Chemistry 123 **Problem Set Solution** **Winter Term 2003**
Assignment #2 **Instructor: R. Rossi**

Common Symbols Rob uses in this key, or more generally when writing stuff on the board in class:

m = mass

m_x = mass of x, for example, m_{cheese} would represent the mass of cheese present

η = moles

η_x = moles of x, for example, η_{beans} would represent the moles of beans present

$\hat{X}$ = The extensive property X measured on a mass basis, for example, an energy in joules per gram would be $\hat{E}$

$\tilde{X}$ = The extensive property X measured on a mole basis, for example, an energy in joules per mole would be $\tilde{E}$

$\widehat{X}$ = The extensive property X measured on a volume basis, for example, an energy in joules per liter would be $\widehat{E}$

$\tilde{m}_x$ = molar mass of substance x

sf = significant figures

$\%_{\text{mass}}$ = percent by mass

$\%_{\text{mol}}$ = mole percent = percent by number

$\%_{\text{vol}}$ = percent by volume

T = temperature

P = pressure

π = osmotic pressure

V = volume

ℓ = liters (litres)

R = universal gas constant

ρ = density

g = the acceleration of gravity at sea level on earth

F = force

a = acceleration

A = area

sat'd = saturated

sol'n = solution

P_x = partial pressure of gas x

P^o_x = pure component vapor pressure of x

m_x = molality of substance x

M = molarity

[A] = molarity of chemical species A

atm = atmosphere(s)

$\underline{x}$ = an exact number For example, 1000 would be understood to have 1 significant figure. $\underline{1000}$ is understood to be *exact*

I employ the standard abbreviations for SI units and prefixes, which appear in Tables 1.1 and 1.2 in Zumdahl.

1. a. method #1 $P = P_0 + \rho g h$ $g = 9.8\ m/s^2$

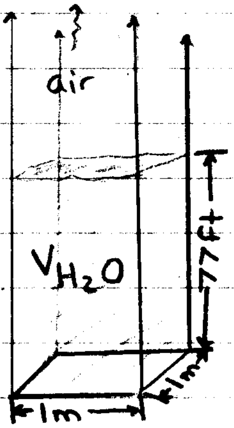
$$\rho g h = (1.0\ g/\cancel{cm^3})(9.8\ m/s^2)(77\ \cancel{feet}) \times \left(\frac{1\ m}{3.2808\ \cancel{ft}}\right) \times \left(\frac{100\ \cancel{cm}}{1\ m}\right)^3$$

$$= 2.3 \times 10^8\ \frac{\cancel{g}\cdot \cancel{m^2}}{\cancel{s^2}\ \cancel{m^3}} \times \frac{1\ \cancel{kg}}{1000\ \cancel{g}} \times \frac{1\ Pa}{1\ \cancel{kg}/\cancel{m}\cdot\cancel{s^2}}$$

$\rho g h = 2.3 \times 10^5\ Pa$ = pressure due to H_2O

$P_0 = P_{atm} = 1\ atm = 101325\ Pa$ so $P_{abs} = 2.3 \times 10^5 + 101325\ Pa$

$$\boxed{\text{The absolute pressure is about } 3.3 \times 10^5\ Pa \text{ at a depth of 77 feet}}$$



method #2 - Based on diagram @ left

$$F_{H_2O} = ma = \rho_{H_2O} \cdot V_{H_2O} \cdot g$$

$$= 1.0\ g/cm^3 \cdot (77 ft \cdot 1m \cdot 1m)(9.8\ m/s^2)$$

$$= 7.5_{46}\ \frac{\cancel{g}\cdot \cancel{ft} \cdot \cancel{m^3}}{\cancel{cm^3}\cdot s^2} \left(\frac{100\ \cancel{cm}}{1\ \cancel{m}}\right)^3 \left(\frac{1\ m}{3.2808\ \cancel{ft}}\right)\left(\frac{1\ kg}{1000\ \cancel{g}}\right)$$

$$= 2.3 \times 10^5\ \frac{kg \cdot m}{s^2} = 2.3 \times 10^5 \text{ Newtons}$$

$$P = \frac{F}{A} = \frac{2.3 \times 10^5\ \cancel{kg \cdot m/s^2}}{1\ \cancel{m^2}} \times \frac{1\ Pa}{1\ \cancel{kg/m s^2}} = 2.3 \times 10^5\ Pa = P_{H_2O}$$

