Ion Speciation

OCN 623 – Chemical Oceanography

Speciation defines the chemical reactivity of elements in the ocean

- Affects residence time e.g. anions vs cations
- Affects biological uptake e.g. Fe species
- Affects transformation paths e.g. $N_2 \rightarrow NO_3$
- Affects other properties of seawater e.g. $MgSO_4^0$ pairing

Speciation follows the rules of chemical equilibrium

Reactions proceed in the direction that lowers energy
Can predict speciation if know basic thermodynamics

Equilibrium:

Reaction: \( aA + bB = cC + dD \)

Equilibrium constant \( K_{eq} = \frac{[C]^c[D]^d}{[A]^a[B]^b} \)

example;

\[ \text{NaCl} \text{ (s)} = \text{Na}^+ \text{ (aq)} + \text{Cl}^- \text{ (aq)} \]

Reaction goes to completion, get 1 mole \( \text{Na}^+ \) and 1 mole \( \text{Cl}^- \)

i.e. 2 moles of ions total

BUT

Colligative properties of solutions depend on number of ions in solution
e.g. lowering of vapour pressure
elevation of boiling point
depression of freezing point

Depression of freezing point:
\[ \Delta t = -nk_f m \]
For water \( k_f \) is \(-1.86^\circ C \text{ kg H}_2\text{O}^{-1} \text{ mol solute}^{-1}\)

e.g.
Take NaCl solution, 2 moles solute, expect depression of
\(-3.72^\circ C\)
but in fact get \(-3.01^\circ C\)

NaCl is acting as though there were less than 2 moles of ions

**Solution is non-ideal**

Ionic interactions cause non-ideality
As ionic strength increases interactions, and non ideality increase
Effective concentration of ions is --

**ACTIVITY**
Affects equilibrium, rewrite equation:

$$K_{eq} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

activity (a) of an ion i is defined:

$$a_i = \gamma_i m_i$$

$\gamma_i$ is the activity coefficient for the ion i

$m_i$ is its total molality

$\gamma$ can be calculated by equations, depend on ionic strength e.g.

Debye-Huckel equation gives

$$\log \gamma_i = -A z_i^2 \sqrt{I}$$

$A$ is a constant for the ion

$z_i$ is its charge

$I$ is the ionic strength

Calculate ionic strength:

$$I = \frac{1}{2} \sum_i m_i z_i^2$$

$I$ is the sum of total charge from ions
As ionic strength $\rightarrow 0 \gamma \rightarrow 1$

Example of calculation of ionic strength of solution

TABLE 5.1
Method for Calculating Ionic Strengths of Solutions

<table>
<thead>
<tr>
<th>Solute</th>
<th>Molality (m)</th>
<th>Ionic Charge (z)</th>
<th>$\gamma$</th>
<th>$m\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$^+$</td>
<td>0.5</td>
<td>+1</td>
<td>1</td>
<td>0.5</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>0.5</td>
<td>-1</td>
<td>1</td>
<td>0.5</td>
</tr>
<tr>
<td>K$^+$</td>
<td>0.2</td>
<td>+1</td>
<td>1</td>
<td>0.2</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>0.1</td>
<td>-2</td>
<td>4</td>
<td>0.4</td>
</tr>
</tbody>
</table>

$\sum m\gamma = 1.6 m$

$I = \frac{1}{2}(1.6)$

$= 0.8 m$

As ionic strength gets larger, formula gets more complex

Seawater is 0.7 M

Uncharged species not affected much by ionic strength

Most interactions are electrostatic

Activity coefficients for uncharged species can be $>1$

TABLE 5.2
Various Expressions for the Calculation of Single Ion Activity Coefficients

