Problem 1: One if by land, two if by sea

Ion	Concentration (M)
Cl^-	0.560
Na^+	0.479
Mg^{2+}	0.109
SO_4^{2-}	0.057
Ca^{2+}	0.021
K^+	0.010
HCO_3^-	0.002

A. On page 546, just above §11.7, Zumdahl describes a portable water desalination system developed for the U.S. Navy. Based on the process of reverse osmosis, these systems are now available to the general public, and have replaced stored water on most life rafts. What they do is actually pretty incredible, given that they must overcome the osmotic pressure difference between sea water and fresh water. The principal ions in sea water are indicated in the table at right. Given this data, calculate the gauge pressure a desalinator charged with sea water must develop in order to start forcing fresh water through its osmotic membrane. Assume the temperature at sea is 73ºF. Please neglect the effects of ion pairing in working this problem, but state whether your answer is therefore actually an over- or an under-estimate.

B. "Road salt" is a general term used to describe a variety of compounds put down on icy roads in wintertime in order to encourage ice to melt. Sodium chloride, NaCl, is the most commonly used compound, but it is entirely possible for temperatures to drop so low that it doesn't work. In such situations, (or in order to try to reduce the environmental damage done by the sodium in road salt,) calcium chloride, $CaCl_2$, is often used instead. Calculate the minimum temperature (in ºC) at which NaCl and $CaCl_2$ can each act to help melt ice, assuming that the solubilities given below apply at all temperatures. Please neglect the effects of ion pairing.

Solubility of NaCl: 35 g of NaCl per 100 g of water   Solubility of $CaCl_2$: 60 g of $CaCl_2$ per 100 g of water

C. Leavening agents (for example, yeast and baking powder) cause a gas to be released into a cake or dough, making it rise and become light and fluffy. If they don't create a large enough volume of gas, you get a rock instead of bread or cake; if they generate a large volume of gas too quickly, you get a giant puffed-up ball of air or a collapsed cake. Lisa Kanner, a Chem 123 student, conducted an interesting investigation into the special techniques required for baking at high altitudes. One of the key tricks she described was reducing the amount of leavening agent used when baking at high altitude, and/or reducing the temperature so that the leavening agents would operate more slowly and less effectively. Why would such changes be needed at high altitudes?

D. Zingitz lives on the planet Zorton, where the seas are full of light crude oil and the skies rain hexane. It's a highly non-polar world, where all the solvents resemble oils and fats. Zingitz is advanced in many ways, but not in the ways of laundry care. Today he has spilled some NaCl on his favorite shirt, and try as he might, he can't wash it off with hexane from his tap. He doesn't have any water, but he does have some detergent he picked up on his last visit to earth. Would a surfactant like this work on a planet where hexane is the readily available solvent, and where polar, hydrophillic materials pose the toughest "dirt" problems? Explain.

E. In trying to determine the molar mass of soap, I carried out the steps described below. Clearly I made at least one mistake, because there's no way soap has the molecular weight I've calculated. Find at least one of my major mistakes, circle it, and explain what I did wrong and why it matters to what I tried to accomplish.

I made a solution of 30.0 g of soap in 1.00 ℓ of Northfield tap water. I put the soapy water into one side of the device shown at right, fitted with a semipermeable membrane I know to be impermeable to both soap ions and sodium ions. I filled the other side of the device with clean tap water until there was no net flow of H_2O across the membrane (the system was at equilibrium). The difference in the height of the two liquid columns was 14.1 cm, as indicated in the picture at right. Then I tried to calculate the molar mass of soap, as shown at right:

$P_{\text{at point "A"}} = \rho g h + P_0 = 0.92\ g/cm^3 \cdot 9.8\ m/s^2 \cdot 14.1\ cm \cdot \frac{100\ cm}{1\ m} + 1.032\ atm$

T = 297 K today

P_{atm} = 1.032 atm today

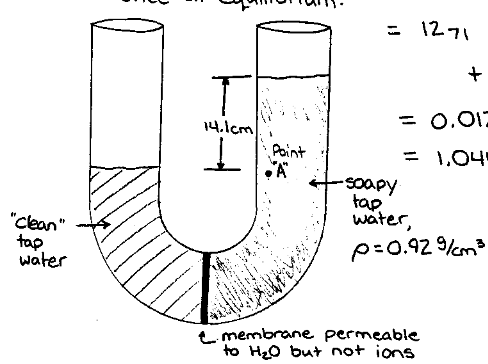
$= 12_{713}\ \frac{g \cdot cm^2}{cm^3 \cdot s^2} \cdot \frac{100\ cm}{m} \cdot \frac{1\ kg}{1000\ g} + 1.032\ atm$