again, adding atmospheric pressure gives us

$$P_{abs} = P_{H_2O} + P_{atm} = 230000 + 101325\ Pa$$

$$= 330000\ Pa$$

1\. b. $$\text{Solubility}_{@77ft} = \left(\frac{P_{@77ft}}{1\,atm}\right) 9.4\,mg\,N_2/1\,l\,H_2O$$

$$= \left(\frac{3.3\times10^5\,Pa}{101325\,Pa}\right)\frac{9.4\,mg\,N_2}{1\,l\,H_2O}\times\frac{1\,l}{1000\,ml}\times\frac{1\,ml}{1.0\,g}$$

$$= 0.030_6\,\frac{mg}{g}\times\frac{1\,g}{1000\,mg}\times\underbrace{10^6\,ppm}_{\text{like }100\%}$$

$$= 30._{61}\,ppm$$

$$\boxed{\text{There's }31\,ppm_{(by\,mass)}\,N_2\text{ in Rob's blood}}$$

c\. When Rob rises back up to the surface, the solubility of N_2 in his blood will return to 9.4 mg/l. 77 feet under water it was $9.4\,\frac{mg}{l}\left(\frac{3.3\times10^5\,Pa}{101325\,Pa}\right) = 30._6\,\frac{mg}{l}$

Thus $$30._6 - 9.4\,\frac{mg\,N_2}{l\,blood} = 21._2\,\frac{mg\,N_2}{l\,blood}$$

will come out of solution and form bubbles in Rob's blood. (ouch!) That's a total of

$$21._2\,\frac{\cancel{mg\,N_2}}{\cancel{l\,blood}}\times 4.5\,\cancel{l\,blood}\times\frac{1\,mol\,N_2}{2(14.007)\,\cancel{g}\,N_2}\times\frac{1\,\cancel{g}}{1000\,mg} = 3.4_1\times10^{-3}\,mol\,N_2$$

N_2 is a rather ideal gas, so we can use $PV = nRT$

$P = 1\,atm = 101325\,Pa$ $T = 37°C + 273.15 = 310._{15}\,K$

$$V_{N_2} = \frac{n_{N_2}RT}{P} = \frac{(3.4_1\times10^{-3}\,\cancel{mol}\,N_2)(8.3145\,\frac{Pa\cdot m^3}{\cancel{mol\cdot K}})(310._{15}\,\cancel{K})}{101325\,\cancel{Pa}}$$

$$= 0.000086_{685}\,\cancel{m^3}\times\frac{1000\,\cancel{l}}{1\,\cancel{m^3}}\times\frac{1000\,ml}{1\,\cancel{l}} = 86._{685}\,ml$$

$$\boxed{\text{87 ml of } N_2 \text{ gas will form in Rob's bloodstream.}}$$

← I'd be a dead man

2. a. The osmotic pressure data in (1) can be used to determine the molecular mass of camphor ($MW_{camphor}$) as described in sample Exercise 11.11 in Zumdahl.

The osmotic pressure is 52.58 cm of diluted solution, or

$$\pi = \rho g h = 0.789\,\mathrm{g/cm^3}\left(9.81\,\frac{m}{s^2}\right) 52.58\,\mathrm{cm}$$

$$= 406_8\,\frac{g\cdot \cancel{cm}}{\cancel{cm^2}\,\cancel{s^2}} \times \frac{1\,\mathrm{Pa}}{1\,\frac{\cancel{kg}}{\cancel{m}\,\cancel{s^2}}} \times \left(\frac{100\,\cancel{cm}}{1\,\cancel{m}}\right)^2 \times \frac{1\,\mathrm{kg}}{1000\,\mathrm{g}} = 406_8\,\mathrm{Pa}$$

Then, $C = \frac{\pi}{RT} = \frac{406_8\,\mathrm{Pa}}{\left(8.314\,\frac{Pa\cdot m^3}{mol\cdot \cancel{K}}\right)(298\,\cancel{K})} = 1.64_{11}\,\frac{mol}{m^3}$ (See O+N's example 4-13)

