Properties of Water and Seawater

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The Nature of Pure Water

Seawater is mostly water (H2O). In fact it is about 96.5 wt % water. Surface sediments are also mostly water. Most fine-grained surface sediments have a porosity (<! = 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.
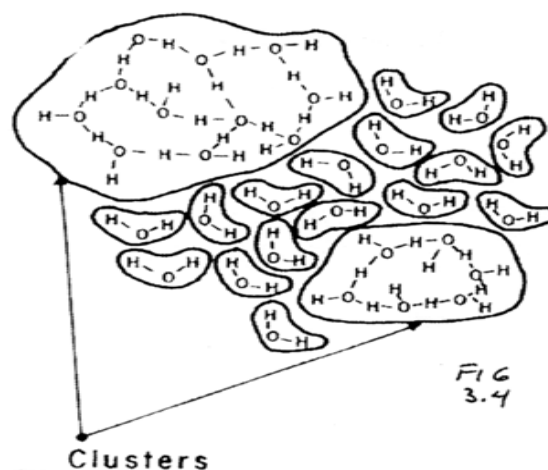
Water has unique and unusual properties both in pure form and as a solvent. These properties influence many of the chemical reactions taking place in the oceans.

Structure of the Water Molecule: The structure of H_2O consists of an oxygen atom with 2 6 electrons that have the electronic configuration of: 1s2 2s2 2pz 2py 2px which merge with two H atoms with 1 electron each resulting in a neutral molecule with 8 electrons which form four pairs called sp3 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.

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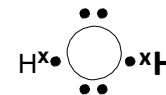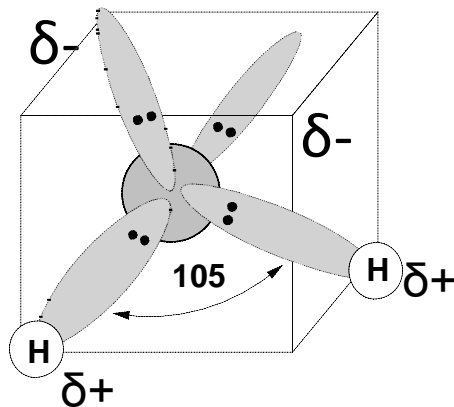
The H-O-H tetrahedral angle is 105° this is less than the ideal tetrahedral angle of 109° this is because of electron repulsion. The bent structure results in a dipole moment, there is separation of charge, which means it is a polar molecule. An important aspect of the water molecule structure is its 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.
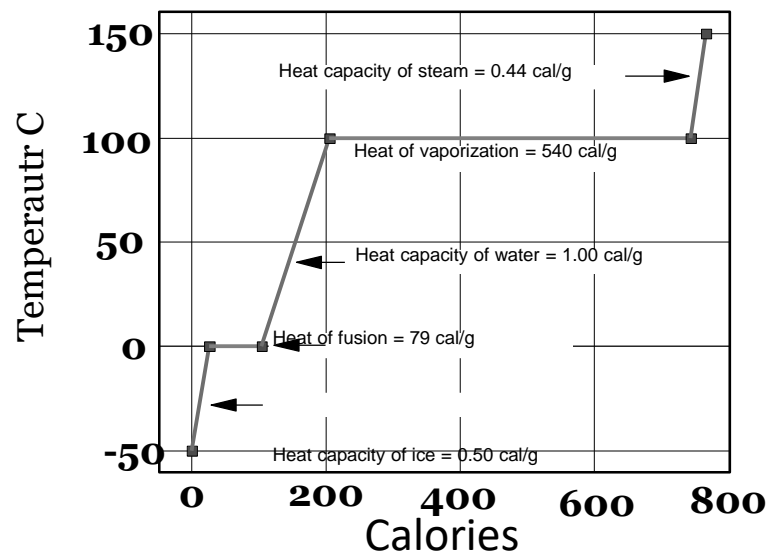
The structure of the H2O molecule and the hydrogen bonding of water explain many of the unique physical properties of water. Water has many physical properties that indicate unusually strong intermolecular associations. It takes a lot of energy to break the hydrogen bonds and change the structure of water, thus the water has a large thermal buffer capacity and acts as a climate moderator.