<table>
<thead>
<tr>
<th>Approximation</th>
<th>Equation</th>
<th>Approximate Applicability (ionic strength (M))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Debye–Hückel</td>
<td>$\log \gamma = -A_0\sqrt{T}$</td>
<td>$&lt;10^{-2}$</td>
</tr>
<tr>
<td>Extended Debye–Hückel</td>
<td>$= -A_0\sqrt{T} + B_0\sqrt{T}$</td>
<td>$&lt;10^{-1}$</td>
</tr>
<tr>
<td>Gintenberg</td>
<td>$= -A_0\sqrt{T}$</td>
<td>$&lt;10^{-1}$ useful in solutions of several electrolytes</td>
</tr>
<tr>
<td>Davies</td>
<td>$= -A_0\sqrt{T}$</td>
<td>$&lt;0.5$</td>
</tr>
<tr>
<td>Brönsted-Guggenheim</td>
<td>$\gamma = \gamma_{ion} + A(C) + \sum B_i(C_i)$</td>
<td>$\leq 4$</td>
</tr>
</tbody>
</table>


*Values for the constants can be found in Stumm and Morgan (1981).*
Interaction types

Non-specific:
interaction between the ion and the solvent
ordered shell-- drops off considerably with distance
well developed hydration shell no other interactions-- free ion (Na\(^+\),Cl\(^-\))

Specific interactions:
continuum
weak ion pairs, sharing hydration shells
→ complex ions that are sharing electrons
Co-ordination complex:

M$^+$ metal is co-ordinated with an electron donor ligand L$^-$

Strongest bonds favoured -- most decrease in energy

Is a chemical equilibrium -- e.g.

\[ aM^+(aq) + bL^-(aq) = M_aL_b(aq) \]

Recast equation in terms of concentration using \( a = \gamma_m \) (is easier)

\[
K_c = \frac{[M_aL_b]}{[M^+]^a[L^-]^b} = \frac{(\gamma_m^+)^a (\gamma_m^-)^b}{\gamma_{MaLb}} K_{eq}^0
\]

\( K_{eq}^0 \) is a thermodynamic equilibrium for I=0 ionic strength, and 25˚C

So, \( K_c \) not really a constant, only valid for conditions that activity coefficients were calculated for
Can calculate ion pairing:

1 mole of MgSO\(_4\), 1 mole of CaF\(_2\) in 1 kg of H\(_2\)O

Species in solution:

Mg\(^{2+}\), Ca\(^{2+}\), SO\(_4^{2-}\), F\(^-\), Mg SO\(_4\)\(^0\),

MgF\(^+\), Ca SO\(_4\)\(^0\), CaF\(^+\)

Can write mass balance for each species, e.g.

\([\text{Mg}] = [\text{Mg}^{2+}] + [\text{Mg}^{2+}]_{\text{MgSO}_4} + [\text{Mg}^{2+}]_{\text{MgF}^+} = 1.00 \text{ m}\)

is same as

\([\text{Mg}] = [\text{Mg}^{2+}] + [\text{MgSO}_4^0] + [\text{MgF}^+] = 1.00 \text{ m}\)

Similarly:

\([\text{Ca}] = [\text{Ca}^{2+}] + [\text{CaSO}_4^0] + [\text{CaF}^+] = 1.00 \text{ m}\)

(SO\(_4^{2-}\)) \([\text{S}] = [\text{SO}_4^{2-}] + [\text{Mg SO}_4^0] + [\text{Ca SO}_4^0] = 1.00 \text{ m}\)

\([\text{F}] = [\text{F}^-] + [\text{MgF}^+] + [\text{CaF}^+] = 2.00 \text{ m}\)

--used CaF\(_2\), therefore are 2 moles of F\(^-\) for each mole of Ca
We can rewrite this equation:

\[ K_{c_{\text{MgSO}_4}}^0 = \left( \gamma_{\text{Mg}^{2+}} \right) \left( \gamma_{\text{SO}_4^{2-}} \right) K_{\text{eq}_{\text{MgSO}_4}}^0 \]

We can substitute the values in the table and in the appendix:

\[ = (0.29)(0.17)10^{2.36} = 10.0 \]

(This is (1.13))

Note: \( \gamma \) values in table 5.3, are for seawater, we use values 0.29 and 0.17

\[ K_{c_{\text{MgSO}_4}}^0 = \frac{[\text{MgSO}_4^0]}{[\text{Mg}^{2+}][\text{SO}_4^{2-}]} = 10.0 \]

rearranging

\[ [\text{MgSO}_4^0] = 10.0 [\text{Mg}^{2+}][\text{SO}_4^{2-}] \]