We had 200 mℓ of solution, containing 0.0500 g of camphor, so

$$1.64_{11}\,\frac{mol}{\cancel{m^3}} \times 200\,\cancel{m\ell} \times \frac{1\,\cancel{\ell}}{1000\,\cancel{m\ell}} \times \frac{1\,\cancel{m^3}}{1000\,\cancel{\ell}} = 3.28_{22} \times 10^{-4}\,mol$$

$$\boxed{\therefore MW_{camphor} = \frac{m}{n} = \frac{0.0500\,g}{3.28_{22} \times 10^{-4}\,mol} = 152._3\,g/mol}$$

b. $$250.0\,g\ camphor \times \frac{1\,mol\ camphor}{152._3\,g\ camphor} = 1.64_{15}\,mol\ camphor$$

It is now pretty easy to use the data in (2) to determine the chemical formula:

$$722\,g\ CO_2 \times \frac{1\,mol\ CO_2}{[12.011 + 2(15.999)]\,g\,CO_2} = 16.4_1\,mol\ CO_2$$

$$235\,g\ H_2O \times \frac{1\,mol\ H_2O}{[2\cdot 1.008 + 15.999]\,g\,H_2O} = 13.0_4\,mol\ H_2O$$

Let camphor have the formula $C_xH_yO_z$

All the carbon in camphor comes out as CO_2:

$$n_{C\,in} = n_{C\,out} \Rightarrow n_{camphor}\left(\frac{x\,\cancel{mol}\,C}{1\,mol\ camphor}\right) = n_{CO_2}\left(\frac{1\,\cancel{mol}\,C}{1\,mol\ CO_2}\right)$$

$$x = \frac{n_{CO_2}}{n_{camphor}}\left(\frac{mol\ camphor}{mol\ CO_2}\right) = \frac{16.4_1\,mol\ CO_2}{1.64_{15}\,mol\ camphor}\left(\frac{mol\ camphor}{mol\ CO_2}\right)$$

$$= 9.99_7 \doteq 10 \text{ (rounded to whole atoms)}$$

Similarily, all the H in the camphor that was burned emerged as H_2O.

2. b. continued...

$$n_{H_{in}} = n_{camphor} \cdot y = n_{H_{out}} = 2n_{H_2O}$$

$$y = \frac{2n_{H_2O}}{n_{camphor}} = \frac{2(13.0_4\text{ mol})}{1.64_{15}\text{ mol}} = 15.8_9 \doteq 16$$

There are a large number of equivalent ways to get z. I think the easiest is to figure out how much of the MW is not due to C or H → and that's due to O:

$$MW = 152._3\,\text{g/mol} = x(12.011) + y(1.008) + z(15.999)$$

$$z = \frac{152._3 - 10(12.011) - 16(1.008)}{15.999} = 1.00_4 \doteq 1$$

$$\boxed{\text{So camphor is } C_{10}H_{16}O}$$

Method #2 (More mathematically challenging)

You can solve this problem starting from the information in (2), but it's a bit tricky. see, Rob is still a ChE

Again, let camphor be $C_xH_yO_z$.

We have 3 variables, we need 3 independent equations in order to solve for x, y, and z.

We can write 4 balances (be they mass or mole balances) but they are not independent.

I'll use mass balances here (they're clearer)

① total mass in = total mass out

② mass of C in = mass of C out

③ mass of H in = mass of H out

④ mass of O in = mass of O out

These add to give this.

Only 3 of these are independent; so we pick the 3 that are easiest to work with.

2. b. method #2, continued...

① total mass in = total mass out

$$m_{camphor_{in}} + m_{O_{2in}} = m_{CO_{2out}} + m_{H_2O_{out}} + m_{O_{2out}}$$

$$m_{O_{2in}} - m_{O_{2out}} = m_{CO_{2out}} + m_{H_2O_{out}} - m_{camphor_{in}}$$

$$m_{O_2}\text{ consumed} = 722g + 235g - 250.0g$$

not really needed for anything → $= 707\ g\ O_2$ added for combustion

② mass of C in = mass of C out

$$x_{C,camphor} \cdot m_{camphor} = x_{C,CO_2}\, m_{CO_2}$$

where $x_{\alpha,\beta}$ is the mass fraction of α in β

$$x_{C,camphor} = \frac{x_{C,CO_2}\, m_{CO_2}}{m_{camphor}}$$

$$= \left(\frac{12.011 g\ C}{44.009 \cancel{g\ CO_2}}\right)\left(\frac{722 \cancel{g\ CO_2}}{250.0 g\ camphor}\right)$$

