Questions and Answers for Lecture 2

(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?

The relation is the lower the molecular weight the lower the freezing and boiling temperatures.
The temperatures for water should be around –68 and –90. The actual temperatures are higher due to hydrogen bond interactions. It is easier to freeze and harder to boil "clusters" make it more like solid.
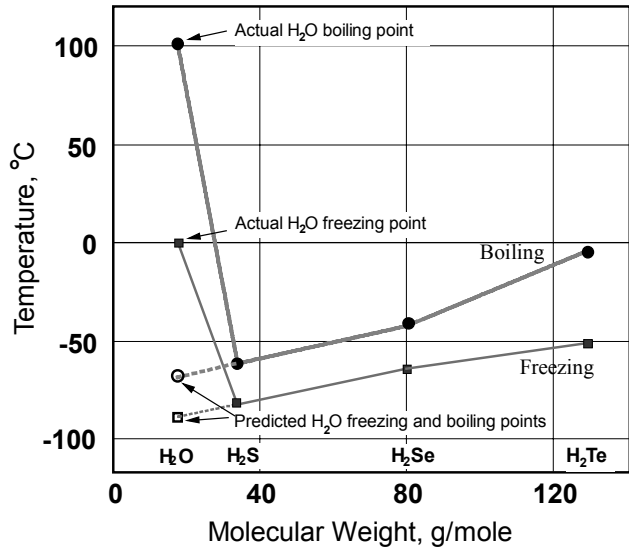
(2)   Why is the heat needed for freezing water less then expected from its mass relative to other similar compounds? Why is it only 1/7 that of vaporization?

Water molecules interact with each other through hydrogen bonds because of the polar nature of the water molecule of these clusters make water "closer" to the solid phase than expected (less bonds need to form).
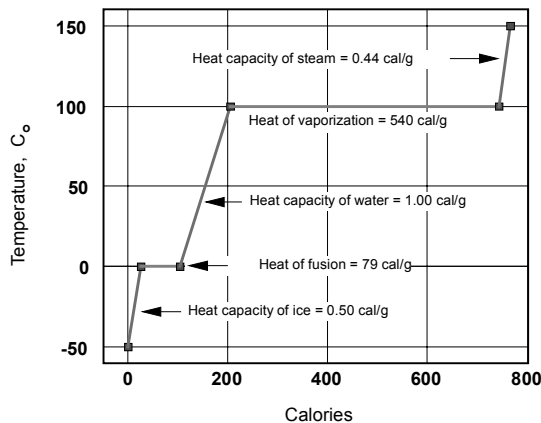
(3)   In what ways are the thermal properties of water the single most important factor in preventing extremes of temperature from being reached at the Earth's surface?

Both the specific heat and the latent heat of fusion and evaporation are extremely high. Large amounts of heat are required to raise the temperature of seawater let alone to evaporate it. The large volume of water provides a huge temperature buffer which confines the range of temperatures on Earth.

(4)   Ice melts and mixes with seawater of salinity 35 g/kg. Will this have the effect of raising or lowering the freezing point of seawater? How would this effect the formation of more sea ice when temperatures fell once more?

This will add fresh water, dilute seawater, make it less saline and raise the freezing point thus facilitate the formation of further sea ice.

(5) If we make a 0.5m NaCl solution we can predict the volume of the solution from the weights and densities of the recipe and compare the predicted volume with that measured.