We can do the same for MgF^+

\[ [\text{MgF}^+] = 18.3 [\text{Mg}^{2+}][\text{F}^-] \]
Too many unknowns: assume that [F] and [SO$_4^{2-}$] are unpaired i.e. equal to 1; 2 for F$^-$. 

therefore:- [Mg SO$_4^0$] = 10.0 [Mg$^{2+}$] 

[MgF$^+$] = 36.6 [Mg$^{2+}$] (F = 2) 

So we can now substitute for Mg SO$_4^0$ and MgF$^+$ back in our original mass balance equation:

$$1.00 = [Mg^{2+}] + 10.0 [Mg^{2+}] + 36.6 [Mg^{2+}]$$

Solving for [Mg$^{2+}$] 

[Mg$^{2+}$] = 0.021 m 

Similarly for Ca$^{2+}$

$$1.00 = [Ca^{2+}] + 7.99 [Ca^{2+}] + 6.55 [Ca^{2+}]$$

[Ca$^{2+}$] = 0.064 m 

We can now use the Mg$^{2+}$ and Ca$^{2+}$ values to substitute back in the equations for SO$_4^{2-}$ [S] and [F]

$$1.00 = [SO_4^{2-}] + ((10.0)(0.021)[SO_4^{2-}]) +((7.99) (0.0644) [SO_4^{2-}])$$

which yields [SO$_4^{2-}$] = 0.058 m
For F⁻:
$$2.00 = [\text{F}^-] + \{(18.3) (0.0210) [\text{F}^-] + \{(3.27) (0.0644) [\text{F}^-]\}$$
$$[\text{F}^-] = 1.3 \text{ m}$$

We can then take these values for [SO₄²⁻] and [F⁻] and recalculate the [Mg²⁺] and [Ca²⁺] we would get:

$$[\text{Ca}^{2+}] = 0.10 \text{ m and } [\text{Mg}^{2+}] = 0.034 \text{ m}$$

This in turn can be used to recalculate the [SO₄²⁻] and [F⁻] etc.

We can keep up these iterations until we find little or no change in the calculated values.
After 10 iterations

\[ [\text{Mg}^{2+}] = 0.050 \text{m} \quad [\text{Ca}^{2+}] = 0.15 \text{ m} \]
\[ [\text{SO}_4^{2-}] = 0.37 \text{ m} \quad [\text{F}^-] = 0.83 \text{ m} \]

These can then be used to calculate

\[ [\text{MgSO}_4^{0}] = (10.0)(0.050)(0.37) = 0.19 \text{ m} \]
\[ [\text{MgF}^+] = (18.3)(0.050)(0.83) = 0.76 \text{ m} \]
\[ [\text{CaSO}_4^{0}] = (7.99)(0.15)(0.37) = 0.44 \text{ m} \]
\[ [\text{CaF}^+] = (3.27)(0.15)(0.37) = 0.41 \text{ m} \]

Results normally presented as % of total species

Normally do by computer program

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Speciation of major ions in sea water

Major cations are mainly present as free ions
Ca and Mg are paired more than Na or K
Significant ion pairing of \( \text{SO}_4^{2-} \)
Chloride assumed to be unpaired.
Because of Cl, other anions are present in lower concentrations than the cations
-- thus are more complexed %-wise

\( \text{MgSO}_4^{0} \) absorbs sound in the kilocycle range,
-- affects sound propagation
Speciation of trace metals

Not well understood, lack of thermodynamic data
More likely to be complexed than major ions (concentration effect)
Numerically has insignificant effect on ligand complexation