$$x_{C,camphor} = 0.788_2\ \frac{g\ C}{g\ camphor}$$

③ mass of H in = mass of H out

$$x_{H,camphor} \cdot m_{camphor} = x_{H,H_2O} \cdot m_{H_2O}$$

$$x_{H,camphor} = \frac{x_{H,H_2O}\, m_{H_2O}}{m_{camphor}}$$

$$= \left(\frac{2 \cdot 1.008\ g\ H}{18.015\ \cancel{g\ H_2O}}\right)\left(\frac{235 \cancel{g\ H_2O}}{250.0\ g\ camphor}\right)$$

$$x_{H,camphor} = 0.105_2\ \frac{g\ H}{g\ camphor}$$

we won't use ④ because it can't tell us anything new. It's a messy equation anyway.

2. b. Method #2, continued...

Instead, we will use the fact that the mass fractions must add up to one:

$$\chi_{O,\text{camphor}} = 1 - \chi_{C,\text{camphor}} - \chi_{H,\text{camphor}}$$

$$= 1 - 0.788_2 - 0.105_2$$

$$= 0.106_6$$

Here's where it gets messy - x, y, and z help. If we take one mole of campor as our "basis",

↑ glorified plumbing term

$$\chi_C = \frac{x(12.011)}{x(12.011)+y(1.008)+z(15.999)} = 0.788_2$$

$$\chi_H = \frac{y(1.008)}{x(12.011)+y(1.008)+z(15.999)} = 0.105_2$$

$$\chi_O = \frac{z(15.999)}{x(12.011)+y(1.008)+z(15.999)} = 0.106_6$$

Bottom sum makes these linearly dependent

Unfortunately, these equations are not independent either. (Solve them & you'll get z=z!) There's a whole family of x, y, and z values that will satisfy them. All they give us is the empirical formula. If we arbitrarily set one, we can get the other two in proper ratio. So lets set x=1. Then

$$0.788_2 = \frac{1(12.011)}{12.011+(1.008)y+(15.999)z} \quad \Rightarrow \text{clear denominator}$$

$$12.011 = 9.46_7 + 0.794_5 y + 12.6_1 z \Rightarrow 12.6_1 z = 2.54_4 - 0.794_5 y$$

$$z = 0.201_7 - 0.0630_0 y$$

$$0.105_2 = \frac{y(1.008)}{12.011+(1.008)y+(15.999)[0.201_7 - 0.0630_0 y]}$$

$$1.26_4 + \cancel{0.106_0 y} + 0.339_5 - \cancel{0.106_0 y} = 1.008y \Rightarrow y = 1.59_1$$

2. b. method #2, continued...

$z = 0.201_7 - 0.0630_0(1.59_1) = 0.101_5$

This gives us $C_1H_{1.59_1}O_{0.101_5}$

To get the empirical formula, we divide through by the smallest coefficient:

$\frac{1}{0.101_5} = 9.85_4 \qquad \frac{1.59_1}{0.101_5} = 15.6_8 \qquad \frac{0.101_5}{0.101_5} = 1$

So our empirical formula is $C_{10}H_{16}O$

The chemical formula could be any whole-number multiple of this. Anyone who started down this path will be sad to discover that now they have to go to the data provided in (1), and they'll probably see how much easier it could have been.

As shown there, (1) tells you

$MW_{camphor} = 152._3 \text{ g/mol}$

If we let the chemical formula be $C_{10a}H_{16a}O_a$,

$MW = a[10(12.011) + 16(1.008) + 15.999] = 152.2_4 a \text{ g/mol}$

so $a = \frac{152._3 \text{ g/mol}}{152.2_4 \text{ g/mol}} \doteq 1$

$\boxed{\text{So the chemical formula is } C_{10}H_{16}O.}$

This method is much harder, but if the data in (1) were not given, this (or something like it) would be the only way to get to the empirical formula.

