**Lecture 2: Properties of Water and Seawater**

The Nature of Pure Water

Seawater is mostly water (H_2O). In fact it is about 96.5 wt % water. Surface sediments are also mostly water. Most fine-grained surface sediments have a porosity (Φ = volume of pores to volume of solids) of greater than 90%. Water affects almost all ocean characteristics (density, salinity, gas solubility) and processes (circulation, heat-exchange, climate, biochemistry). Thus, water has been called the universal solvent.

Water has unique and unusual properties both in pure form and as a solvent. These properties influence many of the chemical reactions taking place in the oceans.

Structure of the Water Molecule: The structure of H_2O consists of an oxygen atom with 6 electrons that have the electronic configuration of: $1s^2\,2s^2\,2p_z^2\,2p_y\,2p_x$ which merge with two H atoms with 1 electron each resulting in a neutral molecule with 8 electrons which form four pairs called sp^3 hybrids. The most stable configuration of these four lobes is a "distorted" tetrahedral arrangement, with two electrons in each lobe. Two lobes are used for O-H bonds (shared electrons) and two lobes have free lone pairs of electrons. The water molecule lacks symmetry; the charge is not evenly distributed (it is polar), electrons are shared unequally between the oxygen and hydrogen.
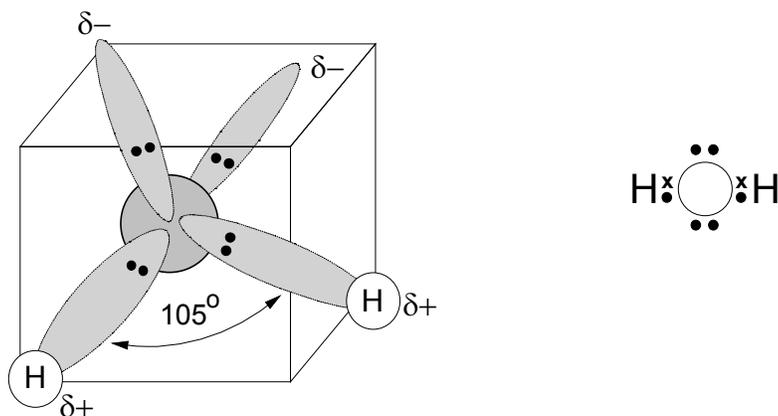
The H-O-H tetrahedral angle is 105° this is less than the ideal tetrahedral angle of 109° this is because of electron repulsion. The bent structure results in a dipole moment, there is separation of charge, which means it is a polar molecule. An important aspect of the water molecule structure is its propensity to form hydrogen bonds (**H-bonds**). These H-bonds also lead to "cooperative bonding" is which water molecules link together to actually form regions with structure. What this means is that formation of one H-bond makes it easier to form a stronger second bond because of the first. In some ways these regions may have a more organized structure "ice like". One line of evidence for this character is that when ice melts only about 15% of the bonds are broken.

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The structure of the H_2O molecule and the hydrogen bonding of water explain many of the unique physical properties of water. Water has many physical properties that indicate unusually strong intermolecular associations. It takes a lot of energy to break the hydrogen bonds and change the structure of water, thus the water has a large thermal buffer capacity and acts as a climate moderator.


FIG 3.4

Clusters
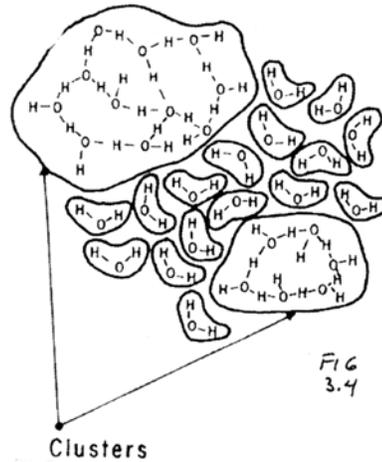
The Anomalous Properties of Water
(originally presented by Sverdrup, Johnson and Fleming in 1942) include:

Property	Comparison	Importance
Heat capacity (Cp; cal g^{-1} $°C^{-1}$) Thermal energy to raise 1 gm of a substance by 1 °C.	Highest of all solids & liquids, except liquid NH_3	Prevents extreme ranges in temperature; Energy transfer by water movements is large
Heat of fusion ($\Delta H = 79$ cal g^{-1}) Energy needed to break the hydrogen bonds.	Highest except for NH_3	Absorption or release of latent heat results in large thermostatic effects. Important for energy transfer and climate.
Heat of vaporization ($\Delta H = 540$ cal g^{-1}) Energy needed to convert water to vapor	Highest of all liquids	Thermostatic effect; Energy transfer
Boiling point (100 °C; projected -68°C) Freezing point (0 °C; projected -90 °C)	Much higher than expected (compared to other hydrides)	Water exists in 3 phases within the critical temperature range that accommodates life
Heat of freezing; only 1/7 that of evaporation	Low; Water structure can move easily into ice.	Implying relatively small difference in the # of bonds between water and ice
Surface tension; water likes itself relative to most other surfaces (7.2 x 10^9 N m^{-1}) Measure of the strength of a liquid surface	Highest of all substances	Waves, drops and aerosol sea salt formation. Cell physiology
Dielectric constant; Charge insulation and dissolving power as a result of ion hydration (87 at 0 °C, 80 at 20 °C)	Highest of all substances except H_2O_2 and HCN	Solubility of salts & ion reactions
Dissolving power	Highest of all liquids both # of substances and quantities	Implications for biological and physical phenomena
Electrolytic dissociation	Very small	A neutral substance, yet contains both H^+ and OH^- ions
Transparency Absorption of radiant energy is large in IR and UV; Relatively uniform in the visible.	Relatively large	Water is "colorless"; Important for photosynthetic and photochemical reactions
Conduction of heat (a molecular process)	Highest of all liquids	Important for small-scale heat transfer, as in living cells.
Molecular viscosity (= 10^{-3} N s m^{-2}) Measure of resistance to distortion (flow)	Less than most other liquids at same temperature.	Water flows readily to equalize pressure differences.
Compressibility	Relatively low (more similar to a solid)	Large increase in presses with depth causes only slight increase in density
Thermal expansion (for pure water it is at 4 °C)	Temperature of maximum density decreases with increasing salinity.	Waters with salinity less than 25 have maximum density at tempemperatures above the freezing point

The high heat capacity and heats of fusion and evaporation provide immense thermostating capacity in the critical temperature range that accommodates most life (-50 to 100°C). It takes 766 calories to raise the temperature of 1 gram of water from −50°C (as ice) to +150°C (as steam). The same number of calories would elevate the temperature of **10 grams** of granite (heat capacity = 0.2 cal g^{-1}) to 383°C. Water is unusual for having two-phase transitions so close together in temperature, thereby allowing large amounts of energy to be exchanged while the temperature of the two-phase system (ice/water or water/steam) remains constant.
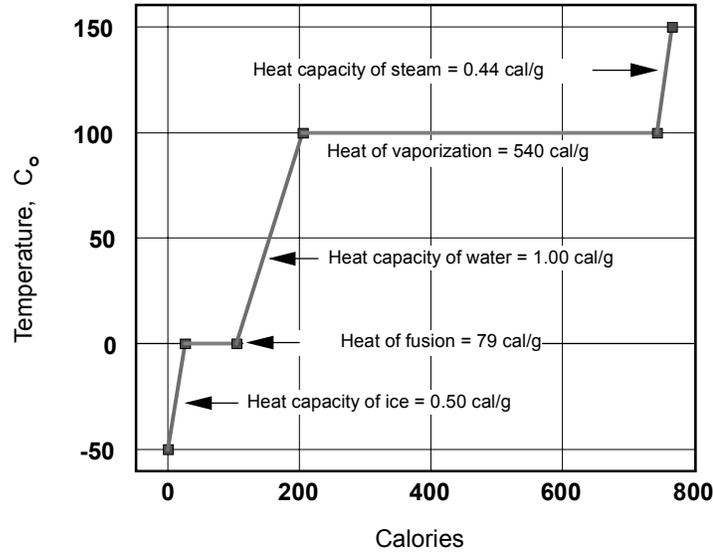

The Structure of the Three Phases of Pure Water

Liquid water is best considered as a mixture of densely packed "monomers" and ice-like "polymers" or clusters; as temperature drops monomers pack more closely together and density increases; as temperature drops more monomers convert to "spaced out" polymers and density drops; the two apposing effect occur <u>simultaneously</u> in proportion to the relative abundance of the two structure types. Liquid water flows but has a heat of fusion only 15% of that which would be needed to break all hydrogen bonds.
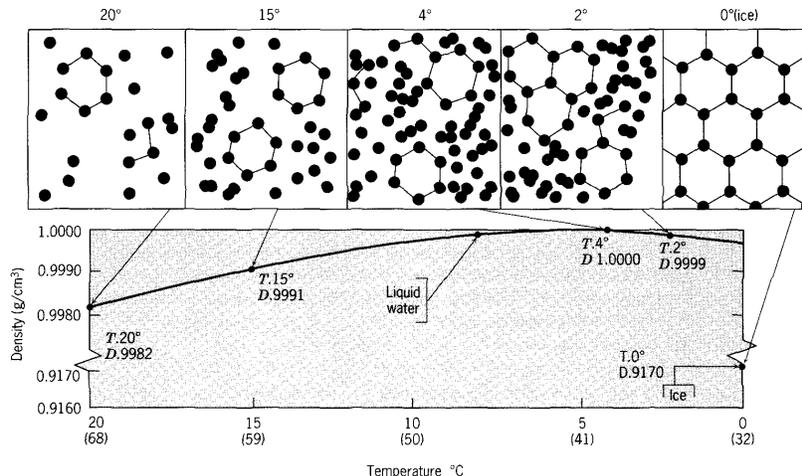