$= 12_{71}\ \frac{kg}{m \cdot s^2} \cdot \frac{1\ Pa}{1\ \frac{kg}{m \cdot s^2}} \cdot \frac{1\ atm}{101325\ Pa} + 1.032\ atm$

$= 0.012_{55}\ atm + 1.032\ atm$

$= 1.044_{55}\ atm$

Device at equilibrium:



This is the pressure at point "A", but the pressure difference across the membrane, π, is just 0.012_{55} atm

Since $\pi = MRT$, $M = \frac{\pi}{RT} = \frac{0.012_{55}\ atm}{0.08206\ \frac{\ell \cdot atm}{mol \cdot K}\ 297 K} = 5.1_5 \times 10^{-4}\ \frac{mol}{\ell}$

So 30.0 g of soap is equal to $5.1_5 \times 10^{-4}$ mol,

and $MW_{soap} = \frac{30.0\ g}{5.1_5 \times 10^{-4}\ mol} = 58_{259}\ g/mol$

∴ The molar mass of the soap is 58000 g/mol

Problem 2: Icestyles of the Wet and Famous

A. A 335 gram chunk of dry ice (solid CO_2) is dropped into an incredibly strong stainless-steel pressure vessel with an internal volume of 2.00 ℓ, which is immediately sealed so that nothing can escape. This chamber sits on your kitchen table until it no longer feels cold. The temperature inside the container, and of its contents, is now 25ºC. It still contains all 335 g of the CO_2. What phase(s) are present inside the pressure vessel, and why? Give quantitative support for your answers. The phase diagram for CO_2 appears on page 500 in Zumdahl. The density of solid CO_2 ranges from 1.3 to 1.6 g/mℓ, while that of liquid CO_2 ranges from 0.9 to 1.1 g/mℓ.

B. Although generally much weaker than chemical bonds, intermolecular forces are nonetheless very important. Mammalian bodies rely on the enthalpy of vaporization (the energy required to pull apart water molecules that are touching each other in the liquid phase) to help cool themselves off. On a hot, dry day in the desert a human can readily sweat away 1.00 ℓ of water per hour. How much heat does this carry away from their skin?

$H_2O_{(\ell)} \rightarrow H_2O_{(g)}$ $\Delta\tilde{H}^\circ_{rxn} = \Delta\tilde{H}^\circ_{vap} = +44$ kJ/mol Assume the density of liquid water is 1.0 g/mℓ.

C. I like ice cream. But I don't eat it very often, and so what I buy sits in the door of my fridge for long periods of time. Pretty much every time I *do* decide to indulge in ice cream, I open the container to find ice crystals lining one of its walls, the one that rests against the door of the fridge. How do those ice crystals get there?

D. Robin, the Boy Wonder, has set out on a frenzied quest to make some crystal-clear ice cubes for his next big bash in the BatCave (which he plans to throw when Batman goes away at the end of the month.) His first attempt at crystal-clear cubes came out really cloudy, and he coyly asked Batman what was wrong. The caped crusader explained that tap water contains dissolved minerals, and that these minerals get forced out of solution as (mostly white) solids when the water molecules arrange themselves into the regular pattern of an ice crystal. He told Robin to set out a tray of water and let it evaporate, he'd see. Robin did so, and sure enough, he found a white powdery residue left behind once all the water had evaporated. So he went to the grocery store and bought a gallon of distilled water. He put this in a tray and let it evaporate to dryness as well. This time there was nothing left behind. Encouraged, Robin tried to cook up another batch of perfect ice cubes, but found that they came out cloudy again, this time looking distinctly like there were little gas bubbles trapped in them. Not wanting to arouse Batman's suspicions about his sudden interest in ice cubes, Robin asks you about it. You relate to him that you have heard that in order to get crystal-clear cubes, you need to boil distilled water just before freezing it. Robin tries it, and sure enough, gets perfectly clear ice cubes. Why?