FIG 3.4

Clusters

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The Anomalous Properties of Water

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 (i'lH = 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 (i'lH =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.


Heat capacity of steam = 0.44 cal/g

Heat of vaporization = 540 cal/g

Heat capacity of water = 1.00 cal/g

Heat of fusion = 79 cal/g

Heat capacity of ice = 0.50 cal/g

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 simultaneously 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
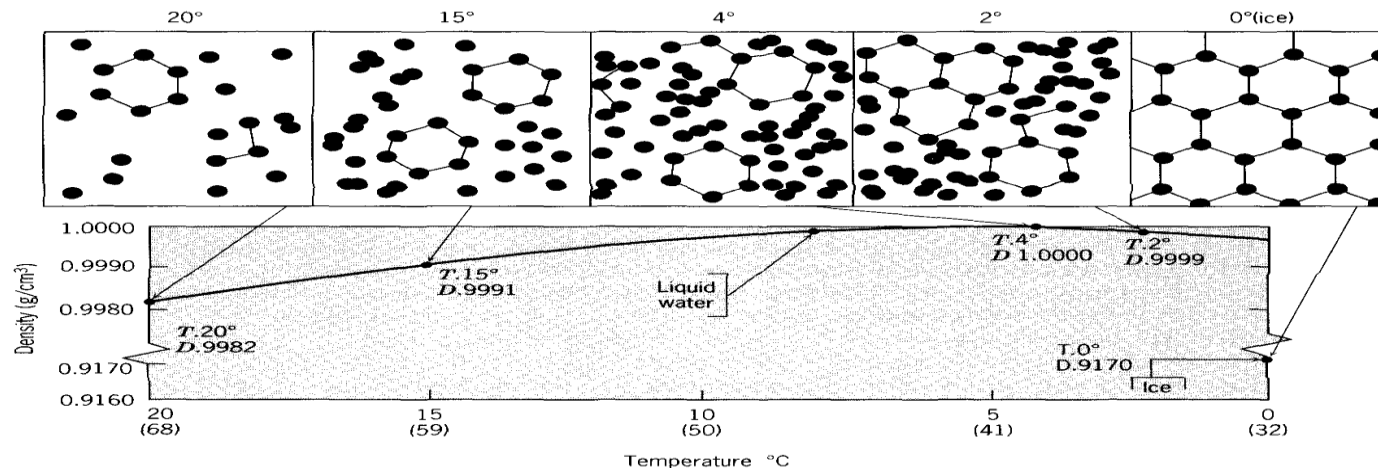

The change in liquid water structure and density with temperature, From Libes, 1992

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.
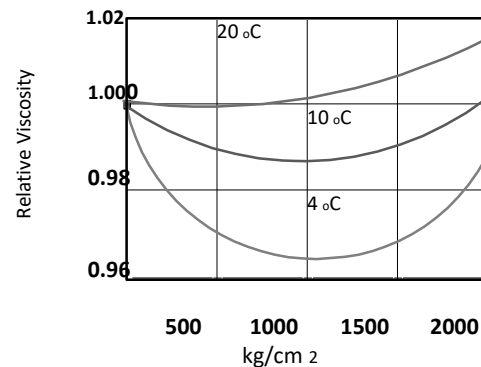

Water vapor has essentially no structure because the molecules are essentially unassociated water "monomers".