2. c. The "correct" molar mass is

$MW_{C_{10}H_{16}O} = 10[12.011] + 16[1.008] + 15.999 = 152.2_4$

The balanced combustion reaction is

$C_{10}H_{16}O + O_2 \rightarrow 10CO_2 + 8H_2O$

$C_{10}H_{16}O \quad \cancel{9O_2} \quad 10CO_2 \quad 8H_2O$

$\cancel{4O_2} \quad \cancel{6O}$

$3O_2$

$\cancel{10O_2}$

$$2C_{10}H_{16}O + 27O_2 \rightarrow 20CO_2 + 16H_2O$$

Theoretical yields:

$$250.0\,\cancel{g\ camphor} \times \frac{1\ \text{mol camphor}}{152.2_4\,\cancel{g\ camphor}} \times \frac{20\,\cancel{CO_2}}{2C_{10}H_{16}O} \times \frac{44.009\ g\ CO_2}{1\,\cancel{mol\ CO_2}} = 722.7\ g\ CO_2$$

$$250.0\,\cancel{g\ camphor} \times \frac{1\,\cancel{mol\ camphor}}{152.2_4\,\cancel{g\ camphor}} \times \frac{16\,\cancel{H_2O}}{2\,\cancel{C_{10}H_{16}O}} \times \frac{18.015\ g\ H_2O}{1\,\cancel{mol\ H_2O}} = 236.7\ g\ H_2O$$

$$\%\ \text{yield}\ CO_2 = \frac{\text{real}}{\text{theory}} = \frac{722\,g}{722.7\,g} \times 100\% = 99.9\%$$

$$\%\ \text{yield}\ H_2O = \frac{\text{real}}{\text{theory}} = \frac{235\,g}{236.7\,g} \times 100\% = 99.3\%$$

$$\boxed{\%\ \text{yields:}\quad 99.9\%\ CO_2 \quad 99.3\%\ H_2O}$$

These can vary by ±0.1%, but they must have three significant figures for full credit. If a) was wrong, partial credit can be given for the method in (b), so long as the result is reasonable. (i.e. not 365% or 22% yield - the calculations for (a) assume 100% yield!)

3. Solving this problem requires that you understand both freezing point depression and how water softeners work…it's not trivial!
   a. Since freezing point depression is a colligative property, we care only about the concentration of particles in the well water, not their identity or charge. We'll stick that into the freezing point depression equation $\Delta T_f = K_f m_{\text{solute particles}}$ to determine the freezing point. The main challenge here is in the units, because while we have to determine the molality of the particles, we are given their concentration in ppm_{mass} units. This isn't as problematic as it may initially appear, because we are told that these are the only impurities having a significant concentration; thus we can total up the mass of these impurities and find that the water contains a total impurity level of less than 500 ppm_{mass}, in other words less than 500 mg of impurities per kilogram of water. That in turn tells us we can safely claim that exactly one kilogram of this solution contains 1000. g of water. (Actually, it would be about 999.5 g of water, and 0.5 g of impurities, but that's within the range indicated by the sig figs written above!) Unlike the sodium hydroxide from the last problem set, this solution is so dilute that its density and water content are effectively indistinguishable from that of pure water at the four sig fig level. So, taking exactly one kilogram of this water as our *basis*, we expect that it will contain

$$216 \text{ mg of Cl}^- \left(\frac{1 \text{ mol Cl}^-}{35.45 \text{ g Cl}^-}\right) = 6.09_{31} \text{ millimoles of Cl}^-$$

$$56 \text{ mg of Na}^+ \left(\frac{1 \text{ mol Na}^+}{22.99 \text{ g Na}^+}\right) = 2.4_{36} \text{ millimoles of Na}^+$$

$$78 \text{ mg of Ca}^{2+} \left(\frac{1 \text{ mol Ca}^{2+}}{40.08 \text{ g Ca}^{2+}}\right) = 1.9_{46} \text{ millimoles of Ca}^{2+}$$

$$30. \text{ mg of Mg}^{2+} \left(\frac{1 \text{ mol Mg}^{2+}}{24.31 \text{ g Mg}^{2+}}\right) = 1.2_{34} \text{ millimoles of Mg}^{2+}$$

$$40. \text{ mg of SO}_4^{2-} \left(\frac{1 \text{ mol SO}_4^{2-}}{(32.07 + 4 \cdot 16.00) \text{ g SO}_4^{2-}}\right) = 0.41_{64} \text{ millimoles of SO}_4^{2-}$$

$$18 \text{ mg of Fe}^{3+} \left(\frac{1 \text{ mol Fe}^{3+}}{55.85 \text{ g Fe}^{3+}}\right) = 0.32_{23} \text{ millimoles of Fe}^{3+}$$