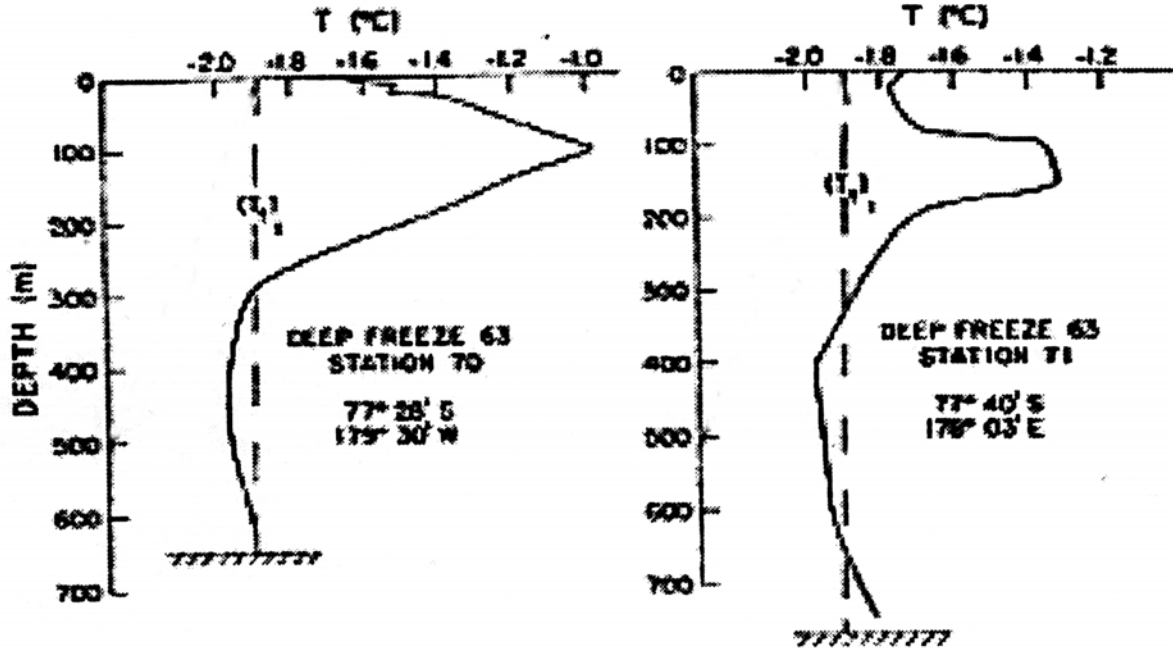(a) calculate the volume of 1000.0 grams of 0.5m NaCl.

NaCl molecular weight is 58.44 $\rho = 2.165$ g cm^{-3}
H$_2$O $\rho = 0.997$ g cm^{-3}

(b) the actual volume is 983 (4.2 less) Why is there a difference?

Thus: Component   density   volume
       29.22 g NaCl ÷ 2.165 g cm^{-3} = 13.50 cm^3
       970.78g H$_2$O ÷ 0.997 g cm^{-3} = 973.70 cm^3
       _____   _____
       1000.0g of 0.5m   = 987.2 cm^3 (predicted)
                                    983.0 cm^3 (actual)
              Volume difference   =   4.2 cm^3

The effect of hydration and electrostriction is in action the reduction of water volume by added ions is a result of ion/dipole interaction. In this case, the net system volume shrunk by ~0.5% because **waters of hydration** about individual ions are oriented and closely packed into a "primary hydration shell".

(6) In the following temperature profile for the Ross Sea notice that temperatures are everywhere below -1.0 °C. Specifically the water from 300-600 m has a temperature as much as 0.07 °C below the one atmosphere freezing point. Why does the Ross Sea not freeze? What will happen if the water is mixed up rapidly (no time for temperature re-equilibration)?

T (°C)

-2.0 -1.8 -1.6 -1.4 -1.2 -1.0

DEPTH (m)

DEEP FREEZE 63
STATION 70

77° 28' S
175° 30' W

T (°C)

-2.0 -1.8 -1.6 -1.4 -1.2

DEEP FREEZE 63
STATION 71

77° 40' S
178° 03' E

The effect of water pressure on the freezing point is demonstrated in the hydrographic data from the Ross Ice Shelf (Countryman and Gsell, 1966). The freezing point is depressed due to the pressure effect. Water brought quickly from this depth to the surface would flash freeze.

(7) At what temperature will seawater freeze out completely (to the bottom)?

Construct a graph that shows the % of the ocean frozen as a function of temperature. Assume that there is no heat source at the ocean floor and that the temperature above the ice surface is always less than the freezing point. Start out with a 0.7M solution of NaCl. The relation between the freezing temperature and salinity is a cubic equation as follows:

$$S = 1.78\ t - 0.0442\ t^2 + 0.000557\ t^3$$

(a) calculate the initial salinity for 0.7M NaCl
(b) remember the total mass of the salt does not change so:
$$4.095 \times 100 = S(100\text{-}F) \text{ and } S = 4.095 \times 100/ (100\text{-}F)$$
(c) calculate S for different F and solve the cubic equation
* you can also use any temp. Solve for S and calculate F
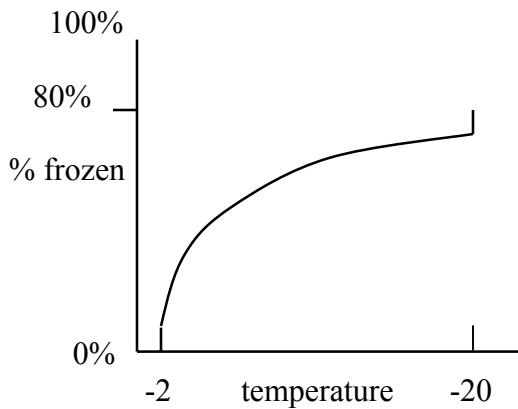
Please note this is a "free hand" line drawn to illustrate the idea and has not based on "real calculations"

When the ocean freezes it becomes a system of two phases a solid phase ice and a liquid phase. Since salt is not incorporated into the ice the liquid phase becomes more and more saline as the ocean freezes.

0.7N NaCl = 4.095%; x = y –b/3a; This is fine but not correct the actual curve will not follow this relation all along it will do so only until the eutectic point which is at –21.12 degrees at this temperature 84.9% of the ocean will be frozen, after that every thing freezes.

(8) (a)What would the ionic strength of seawater be if only sodium and chlorine were in this solution? (b) How does this change if the divalent ions are included? (c) Compare the ionic strength of freshwater and seawater.

Remember $\quad\quad\quad\quad I = 1/2\ \Sigma m_i\ x\ Z_i^2$

Molality (moles solute per kg solvent)

	Seawater (SW)	Lake Water (LW)
Na^+	0.49	$0.2\ x\ 10^{-3}$
Mg^{2+}	0.053	$0.14\ x\ 10^{-3}$
Ca^{2+}	0.010	$0.22\ x\ 10^{-3}$
K^+	0.010	$0.03\ x\ 10^{-3}$
Cl^-	0.57	$0.09\ x\ 10^{-3}$
SO_4^{2-}	0.028	$0.102\ x\ 10^{-3}$
HCO^{3-}	0.002	$0.816\ x\ 10^{-3}$

(a) 0.53
(b) 0.712
$I_{SW} = 1/2\ (m_{Na}\ x\ 1^2 + m_{Mg}\ x\ 2^2 + m_{Ca}\ x\ 2^2 + m_K\ x\ 1^2 + m_{Cl}\ x\ 1^2 + m_{SO4}\ x2^2 + m_{HCO3}\ x\ 1^2) = 0.72\ mol\ kg^{-1}$
$I_{LW} = 0.0015 = 1.5\ x\ 10^{-3}\ mol\ kg^{-1}$

So the ionic strength of seawater is about 500 times larger than that of fresh water.

(9)   Is $SrSO_4$ more soluble in distilled water or in 0.7 M NaCl solution? Why? What about in seawater? Will the solubility of $CaCO_3$ be higher at 1m solution made of NaCl or at 1m solution made of a mixture of NaCl and MgCl
$SrSO_4$ is more soluble in 0.7M NaCl because of the ion shielding effect. It will be even more soluble in seawater where there are more doubly charged ions and in particular more CO_3^{2-} which makes complexes with Sr lowering its free content.

(10) Suppose you have a solution of 0.7 mol/l NaCl and another solution of 0.1 mol/l $MgCl_2$.
    (a) What are the ionic strengths of these solutions? $I = 1/2\ \Sigma m_i\ x\ Z_i^2$
0.7 and 0.3 respectively

(b) How much NaCl do I need to add to my $MgCl_2$ solution so both solutions will have the same ionic strength?
0.4 M

(c) Which of these solutions will have more Cl in?
The first 0.7 vs 0.8

(d) Accordingly in which solution could you dissolve more AgCl?
In the solution with less Cl, because $Ksp = [Ag^+]\gamma_{Ag+}\ [Cl^-]\gamma_{Cl-}$

(11) (a) Calculate the total activity coefficient of free ions in a seawater.

The values for the %free and γi for different ions in seawater are given below for the Garrels and Thompson model for major ion speciation.

