the freedom of action of each ion approaches a maximum, and the activity coefficient approaches 1.

- The ionic strength, I, is calculated as follows:

$$I = \frac{1}{2}\sum m_i \left(z_i^2\right)$$

m_i = The molal concentration of the i ion

z_i = The charge on the i ion

- Seawater is a mixture of many ions: it is about 0.5 molal in each of the two most concentrated ions, and it has an ionic strength, I, of about 0.7, so it is both complex and relatively concentrated.

Estimated free-ion activity coefficients for some seawater constituents (S=35‰ t=25 °C)			
Cations	**Activity coefficients**	**Anions**	**Activity coefficients**
H^+	0.967	OH^-	0.863
Na^+	0.707	Cl^-	0.623
K^+	0.623	Br^-	0.642
NH_4^+	0.618	NO_3^-	0.490
Mg^{2+}	0.285	SO_4^{2-}	0.219
Ca^{2+}	0.256	CO_3^{2-}	0.205