Problem 3: Mommy! Mommy! The Entropy Monster is coming to get me!

A. Cleaning out your dorm room one day, you happen upon a remarkable artifact of an advanced civilization: it is a real, live, honest-to-goodness "magic" syringe in a time stasis field, containing 0.0100 moles of $N_{(g)}$, that is, individual nitrogen atoms. You know that if you deactivate the stasis field, many of the N atoms will combine to form N_2, molecular nitrogen, and that the syringe volume will change. The chemical reaction in question is

$$2\,N_{(g)} \rightarrow N_{2(g)}$$

a. Calculate an approximate value for this reaction's $\Delta\tilde{H}^{\circ}_{rxn}$ (You may not find the data you need to do this the first way you think of, so be creative and try another approach if you hit a roadblock on your first try.)

b. Given your answer to (a), will the magic syringe dump heat into or take heat out of its surroundings if it is exposed to the earth's atmosphere when the stasis field is turned off? Justify your answer.

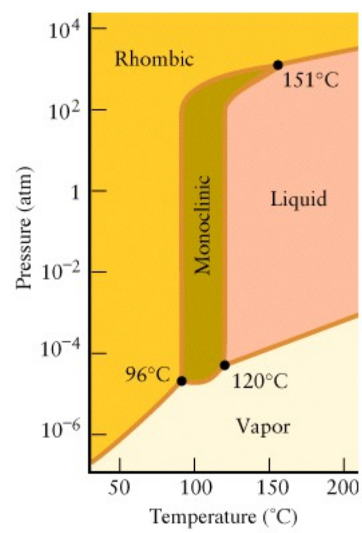
c. Will the contents of the magic syringe do work on their surroundings, or have work done on them, if the syringe is exposed to the air in your room when the stasis field is turned off? Justify your answer. Assume the syringe and its contents start out at the same temperature and pressure as the air in your room, and that the temperature and pressure of the air in your room are not much affected by the syringe.

d. Suppose you balanced your chemistry book on top of the magic syringe before turning off the stasis field, such that it was launched neatly out your window when the reaction started. Would the warming or cooling of your room be more or less pronounced relative to the situation in (c)? Why?

e. Is ΔS° for this reaction going to be positive or negative? Explain why. (Stuck? Consider analogous reactions for which you *can* calculate ΔS° using the data in Appendix 4 of Zumdahl.)

C. Several companies sell emergency cold packs, which contain a combination of chemicals that get quite cold when they react. These chemicals are kept separate from each other until the cold pack is activated by twisting or bending it. They then provide cooling for several hours, until the chemicals inside have reacted with each other as much as they are going to, and the chemical reaction stops. What combination of ΔH^o and ΔS^o (positive and negative, negative and positive, etc.) will make a reaction a good candidate for use in emergency cold packs, and why?

D. Zumdahl provides a phase diagram for sulfur on page 509, but it is really pretty ugly. So take a look at the one at right, which is from Jones and Atkins, Chemistry: Molecules, Matter and Change, 4th ed., W. H. Freeman: New York (2000). Use this phase diagram to help you answer the following questions:



Rhombic and monoclinic are distinct, solid allotropes of solid sulfur. Both can be obtained, but only one will be stable at a given temperature and pressure.

a. Which is the denser solid allotrope, rhombic or monoclinic, and why?

b. Consider the phase transition described by the following chemical reaction:

$$S_{(s,\ rhombic)} \rightarrow S_{(s,\ monoclinic)}$$

Is the entropy change (ΔS) for this reaction positive or negative? Justify your answer. You may *check* your answer using the data in Appendix 4, but your justification must be based on the phase diagram.

c. Polymeric sulfur is soft and rubbery, and does not appear on this phase diagram, even though it can exist for a while at room temperature. What will eventually happen to a sample of polymeric sulfur if it is stored at 25ºC and 1 atm for an extended period of time, and why?

Problem 4: Hot Time in the Lab Tonight

A. My second cousin Billy-Bob Rossi came up to visit me for our yearly chemistry barbecue! We went into the lab and set up a simple constant-pressure calorimeter, just like the one you used in lab. We used 250. mℓ of distilled water and a thin-walled 300 mℓ flask, and calibrated our calorimeter using an ethanol lamp. B.B. and I got an average heat capacity of 3.5 ± 0.9 kJ/Kº over five calibrations. Then we took a crack at determining the identity of an "unknown" fuel that Julie chose for us. We tried plying the identity of the mystery fuel out of her with a few beers, but she wasn't talking. All she would tell us was that the mystery fuel had a formula weight of 74.12 g/mol, and that it would undergo nearly complete combustion in an alcohol lamp. So we went to work.