Ion	γi	% Free	γT
Ca^{2+}	0.28	0.91	0.25
Mg^{2+}	0.36	0.87	0.31
Na^+	0.76	0.99	0.75
K^+	0.64	0.99	0.63
SO_4^{2-}	0.12	0.54	0.065
$HCO3^-$	0.68	0.69	0.42
$CO3^{2-}$	0.20	0.09	0.018
Cl^-	0.63	1.00	0.63

γT = % Free x γi

The **major ions** (>1mg/kg seawater) at S‰ = 35.000 (from Pilson)

Ion	Formula	g/Kg	mmol/Kg
Sodium	Na^+	10.781	468.96
Magnesium	Mg^{2+}	1.284	52.83
Calcium	Ca^{2+}	0.4119	10.28
Potassium	K^+	0.399	10.21
Strontium	Sr^{2+}	0.00794	0.0906
Chloride	Cl^-	19.353	545.88
Sulfate	SO_4^{2-}	2.712	28.23
Bicarbonate	HCO_3^-	0.126	2.06
Bromide	Br^-	0.067	0.844
Borate	$H_3BO_4^-$	0.0257	0.416
Fluoride	F^-	0.00130	0.068
Totals	11	35.169	1119.87

(b) Write the expression for f_{Ca2+} x γ_{Ca2+} in terms of the different species concentrations assume that Ca interacts only with sulfate and carbonate to form $CaSO_4$ and $CaCO_3$ complexes.

$$\gamma T = f_{Ca2+} \times \gamma_{Ca2+} = ([Ca^{2+}]/ Ca_T) \times \gamma_{Ca2+} = ([Ca^{2+}]/ ([Ca^{2+}]+ [CaSO_4] + [CaCO_3])) \times \gamma_{Ca2+}$$

(c) Using this information calculate what is the concentration of free Ca^{2+} in seawater

$$m_i = m_T \times f_i$$

$[Ca^{2+}] = [Ca_T]$ x fi $[Ca^{2+}] = 0.010$ moles/kg x 0.91 = 0.0091 moles/kg

(12) Element M is known to be toxic to plankton at concentrations of about 1×10^{-9} mol/kg. Recent concentration measurements of this element M in Trout Lake indicate exactly this level. Dr. Lou Hiss, a biological oceanographer working as a consultant to GVRD, states that the lake is in imminent danger of all the plankton dying and proposes a massive clean up. Because you are a graduate of *Marine Chemistry*, "Lorax Consulting Co." has hired you and Dr. Suess to predict if the plankton are in danger of dying. Dr. Suess is at a loss to come up with an alternative explanation and spends all day doodling. In your prediction make sure to include all the necessary equations and calculations.

Data: total concentration of M, $[M]_{tot} = 1 \times 10^{-9}$ mol/kg

M^{2+} forms strong ion pairs with CO_3^{2-} but no other ion pairs

$K_{ion\ pair} = 2.5 \times 10^{-5}$ mol/kg

concentration of carbonate ion, $[CO_3^{2-}] = 10^{-3}$ mol/kg

$\gamma CO_3^{2-} = \gamma_m = 0.5$ $\gamma_{MCO3} = 1.13$

In order to be paid by Lorax consultants, you must show your **quantitative** reasoning.

Need to calculate the   %free M= [M]/Mt or show the free [M] is less than 1×10^{-9}

$M_T = [M] + [MCO_3] = 1 \times 10^{-9}$

$[MCO_3] = 1 \times 10^{-9} - [M]$

$K_{MCO3} = (M)(CO_3)/(MCO_3) = [M]\gamma_M \times [CO_3]\gamma_{CO3} / [MCO_3]\gamma_{MCO3}$

$K_{MCO3} = [M]\gamma_M \times [CO_3]\gamma_{CO3} / \{ 1 \times 10^{-9} - [M]\}\gamma_{MCO3}$

Solve for [M]

$$2.5 \times 10^{-5} = \frac{\gamma_M \times [CO_3]\gamma_{CO3}}{\gamma_{MCO3}} \times \frac{[M]}{1 \times 10^{-9} - [M]}$$

$$\frac{[M]}{1 \times 10^{-9} - [M]} = 0.113$$

$0.113 \times 10^{-9} - 0.113 [M] = [M]$

$1.113 [M] = 0.113 \times 10^{-9}$

$[M] = 1.015 \times 10^{-10}$