The change in liquid water structure and density with temperature, From Libes, 1992

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This also explains the minimal relative viscosities of pure liquid water at pressure near ~1000 kg cm^{-2}; increasing pressure forces monomers closer together, they then attract each other more and viscosity increases; further pressure increases "squeezes out" polymers which are lumpy and lead to high viscosity; net viscosity increases with increasing pressure are more pronounced at low temperature, because polymers have a higher relative abundance in colder water.
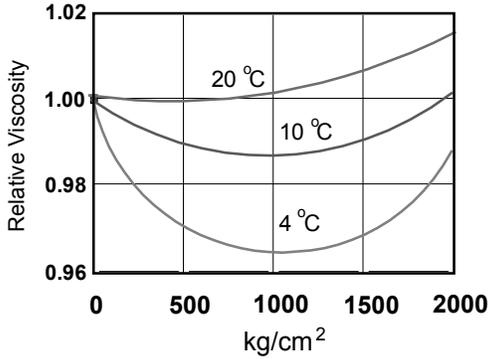
Water vapor has essentially no structure because the molecules are essentially unassociated water "monomers".

Ice has a well-defined structure at 1 atmosphere pressure (Ice-I) with the following characteristics; (a) Every hydrogen atom is in an oriented H-bond between 2 oxygen atoms, which are spaced about 2.76 Å apart; (b) Every O is bonded to 4 H's in an undistorted tetrahedron (c) The O atoms lie in a network of puckered hexagonal rings with H's cementing the O network together; (d) The network is full of holes thus it is less dense than water. It floats! At 0°C the density of ice, $\rho_{ice} = 0.915$ while the density of water at that temperature is, $\rho_{water} = 0.999$. There are several different phases of ice that are stable at different T-P conditions.

Ice-I

Molecular alignment

TOP VIEW

SIDE VIEW

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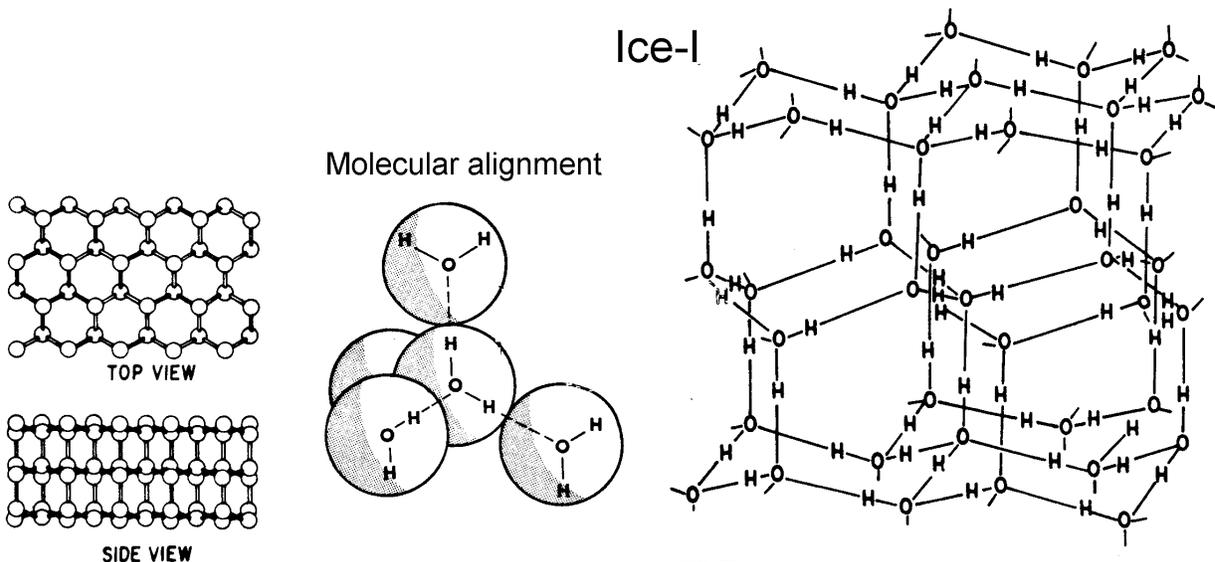
Sea-ice is formed by the freezing of seawater itself. When seawater first begins to freeze, relatively pure ice is formed, so that the salt content of the surrounding seawater is increased, which both increases its density and depresses its freezing point further. Most of the salt in sea-ice is in the form of concentrated brine droplets trapped within the ice as it forms, this brine is much more saline than the ice itself (brine remains liquid).