 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, p_{ice} = 0.915 while the density of water at that temperature is, p_{water} = 0.999. There are several different phases of ice that are stable at different T-P conditions.
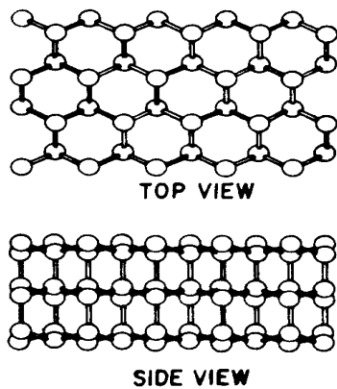
Ice-I

Molecular alignment

TOP VIEW

SIDE VIEW
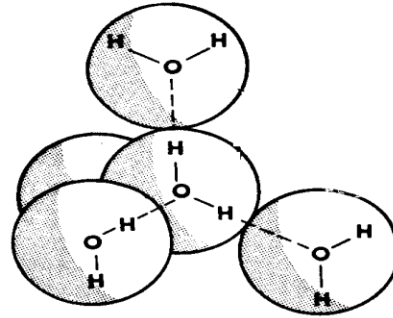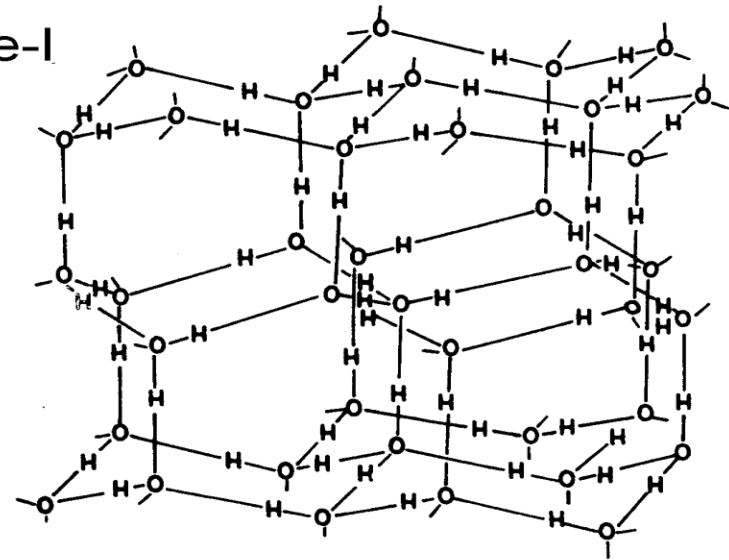
Sea-ice is formed by the freezing of seawater itself. When seawater first begins to freeze, relatively pure ice is formed, so that the salt content of the surrounding seawater is increased, which both increases its density and depresses its freezing point further. Most of the salt in sea-ice is in the 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.
- The freezing point is depressed.
- The boiling point is elevated.
- The conductivity is increased.

Comparison of Seawater and Pure Water Properties

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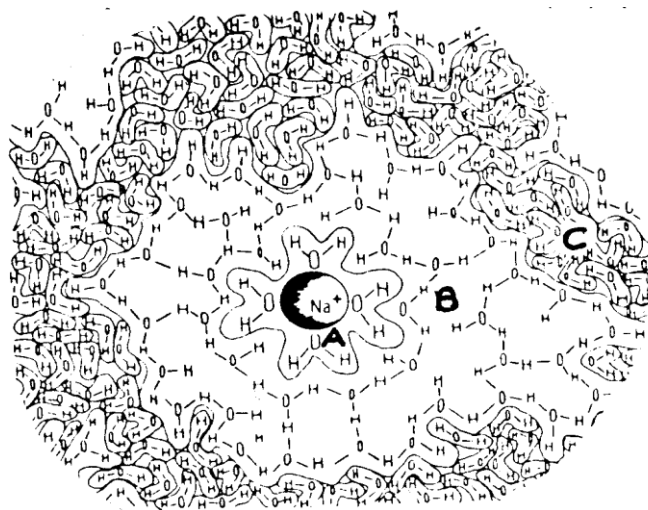
Heat Capacity of Seawater

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.