for a grand total of

$$\begin{array}{rl} & 6.09_{31} \text{ mmol of Cl}^- \text{ ions} \\ & 2.4_{36} \text{ mmol of Na}^+ \text{ ions} \\ & 1.9_{46} \text{ mmol of Ca}^{2+} \text{ ions} \\ & 1.2_{34} \text{ mmol of Mg}^{2+} \text{ ions} \\ & 0.41_{64} \text{ mmol of SO}_4^{2-} \text{ ions} \\ + & 0.32_{23} \text{ mmol of Fe}^{3+} \text{ ions} \\ \hline & 12.4_{478} \text{ mmol of particles} \end{array}$$

Since we have 1.000 kg of water, our solvent, the molality of particles in our solution is

$$\frac{12.4_{478} \times 10^{-3} \text{ mol of particles}}{1.000 \text{ kg of solvent}} = 12.4_{478} \times 10^{-3} \text{ molal particles}$$

The freezing point depression constant for water is given in Table 11.5 of Zumdahl to be 1.86 C°·kg·mol^{-1}. (Note: I use C° rather than °C, because they are actually different things. °C refers to a temperature measured on the Celsius scale. C° refers to a temperature *difference* measured in Celsius-sized units. There is a difference, which Zumdahl glosses over!) The freezing point of the water will therefore be depressed by

$$\Delta T_f = K_f m_{\text{solute particles}} = 1.86 \frac{\text{C}^\circ \cdot \text{kg}}{\text{mol}} \left(12.4_{478} \times 10^{-3} \frac{\text{mol}}{\text{kg}}\right) = 0.0231_{53} \text{ C}^\circ$$

Which, unfortunately for the Kiersaw-Bartons, isn't squat. Chances are really good that the well water pipe will burst.

$$\boxed{\text{The unsoftened well water will freeze at -0.0232°C}}$$

Note that the charge of the ions in the water is irrelevant to this part of the problem: freezing point depression is a colligative property, oblivious to the identity of the particles in the solution that bring it about!

b. To answer this problem correctly, we need to understand an important detail about how common (ion-exchange) water softeners work. They pull a bait-and-switch maneuver, in which they remove the positively-charged ions normally found in your water with sodium ions having the same total charge. Thus a Cl^- ion isn't touched by a water softener at all, because it is negatively charged. A Ca^{2+} ion is replaced by *two* Na^+ ions, because it takes two +1 ions to match the vitamin nutrition in one +2 ion like calcium. Iron (III) ions, Fe^{3+}, are actually replaced by *three*, count 'em, *three* Na^+ ions in order to maintain charge equilibrium in your water and the overall sanity of the universe. So the composition of the stuff coming out of the water softener in the Kiersaw-Barton home will be such that one kilogram will contain:

$$6.09_{31}\ \text{mmol of Cl}^-\ \text{ions (which are unaffected by the water softener)}$$

$$2.4_{36}\ \text{mmol of Na}^+\ \text{ions (which were present in the original water)}$$

$$1.9_{46}\ \text{mmol of Ca}^{2+}\left(\frac{2\ \text{mol Na}^+}{1\ \text{mol Ca}^{2+}}\right)=3.8_{92}\ \text{mmol of Na}^+\ \text{ions, pushed in by the softener to remove Ca}^{2+}$$

$$1.2_{34}\ \text{mmol of Mg}^{2+}\left(\frac{2\ \text{mol Na}^+}{1\ \text{mol Mg}^{2+}}\right)=2.4_{68}\ \text{mmol of Na}^+\ \text{ions, pushed in by the softener to remove Mg}^{2+}$$

$$0.41_{64}\ \text{mmol of SO}_4^{2-}\ \text{ions (which are unaffected by the water softener)}$$

$$0.32_{23}\ \text{mmol of Fe}^{3+}\left(\frac{3\ \text{mol Na}^+}{1\ \text{mol Fe}^{3+}}\right)=0.96_{69}\ \text{mmol of Na}^+\ \text{ions, pushed in by the softener to remove Fe}^{3+}$$