Properties of Seawater

Water is called the universal solvent because of its ability to dissolve at least a little of virtually every substance. Water is a particularly good solvent for substances held together by polar or ionic bonds. Indeed the most abundant substances dissolved in seawater are ionic solids (salts such as sodium chloride). When we add salt to water we observe the following:

The density is increased: Any substance dissolved in a liquid has the effect of increasing the density of that liquid. The greater the amount of solute, the greater the effect. As a result of the salt content in seawater the density of seawater increases continuously with decreasing temperature and there is no density maximum like for freshwater. The density of seawater increases with falling temperature right down to the freezing point.

The freezing point is depressed: Salts lower the temperature at which water freezes (this is why salt is spread on frozen roads.). That is because dissolved salts inhibit the tendency of water molecules to form direct bonds with other water molecules.

The boiling point is elevated: The salts have the effect of making the water molecules cluster and become more "ordered" thus harder to pull apart and evaporate.

The conductivity is increased: The transport of electrons causing and electric current to flow is enhanced by the strong electrolyte nature of salts. If an electromagnetic field is applied to a solution of strong electrolytes, the ions will migrate, producing an electric current (e.g. conductivity is increased).

Comparison of Seawater and Pure Water Properties

Property	Seawater (35‰)	Pure Water
Density, g cm^{-3}, 25 ºC	1.02412	1.0029
Specific conductivity, ohm^{-1} cm^{-1}, 25 ºC,	0.0532	-
Viscosity, millipoise, 25 ºC	9.02	8.90
Vapor pressure, mm Hg, 20 ºC	17.4	17.34
Isothermal compressibility, vol/atm, 0 ºC	46.4 x 10^{-6}	50.3 x 10^{-6}
Temperature of maximum density, ºC	-3.25	3.98
Freezing point ºC	-1.91	0.00
Surface tension, dyne cm^{-1}, 25 ºC	72.74	71.97
Velocity of sound, m s^{-1}, 0 ºC	1450	1407
Specific heat, J g^{-1} ºC^{-1}, 17.5 ºC	3.898	4.182

Water is a good solvent, it attracts anions and cations. When a salt dissolves in solution, water molecules surround each ion in a process called **hydration**. Such hydration numbers are difficult to measure but the strength of hydration is proportional to the charge to radius ratio (q/r) of the central ion. Thus Mg^{2+} hydrates more strongly than Ca^{2+}. Hydration isolates ions from each other and enhances solubilization. The waters around a central ion are called the hydration sphere. The water molecules arrange themselves into an inner sphere of tightly bound waters and an outer sphere that is less tightly bound. The water molecules are oriented with their oxygen pointed toward a cation. The process of hydration usually results in a decrease in volume and is called **electrostriction**. In other words water with salt occupies less volume than expected from adding the volumes of each component separately, this is due to ion/dipole interaction and "close packing" of waters of hydration. Most ions increase net water structure and hence viscosity and conductivity.
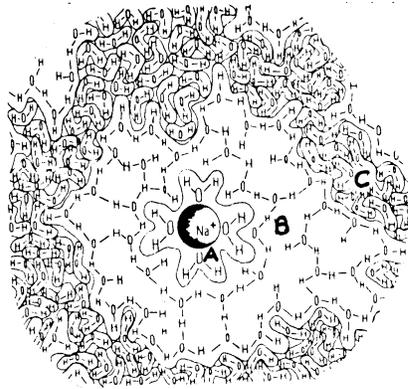
Heat Capacity of Seawater

When two bodies of seawater with different salinity and temperature are uniformly mixed, it is important to be able to calculate precisely the temperature, salinity, and density of the resulting water mass. These calculations require knowledge of the heat capacity of seawater and its temperature and pressure variations. Cox and Smith (1959) found that over the temperature range of -2 to 30 °C, the heat capacity of pure water decreases with increasing temperature. The addition of sea salt dampens this decrease, and at salinity of 20 the effect of temperature is reversed and heat capacity increases with temperature.

Freezing Point of Seawater

The freezing point of seawater is the temperature, T_f, at which pure ice and seawater are in thermodynamic equilibrium. This temperature decreases with increasing salinity and increasing water pressure (e.g. temperatures below the atmospheric freezing point have been observed for waters at 200 to 500 m near the ice shelves of Antarctica).

The pressure dependence of T_f is essentially constant over the range of 0 to -2 °C and 1 to 40atm. Using an average value of $dT_f / dP = - 0.00758$ °C atm, the *in situ* freezing point can be expressed as:

$$T_f = -0.0137 - 0.051990\ S - 0.00007225\ S^2 - 0.000758\ z$$

Where   S is the salinity and z is depth in meters.