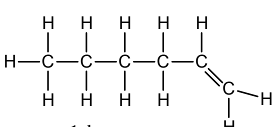
a. Following the same procedure you did, but using our unknown, we got an initial lamp mass of 126.42 g and a final mass of 124.29 g. Our calorimeter started out at 24.5 ºC and topped out at 45.5 ºC. Calculate $\Delta\tilde{H}^{\circ}_{combustion}$ for our unknown fuel. [Uncertainties are as implied by significant figures, unless specified.]

b. Do a worst case error analysis on your result from part (a) and, based on that, identify which fuels from the list of possibilities below can be eliminated from consideration because they do not fall within the range of "possible" $\Delta\tilde{H}^{\circ}_{c}$ values consistent with our calorimetry result. Assume our calorimeter is as reliable as our C_p value suggests it is, so that the worst case error gives a good upper bound on the uncertainty in $\Delta\tilde{H}^{\circ}_{c}$.

Fuel Name	$\Delta\tilde{H}^{\circ}_{combustion}$ (kJ/mol)
Methyl Acetate	–1596
Propane	–2220
Ethyl Acetate	–2247
n-butanol	–2677
Benzoic Acid	–3228
Isopentane	–3528
n-pentane	–3537
n-hexane	–4165

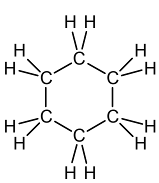
B. Wally Phish, science know-it-all, is in your face in a big way today. Having just learned about enthalpy, he's all excited about how he can calculate exactly how much heat is released in any chemical reaction. Specifically, based on the heat of combustion of Steno fuel, he has calculated the exact amount of heating power that a full can of Steno should offer up. Suppose the specific enthalpy change for the complete combustion of Steno fuel is (just as he says it is) -31.4 kJ/g. Wally says if a can of Steno labeled as containing 100. grams (net) of fuel is lit under a pot containing 10.0 liters of water at 20.0ºC, the temperature of the water will be exactly 95ºC when the can stops burning. Wally sets a pot containing 10.0 ℓ of 20.0ºC water on a ring stand, opens a (stinky) can of Steno, and wafts it before your nose while he jabbers on at length about what a smart dude he is. He finally gets around to lighting the can and sticking it under the pot of water. Under duress, you stick around to see how smart he is. The pot's temperature is only 72.1ºC when the can burns out. Convinced he was the victim of bad luck, Wally repeats the experiment, only to have the pot end up at only 70.5ºC on the next attempt. Wally tries it one more time, and manages 73.6ºC, but not a degree more. Wally is peeved and goes storming off to tell the company they are not filling their cans with the stated amount of fuel. You know better. Give four plausible reasons why the pot of water didn't get as hot as Wally's thermodynamic calculations said it "should" have.

C. Shown below are the (balanced) complete combustion reactions of two different isomers of $C_6H_{12(g)}$:



1-hexene$_{(g)}$

$+\ 9\ O_{2(g)} \rightarrow 6\ CO_{2(g)} + 6\ H_2O_{(\ell)}$ $\quad \Delta\tilde{H}^\circ_{rxn} = \Delta\tilde{H}^\circ_c$[1-hexene] = -4010 ± 20 kJ/mol



cyclohexane$_{(g)}$

$+\ 9\ O_{2(g)} \rightarrow 6\ CO_{2(g)} + 6\ H_2O_{(\ell)}$ $\quad \Delta\tilde{H}^\circ_{rxn} = \Delta\tilde{H}^\circ_c$[cyclohexane] = -3930 ± 20 kJ/mol

Based on the bond energies given in Table 8.4 on page 373 of Zumdahl, explain why $\Delta\tilde{H}^\circ_c$[1-hexene] is more negative than $\Delta\tilde{H}^\circ_c$[cyclohexane], and thus why a mole of 1-hexene provides more heat when burnt completely than does one mole of cyclohexane. Your answer to this question need not be quantitative, but it's OK if it is.