So the total concentration of particles in the water has gone up appreciably:

$$\begin{array}{rl}
6.09_{31} & \text{mmol of Cl}^-\ \text{ions} \\
2.4_{36} & \text{mmol of Na}^+\ \text{ions} \\
3.8_{92} & \text{mmol of Na}^+\ \text{ions} \\
2.4_{68} & \text{mmol of Na}^+\ \text{ions} \\
0.41_{64} & \text{mmol of SO}_4^{2-}\ \text{ions} \\
+\ \ 0.96_{69} & \text{mmol of Na}^+\ \text{ions} \\
\hline
16.2_{72} & \text{mmol of particles}
\end{array}$$

While the total $\%_{\text{mass}}$ of impurities may have increased slightly as a result of all this, it certainly wasn't enough to make one kilogram of this water contain less than 999 g of water, so we can still treat molalities as synonymous with the moles of an ion present in one kilogram of water, at the three sig fig level. The freezing point depression of the softened water is greater than that of the unsoftened water, but still really piddly:

$$\Delta T_f = K_f\, m_{\text{solute particles}} = 1.86\,\frac{\text{C}^\circ\cdot\text{kg}}{\text{mol}}\left(16.2_{72}\times10^{-3}\,\frac{\text{mol}}{\text{kg}}\right)=0.0302_{67}\,\text{C}^\circ$$

$$\boxed{\text{The softened water will freeze at -0.0303 °C}}$$

Sadly, it seems the Kiersaw-Barton clan will learn an expensive lesson when they return from their visit with Mickey.

4. The answer to the fundamental puzzle posed by this question was actually given in class. **Sea water can remain a liquid well below the freezing point of pure water because of the large amount of stuff dissolved in it, and the phenomenon of freezing point depression.** The more concentrated a solution, the harder it becomes to boil or freeze it, because, in effect, the things dissolved in it are happiest by far with the water in a liquid state. They exert what influence they can to keep it that way. Icebergs, being made of almost pure water (kind of an exclusive club for water molecules, in which dissolved solutes are not very welcome), can remain solid at the very same temperatures at which sea water remains liquid; in fact, their melting resembles far more the melting of ice on a salted sidewalk than that of ice cubes in a glass of fresh water.

   This question actually does ask us to do some quantitative work, however, so let's get to that. We are asked whether the presence of liquid (sea) water at 28ºC is consistent with the solubility of NaCl in water. (That turns out to be at best an approximation to the "right" question to ask…see below!) There are lots of places to find the solubility of NaCl in water, and they'll give it to you in lots of funny units. The web is by far the *easiest* place to go *looking* for this information, **but it need not be the easiest place to actually find a reliable value**. You should try to get at least one second opinion on any answer you get from the web:

- According to http://www.as.ysu.edu/~jjackson/CHEM3719L/Dehydration_of_Cyclohexanol.PDF, accessed on 1/19/03, "The solubility of NaCl in water is about 35 g/100 mℓ."
- www.engr.usask.ca/classes/CHE/421/solutions/che421-a2solution.doc, accessed on 6/22/02, used to claim "Solubility of NaCl in water at 25ºC = 0.3615 g NaCl per 100 g water." (But it's no longer available online.)
- According to http://www.rtol.net/anthony/nacl.htm, accessed on 1/19/03, the solubility of NaCl at 20ºC is 30.1 g per 100 mℓ of water. (I think this is the work of a student…this was from his "secret" chemistry lab web page.)
- Okay, I tried hard to find some variation…to make the point that the web isn't always reliable. But the vast majority of web pages will tell you the solubility of NaCl is 36g /100 g of water, and most will specify that's for room temperature (~25ºC).
- According to the Merck Index, 11th Ed, one gram of NaCl will dissolve in 2.8 mℓ of water at 25ºC (and in 2.6 mℓ of boiling water, suggesting the solubility doesn't vary wildly with temperature).
- The site http://dl.clackamas.cc.or.us/ch105-04/solubili.htm, accessed on 1/12/03, says that a saturated aqueous NaCl solution is 6M; which is about right, but we learned in Assignment 1 how hard it can be to go from molarity to molality!
- Data in http://www.tenet.edu/teks/science/instruction/tutorial/examples_chemistry.pdf, accessed on 1/19/03, not only agrees with the general numbers given above, but suggests the solubility of NaCl at 20ºC doesn't differ appreciably from that at 0ºC.
- http://www.dac.neu.edu/physics/b.maheswaran/phy1121/data/ch10/fig/fig1013.htm, accessed on 1/19/03, corroborates the weak temperature dependence of NaCl's aqueous solubility, and in the caption of the previous figure indicates that "The solubility of NaCl is 36 g per 100 g of water at 20° C."
- According to http://www.chem.arizona.edu/~salzmanr/103a004/nts004/l41/l41.html, accessed on 1/19/03, "The solubility of NaCl in water at 0ºC is about 35.7 g/100mℓ." They even go on to answer the question posed here, in detail.