Ion-ion interactions, Activity Scales and Activity Corrections

Electrostatic forces between individual ions can be attractive (different charges) or repulsive (same charges) and are relatively long ranging. The net result for a system is always attractive – ions hold each other, restricting each other's ability to take part in reactions within aqueous systems. For charged species, concentrations (total amount present in solution; indicated by [x] or Ci) almost always overestimate reaction potential (the amount "free" and available for reaction).
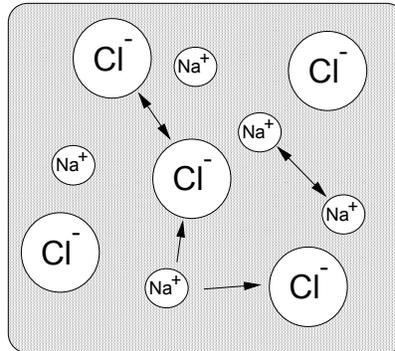
Activity: Ions in solution interact with each other as well as with water. At low concentrations of salts these interactions can sometimes be ignored, but at higher concentrations the ions behave like they are less concentrated than they really are. Therefore, correction factors must be applied to concentrations in order to express them in terms of ion reactivity (the concentrations of ions that are available for participation in chemical reactions). Equilibrium constants calculated from the standard free energy of reaction (e.g. $\Delta G_r°$) are expressed in terms of this **effective concentration** or activity, which is the concentration available for reaction. Thus we define activity as:

      Activity $\left(a_i\right)$ = Effective amount (less then total amount)

In infinitely dilute solutions where ionic interactions are not important: $a_i = Ci$

In concentrated solutions like seawater: $a_i < Ci$
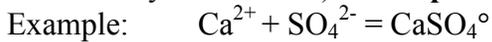
There are two main reasons for these differences:

The Shielding Effect (Electrostatic Interactions)
The background ions in solution shield the interactions between ions.
Example: Say we have a solution of calcium and sulfate in water. The tendency of Ca^{2+} and SO_4^{2-} ions to hydrate induces shielding which affects the ability of Ca^{2+} and SO_4^{2-} to meet and react (and precipitate as a solid in this case) increasing the solubility. If we add other ions like Na^+ and Cl^- to the solution, they are attracted to the ions of opposite charge and we effectively increase the amount of electrostatic shielding. Therefore, gypsum or $CaSO_4 \bullet 2H_2O$, will appear more soluble in seawater than in freshwater. These interactions result in **non-ideal solutions**. Ions with higher charge are more effective than ions with lower charge at this shielding effect.

Ion Complexes
In some cases there are specific interactions between ions – solutes may come close enough to each other that they make direct contact and are considered a new species. These new species are called **ion pairs** (ions are separated by H_2O molecules but share their first hydration shell) or **complexes** (ions are in contact and share electrons).
Example: $Ca^{2+} + SO_4^{2-} = CaSO_4°$
Let's say we have a solution containing some of the major ions: Ca^{2+}, K^+, F^-, and SO_4^{2-} Because of the interaction between ions, not only do we have the free ions present (e.g. Ca^{2+}, K^+, F^-) but also complexes such as: CaF^+, $CaSO_4$, KF and KSO_4^-. Like shielded or hydrated ions these complexes are less able to react with other ions so their formation lowers the effective concentration of these species. In some cases complexes are so dominant that the "free ion" population is only a small fraction of the total. We can ignore higher order complexes involving more than one cation and one anion because their concentrations are very small.

The Activity Coefficient
Activity coefficients are used to correct total concentrations to the effective amount. In most cases we only know the total concentration of an element $[m_T]$ which is most easily measured analytically. We need to convert the total concentration to the concentration of the ion or species that is not "complexed" $[m_i]$ e.g. the free ion concentration. In order to calculate m_i from m_T we need to calculate the percent, or fraction of this ion that is free (f_i) and not complexed.

Thus: $m_i = m_T \times f_i$

For example in the case where we have Ca_T but we want Ca^{2+} we need to calculate the ratio: $f_{Ca2+} = [Ca^{2+}]/ Ca_T = [Ca^{2+}] / ([Ca^{2+}]+ [CaSO_4]+ [CaCO_3])$

Once we have the concentration of the free ion we need to convert it to the activity of the free ion (a_i). To do that we use the free ion activity coefficient (γ_i) that corrects for electrostatic shielding by other ions. This correction is written as:

Activity of free ion $\rightarrow$ $a_i = \gamma_i \times m_i$ $\leftarrow$ concentration of a free ion
$\uparrow$
free ion activity coefficient for that species

The total expression with both correction factors is then written as:

Activity of free ion $\rightarrow$ $a_i = \gamma_i \times f_i \times m_T$ $\leftarrow$ the total ion concentration
$\uparrow$ $\uparrow$
Activity coefficient,   % of the total concentration that is free

How do we obtain values for γ_i and f_i ?