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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).
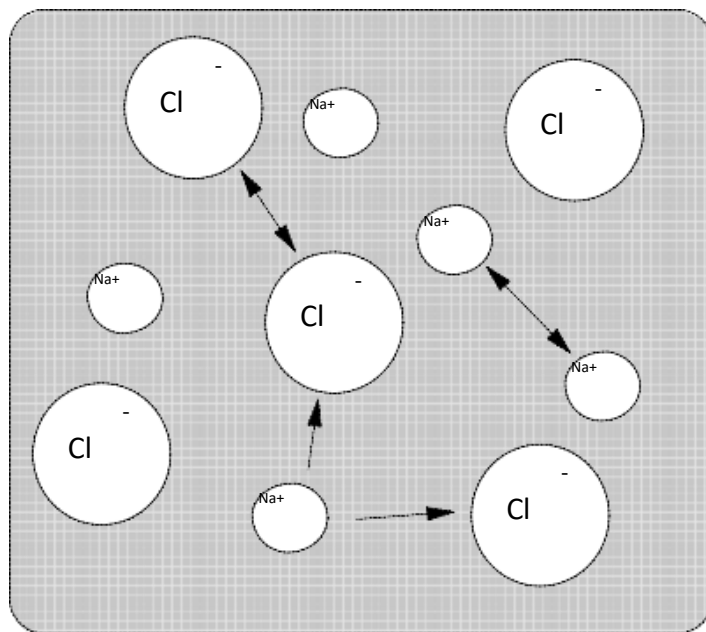
Activity: Ions in solution interact with each other as well as with water. At low concentrations of salts these interactions can sometimes be ignored, but at higher concentrations the ions behave like they are less concentrated than they really are. Therefore, correction factors must be applied to concentrations 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. $\Delta Gr°$) are expressed in terms of this **effective concentration** or activity, which is the concentration available for reaction. Thus we define activity as:

Activity ($\mathbf{a}_i$) = Effective amount (less then total amount)

In infinitely dilute solutions where ionic interactions are not important: $\mathbf{a}_i = C_i$ In concentrated solutions like seawater: $\mathbf{a}_i < C_i$.

There are two main reasons for these differences:

1- The Shielding Effect (Electrostatic Interactions).

2- Ion Complexes.

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: $f_{Ca}{}^{2+} = [Ca^{2+}]/ Ca_T = [Ca^{2+}] / ([Ca^{2+}]+ [CaSO4]+ [CaCO3])$

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 ⟶ $a_i = \gamma_i \times m_i$ ⟵ concentration of a free ion

⬆

free ion activity coefficient for that species

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

Activity of free ion ⟶ $a_i = \gamma_i \times f_i \times m_T$ ⟵ the total ion concentration

⬆ ⬆

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:

$$\text{Ionic strength} \longrightarrow I = 1/2 \; \Sigma m_i \; x \; Z_i^2 \longleftarrow \text{charge of i}^{\text{th}} \text{ ion squared}$$

$$\uparrow$$
$$\text{concentration of i}^{\text{th}} \text{ ion}$$

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

Ion Complexes

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

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

Ion pair = a direct association of **two** ions of opposite charge:

$$Ag^+ + Cl^- \Longleftrightarrow AgCl^0$$

Example:

Consider the following complexation reaction (in seawater):

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

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

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

1. At equilibrium:

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

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).

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

$$([MgF^-]/[F^-]) = (K[Mg^{2+}]\,\gamma_{Mg}^{2+}\,(\%\text{ free }_{Mg}^{2+}/100)\,\gamma_{F^-})\,/\,\gamma_{MgF^+}$$

$$([MgF^-]/[F^-]) = (63.1)(5.4 \times 10^{-2})(0.36)(0.87)(0.63) = 0.98$$

Homework

1- What is the relation between molecular weight and freezing/boiling temp? Where would you expect water to be on this graph?

Where does it actually plot? Why?

2- Why is the heat needed for freezing water less then expected from its mass relative to other similar compounds? Why is it only 1/7 that of vaporization?

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