You certainly don't need to look at this many sources, but do I suggest comparing data from at least two or three independently selected pages when you pull information off the web, where any Bozo can post anything they want to and have a decent hope of tricking you into considering them authoritative and/or unbiased. We are just doing a reality check here, so a solubility value of 36 g NaCl in 100 g of water is just dandy for our purposes. Let's figure out what that would be in terms of molality:

$$\text{Saturated NaCl} = \frac{36\ \text{g NaCl}}{\underline{100}\ \text{g H}_2\text{O}}\left(\frac{1\ \text{mole NaCl}}{22.99+35.45\ \text{g}}\right)\left(\frac{\text{molal}}{\left(\frac{\text{mole of solute}}{\text{kg of solvent}}\right)}\right)\left(\frac{\underline{1000}\ \text{g}}{\underline{1}\ \text{kg}}\right) = 6.1_6\ \text{molal NaCl}$$

That's nifty, but we now want to determine what the freezing point of a saturated solution of aqueous NaCl would be, and in order to do so it is critical to realize that **one mole of NaCl dissolves to form one mole of Na^+ ions *and* one mole of Cl^- ions.** Thus a 6.1_6 molal solution of NaCl in water actually contains $12._{32}$ moles of particles per kilogram of water. *(This neglects the effect of ion pairing, which could become quite pronounced in that concentrated a solution; however, we can safely assume the molarity of particles in a saturated aqueous NaCl solution is actually somewhere between 6 and 12 molal. That'll turn out to be enough!)* The freezing point depression constant, K_f, depends only on the identity of the solvent, in this case water. According to Table 11.5 in Zumdahl, the freezing point depression constant for aqueous solutions is 1.86 Cº·kg/mol. Thus our sea water will freeze at

$$\Delta T_f = -K_f m_{solute} = -\left(1.86\frac{\text{C}^\circ\cdot\text{kg of solvent}}{\text{mol of solute particles}}\right)\left(12._{32}\frac{\text{mol of solute particles}}{\text{kg of water}}\right) = -22._9\ \text{C}^\circ$$

Golly, even with major ion pairing, this will be somewhere between $-11._5$ Cº and $-22._9$ Cº, and the problem said the water temperature was only

$$28°\text{F} = \frac{5}{9}(28-32)\,°\text{C} = -2._{22}°\text{C}$$

(Note that this has only one sig fig!!!)

so there's little doubt of this scenario being plausible, at least in light of the solubility of NaCl in water.

Note: Sea water isn't actually even close to being saturated with sodium chloride, and it contains many ions in addition to Na^+ and Cl^-. According to http://www.dartmouth.edu/~chemlab/chem3-5/ionx2/full_text/appendix.html, accessed on 1/12/03, the actual concentration of dissolved ions in sea water is

$$\left(0.479\ \text{M Na}^+ + \frac{0.109\ \text{M Mg}^{2+}}{2} + \frac{0.021\ \text{M Ca}^{2+}}{2} + 0.010\ \text{M K}^+\right) + \left(0.560\ \text{M Cl}^- + \frac{0.057\ \text{M SO}_4^{2-}}{2} + 0.002\ \text{M HCO}_3^-\right)$$

for a total of 1.155 Molar ions. At that reasonably dilute concentration, molarity and molality are almost numerically equal in water (the density of sea water is about 1.03 g/mℓ), and so sea water contains about 1.1_{55} molal ions. That suggests a freezing point depression of -2.1_5 Cº, in remarkably good agreement with the water temperature stipulated in the problem.
Salinity actually varies slightly with location in the ocean, as per the entry "ocean" in the Encyclopædia Britannica, <http://search.eb.com/eb/article?eu=115012>, accessed on 1/12/03; but the north Atlantic is of about average salinity, and we aren't out to split hairs here, anyway. It's important to realize how precise and accurate one needs to be to answer a given question, lest you make the problem more difficult than it need be, possibly even impossible to answer!