The free ion activity coefficient can be calculated from the ionic strength of an electrolyte solution and a few corresponding constants for the ions in question. We typically use either some form of the Debye-Huckel type equations or the mean salt method to derive this value.

First you need to know the **ionic strength (I)** of the solution because the electrostatic interactions depend on the concentration of charge. The value of I is calculated as follows:

$$\text{Ionic strength} \rightarrow I = 1/2\ \Sigma m_i \text{ x } Z_i^2 \leftarrow \text{charge of i}^{\text{th}} \text{ ion squared}$$
$$\uparrow$$
$$\text{concentration of i}^{\text{th}} \text{ ion}$$

Note that the ionic strength places greater emphasis on ions with higher charge. A 2+ charged ion contributes 4 times more to the ionic strength than a 1+ ion.

Free Ion Activity Coefficients: There are several theoretically based expressions that can be used to estimate single ion activity coefficients. However each is only good for a limited range of ionic strength and none are to good to apply directly to seawater.

Approximation	Equation[a]	Approximate Applicability [ionic strength (M)]
Debye–Hückel	$\log\gamma = -Az^2\sqrt{I}$	$<10^{-2}$
Extended Debye–Hückel	$= -Az^2\dfrac{\sqrt{I}}{1 + Ba\sqrt{I}}$	$<10^{-1}$
Güntelberg		$<10^{-1}$ useful in solutions of several electrolytes
Davies	$= -Az^2\dfrac{\sqrt{I}}{1 + \sqrt{I}}$	
	$= -Az^2\left(\dfrac{\sqrt{I}}{1 + \sqrt{I}} - 0.2I\right)$	<0.5
Brönsted–Guggenheim	$\ell n\gamma_S = \ell n\gamma_{DH_S} + \sum_j A_{S_j}(C_j) + \sum_j\sum_k B_{S_{jk}}(C_j)(C_k) + \cdots$	≤ 4

Source: From *Aquatic Chemistry*, W. Stumm and J. J. Morgan, copyright © 1981 by John Wiley & Sons, Inc., New York, p. 135. Reprinted by permission.
[a]Values for the constants can be found in Stumm and Morgan (1981).

The Debye-Huckel equation, or its extended form, are commonly used in fresh water where:

1. Z = charge on the ion, A= ~0.5 in water at 25 °C, B = 0.33, and a is an adjustable parameter of values between 3 and 9.
2. I = the "ionic strength" of the entire solution
3. Note that the Debye-Huckel equations are limited in their applications to ionic strengths of < 0.1. The expanded Debye-Hückel equations is applicable to average river water ($I < $~0.002), but not to seawater, whose I is approximately 0.7. Empirical techniques are typically used for high ionic strength solutions such as seawater.

The Davies equation is empirical and is often used because of its simplicity and applicability for seawater. In this equation all ions of the same charge have the same value of γ_i; for seawater ionic strength ($I = 0.72$) we get the following values:
monovalent ions $\gamma_i = 0.69$
divalent ions $\gamma_i = 0.23$
trivalent ions $\gamma_i = 0.04$

Activity coefficients for the major ions and their ion pairs at salinity of 35, 25 °C and 1atm are given in the table.

Dissolved Species	Activity Coefficient
$NaHCO_3$	1.13
$MgCO_3$	1.13
$CaCO_3$	1.13
$MgSO_4$	1.13
$CaSO_4$	1.13
Na^+	0.76
HCO_3^-	0.68
$NaCO_3^-$	0.68
$NaSO_4^-$	0.68
KSO_4^-	0.68
$MgHCO_3^+$	0.68
$CaHCO_3^+$	0.68
K^+	0.64
Mg^{2+}	0.36
Ca^{2+}	0.28
SO_4^{2-}	0.12
CO_3^{2-}	0.20

General Rules for Free Ion activity Coefficients
1. $\gamma_i \rightarrow 1$ as $I \rightarrow 0$ i.e. activity = concentration at infinite dilution
2. $\gamma_i \downarrow$ as $I \uparrow$ i.e., the free ion activity coefficient decreases with ionic strength
3. $\gamma_{i2+} < \gamma_{i+}$ i.e., the activity corrections increase with charge
4. $\gamma_i \uparrow$ at high I i.e., in very concentrated salt solutions the free ion activity coefficients become greater than 1. This is called the salting out effect.