Functional groups on DOM can act as ligands
e.g. R-COOH; R-OH; R$_2$-NH; R-NH$_2$; R-SH
<table>
<thead>
<tr>
<th>Element</th>
<th>Maximum Concentration in Ocean Water</th>
<th>Range of Average Concentration in Oozed Material</th>
<th>Type of Distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>0.005–1 ppm (1)</td>
<td>0.005–1 ppm (1)</td>
<td>Soret type</td>
</tr>
<tr>
<td>Cd</td>
<td>0.2–100 ppm (2)</td>
<td>0.2–100 ppm (2)</td>
<td>Soret type</td>
</tr>
<tr>
<td>In</td>
<td>4–100 ppm (3)</td>
<td>4–100 ppm (3)</td>
<td>Soret type</td>
</tr>
<tr>
<td>Sb</td>
<td>10–100 ppm (4)</td>
<td>10–100 ppm (4)</td>
<td>Soret type</td>
</tr>
<tr>
<td>Te</td>
<td>1–10 ppm (5)</td>
<td>1–10 ppm (5)</td>
<td>Soret type</td>
</tr>
<tr>
<td>I</td>
<td>0.1–1 ppm (6)</td>
<td>0.1–1 ppm (6)</td>
<td>Soret type</td>
</tr>
<tr>
<td>Cs</td>
<td>1–100 ppm (7)</td>
<td>1–100 ppm (7)</td>
<td>Soret type</td>
</tr>
<tr>
<td>Ba</td>
<td>0.1–100 ppm (8)</td>
<td>0.1–100 ppm (8)</td>
<td>Soret type</td>
</tr>
<tr>
<td>Ce</td>
<td>0.1–100 ppm (9)</td>
<td>0.1–100 ppm (9)</td>
<td>Soret type</td>
</tr>
<tr>
<td>Ho</td>
<td>0.1–10 ppm (10)</td>
<td>0.1–10 ppm (10)</td>
<td>Soret type</td>
</tr>
<tr>
<td>Er</td>
<td>0.1–100 ppm (11)</td>
<td>0.1–100 ppm (11)</td>
<td>Soret type</td>
</tr>
<tr>
<td>Tm</td>
<td>0.1–100 ppm (12)</td>
<td>0.1–100 ppm (12)</td>
<td>Soret type</td>
</tr>
<tr>
<td>Dy</td>
<td>0.1–100 ppm (13)</td>
<td>0.1–100 ppm (13)</td>
<td>Soret type</td>
</tr>
<tr>
<td>Ho</td>
<td>0.1–100 ppm (14)</td>
<td>0.1–100 ppm (14)</td>
<td>Soret type</td>
</tr>
<tr>
<td>Er</td>
<td>0.1–100 ppm (15)</td>
<td>0.1–100 ppm (15)</td>
<td>Soret type</td>
</tr>
<tr>
<td>Tm</td>
<td>0.1–100 ppm (16)</td>
<td>0.1–100 ppm (16)</td>
<td>Soret type</td>
</tr>
<tr>
<td>Dy</td>
<td>0.1–100 ppm (17)</td>
<td>0.1–100 ppm (17)</td>
<td>Soret type</td>
</tr>
<tr>
<td>Ho</td>
<td>0.1–100 ppm (18)</td>
<td>0.1–100 ppm (18)</td>
<td>Soret type</td>
</tr>
<tr>
<td>Er</td>
<td>0.1–100 ppm (19)</td>
<td>0.1–100 ppm (19)</td>
<td>Soret type</td>
</tr>
<tr>
<td>Tm</td>
<td>0.1–100 ppm (20)</td>
<td>0.1–100 ppm (20)</td>
<td>Soret type</td>
</tr>
<tr>
<td>Dy</td>
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<td>0.1–100 ppm (21)</td>
<td>Soret type</td>
</tr>
<tr>
<td>Ho</td>
<td>0.1–100 ppm (22)</td>
<td>0.1–100 ppm (22)</td>
<td>Soret type</td>
</tr>
<tr>
<td>Er</td>
<td>0.1–100 ppm (23)</td>
<td>0.1–100 ppm (23)</td>
<td>Soret type</td>
</tr>
<tr>
<td>Tm</td>
<td>0.1–100 ppm (24)</td>
<td>0.1–100 ppm (24)</td>
<td>Soret type</td>
</tr>
</tbody>
</table>


See Chapter 11 for a discussion of the distribution of elements.
Major ions compete for sites

Some biomolecules highly specific for certain trace metals
e.g. siderophores, hydroxamate for Fe etc.

Affects bioavailability (whether toxic or required)
Some species in upper waters may be predominantly complexed

Increases solubility in seawater