Rules of Thumb for free ion activity coefficients in seawater (when other data not available).
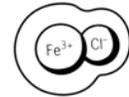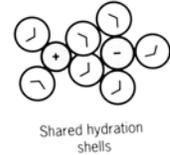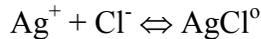
ion charge	range
±1	0.6 to 0.8 avg = 0.7
±2	0.1 to 0.3 avg = 0.2
±3	0.01
±4	< 0.01

Ion Complexes

Ion complex ≡ any indirect association between cations and anions in solution (usually sharing a common hydration sphere):

$$Ag^+ + 2Cl^- \Leftrightarrow AgCl_2^-$$

Ion pair ≡ a direct association of **two** ions of opposite charge:
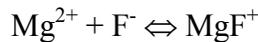
$$Ag^+ + Cl^- \Leftrightarrow AgCl^0$$

Ion Complex Calculation:

The free ion fraction is obtained from a chemical speciation calculation done by hand or using a computer program like MINTEQA2 or HYDRAQL.

Examples:

Consider the following complexation reaction (in seawater):

$$Mg^{2+} + F^- \Leftrightarrow MgF^+$$

Calculate the ion <u>concentration</u> ratio, $[MgF^+]/[F^-]$, at equilibrium in seawater (at 1 atmosphere pressure and 25 °C):

Ion	λ_i	%free
Mg^{2+}	0.36	87
F^-	0.63	-
MgF^+	0.68	-

1. At equilibrium:

$$K = \frac{(MgF^+)}{(Mg^{2+})(F^-)} = 10^{1.8} = 6.31 \times 10^1$$

2. Given the information in the above table, and that the total $[Mg^{2+}] = 5.4 \times 10^{-2}$ m (m = molality = the moles of solute dissolved in one kilogram of solvent):

$$K = 6.31 \times 10^1 = \frac{[MgF^+]\gamma_{MgF^+}}{[Mg^{2+}]\gamma_{Mg^{2+}}(\%free_{Mg^{2+}}/100)[F^-]\gamma_{F^-}}$$

$$\frac{[MgF^+]}{[F^-]} = \frac{K[Mg^{2+}]\gamma_{Mg^{2+}}(\%free_{Mg^{2+}}/100)\;\gamma_{F^-}}{\gamma_{MgF^+}}$$

$$\frac{[MgF^+]}{[F^-]} = \frac{(63.1)(5.4x10^{-2})(0.36)(0.87)(0.63)}{0.68} = 0.98$$

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Calculating Speciation in a Multi-ion Solution (example from Libes, p. 66)

Completely dissolve 1 mole each of $MgSO_4$ and CaF_2 in 1 kg of water and allow all possible ion pairs to form (but no precipitates or "higher" ion complexes):

Components:
$\quad\quad$ free ions = Mg^{2+}, Ca^{2+}, SO_4^{2-} and F^-
$\quad\quad$ Ion pairs = $MgSO_4^{o}$, MgF^+, $CaSO_4^{o}$, and CaF^+

To completely solve for these 8 unknowns we need 8 independent equations

Mass balance equations for total element concentrations:
$$[Mg]_t = [Mg^{2+}] + [MgSO_4^{o}] + [MgF^+]$$
$$[Ca]_t = [Ca^{2+}] + [CaSO_4^{o}] + [CaF^+]$$
$$[S]_t = [SO_4^{2-}] + [MgSO_4^{o}] + [CaSO_4^{o}]$$
$$[F]_t = [F^-] + [MgF^+] + [CaF^+]$$

At this point we need another 4 equations to solve the system

Equilibrium equations can be written for the formation (or dissociation) of the 4 ion pairs:

for $[MgSO_4^{o}]$ where $K_{MgSO4o} = 10^{2.36}$ (Note that this is for <u>formation</u> of $MgSO_4^{o}$)

$$K_{MgSO4o} = \frac{(MgSO_4^{o})}{(Mg^{2+})(SO_4^{2-})} = \frac{[MgSO_4^{o}]\gamma_{MgSO_4^{o}}}{[Mg^{2+}]\gamma_{Mg^{2+}}[SO_4^{2-}]\gamma_{SO_4^{2-}}} = K'_{MgSO4}^{o}\frac{\gamma_{MgSO_4^{o}}}{\gamma_{Mg^{2+}}\gamma_{SO_4^{2-}}} = 10^{2.36}$$

Assuming now that we can assign the same ion activity coefficients as in seawater, then:

$$K'_{MgSO4}^{o} = \frac{\gamma_{Mg^{2+}}\gamma_{SO_4^{2-}}}{\gamma_{MgSO_4^{o}}} K_{MgSO4}^{o} = \frac{(0.36)(0.12)}{1.13}10^{2.36} = 8.76$$

$$\frac{[MgSO_4^{o}]}{[Mg^{2+}][SO_4^{2-}]} = 8.76 \text{ and therefore } [MgSO_4^{o}] = 8.76[Mg^{2+}][SO_4^{2-}]$$

Similarly: $[MgF^+] = 22.7[Mg^{2+}][F^-]$, $[CaSO_4^{o}] = 6.07[Ca^{2+}][SO_4^{2-}]$, $[CaF^+] = 3.52[Ca^{2+}][F^-]$

4. Combining the mass balance and equilibrium equations:
$\quad\quad$ $[Mg]_t = [Mg^{2+}] + 8.76[Mg^{2+}][SO_4^{2-}] + 22.7[Mg^{2+}][F^-] = 1.0$ m, and likewise
$\quad\quad$ $[Ca]_t = [Ca^{2+}] + 6.07[Ca^{2+}][SO_4^{2-}] + 3.52[Ca^{2+}][F^-] = 1.0$ m
$\quad\quad$ $[S]_t = [SO_4^{2-}] + 8.76[Mg^{2+}][SO_4^{2-}] + 6.07[Ca^{2+}][SO_4^{2-}] = 1.0$ m
$\quad\quad$ $[F]_t = [F^-] + 22.7[Mg^{2+}][F^-] + 3.52[Ca^{2+}][F^-] = 2.0$ m

5. The step-wise iterative solution:
a. assume anions are uncomplexed (100% free) it must follow that

$[SO_4^{2-}] = 1.0$ M and $[F^-] = 2.0$ m

b. now the cation mass balance equations (in 4.) can be solved, thus for Mg:
$$[Mg]_t = [Mg^{2+}] + 8.76[Mg^{2+}][SO_4^{2-}] + 22.7[Mg^{2+}][F^-] = 1.0 \text{ m}$$
$$[Mg]_t = [Mg^{2+}] + 8.76[Mg^{2+}]1 + 22.7[Mg^{2+}]2 = 1.0 \text{ m, therefore}$$
$$55.1[Mg^{2+}] = 1.0 \quad \text{and } [Mg^{2+}] = 0.018 \text{ m, and similarly } [Ca^{2+}] = 0.071 \text{ m}$$

c. the above cation concentrations can be substituted into the two anion equations (in 4.):
$$[S]_t = [SO_4^{2-}] + 8.76[Mg^{2+}][SO_4^{2-}] + 6.07[Ca^{2+}][SO_4^{2-}] = 1.0 \text{ m}$$
$$[S]_t = [SO_4^{2-}] + 8.76[0.018][SO_4^{2-}] + 6.07[0.071][SO_4^{2-}] = 1.0 \text{ m}$$
$$1.59[SO_4^{2-}] = 1 \text{ and } [SO_4^{2-}] = 1/1.59 = 0.63 \text{ m, and similarly } [F^-] = 1.20 \text{ m}$$

d. the above anion concentrations can be substituted into the two cation equations in 4., and the iteration continued between ion types until all four free ion concentrations converge to essentially constant numbers (see figure on next page): Getting the complex ion concentrations is now easy, because the above free ion concentrations can be substituted into the K' equations (in 3.):
$$\text{e.g.} \quad [MgSO_4^{\circ}] = 8.76[Mg^{2+}][SO_4^{2-}])$$

6. Results of the previous type of calculation are given below - these are based on Libes' iteration using slightly different γ values:

Ion	Molality (m)	%[Ca]$_t$	%[Mg]$_t$	%[S]$_t$	%[F]$_t$
$[Ca^{2+}]$	0.15	15			
$[Mg^{2+}]$	0.05		5		
$[SO_4^{2-}]$	0.37			37	
$[F^-]$	0.83				42
$[CaSO_4^{\circ}]$	0.44	44		44	
$[CaF^+]$	0.41	41			20
$[MgSO_4^{\circ}]$	0.19		19	19	
$[MgF^+]$	0.76		76		38

7. How the free ion concentrations converge in the previous calculation (From Libes)

FIGURE 5.4. Change in free ion concentration with increasing iteration of the sample speciation calculation.
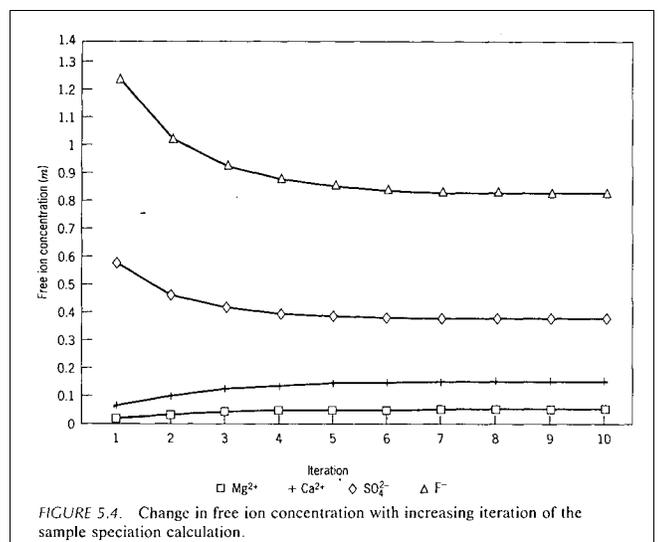
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