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

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.

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

The gauge pressure required to pull this off will be the osmotic pressure difference between the sea water inside the desalinator and the fresh water that comes out of it. The fresh water will have an osmotic pressure of (effectively) zero, and emerge at ambient pressure. (It will drip off the osmotic membrane into a collection vessel, so the pressure difference between the atmosphere and the desalinator piston will be the gauge pressure we are looking for, and it will be equal to $\pi_{\text{sea water}}$). So we just need to calculate the osmotic pressure of sea water, which is given by the formula $\pi = MRT$ = (molarity of particles)(ideal gas constant)(absolute temperature). To determine the molarity of particles in sea water, we just add up the concentrations in the table above. All the given values are good to the nearest millimole, so the sum is as well: M = 0.560 + 0.479 + 0.109 + 0.057 + 0.021 + 0.010 + 0.002 M = 1.238 Molar (moles of solute ions per liter of sea water). We don't need to worry about the identity or charge of the ions, just how many there are. This particular colligative property depends on molarity rather than molality, so we don't need to correct for the density of sea water. We just need to convert the given temperature absolute units (we are using the ideal gas law constant, all the gas law rules apply!), Kelvins to match R:

$$T = 73\,°F = \frac{5}{9}(73-32)\,°C = \frac{5}{9}(41)\,°C = 22._{78}\ °C = \left(22._{78}+273.15\right)K = 295._{93}\ K$$

$$\pi = MRT = \left(1.238\ \frac{\text{moles}}{\ell}\right)\left(0.08206\ \frac{\ell\cdot\text{atm}}{\text{mol}\cdot\text{K}}\right)\left(295._{93}\ \text{K}\right) = 30.0_6\ \text{atm}$$

The desalinator must develop an internal pressure at least 30.0$_6$ atmospheres higher than that outside it in order to start forcing fresh water out through its osmotic membrane. That's a lot! It's 442 psi, a heackuva lot more than even the skinniest bike tire can take!

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

These salts depress the freezing point of the water they dissolve in. (Yep, the water has to "melt" in the first place, in order for the salt to dissolve in it, but how and why that happens is a whole other ball of wax that will make more sense after we learn about equilibria. In an nutshell, there are always a few "liquid" molecules on the surface of an ice cube, even way below the freezing point. The salt acts to make the few hyperactive water molecules that appear every few seconds on the ice surface stay in the liquid state even after they cool off and start moving more slowly.) We just need to figure out by how much these salts depress the freezing point of water. That's going to call for this nifty little formula: $\Delta T_f = -K_f\, m_{\text{solute particles}}$
in which it is very important we remember that freezing point depression is a colligative property and thus depends on the *total concentration of solute particles*. K_f for water can be found in Table 11.5 on p. 537 of Zumdahl, and has a value of 1.86 Cº·kg·mol^{-1}. Then it is just a matter of determining $m_{\text{solute particles}}$ for saturated aqueous solutions of each of our salts:

$$\tilde{m}_{NaCl} = 22.99\frac{g}{mol} + 35.45\frac{g}{mol} = 58.44\frac{g}{mol} \qquad \tilde{m}_{CaCl_2} = 40.08\frac{g}{mol} + 2\left(35.45\frac{g}{mol}\right) = 40.08\frac{g}{mol} + 70.90\frac{g}{mol} = 110.98\frac{g}{mol}$$

Note that the latter molar mass has *five* significant figures, because we can trust the two things we added together in order to get it to the nearest 0.01 g/mol, and thus we can trust the sum to the nearest 0.01 g/mol. Now we can translate the solubilities above from the given units into the molality units we want for our ΔT_f expression. Note that the 60 in $CaCl_2$'s solubility has only one significant figure, because there is no decimal point after the zero. That was a conscious choice on my part! The solubility of $CaCl_2$ has a much wackier and stronger temperature dependence than does the solubility of NaCl, so I couldn't be as precise about what its value would be in the range of sub-zero temperatures we are working with here. I only had solubility data for 0 to 100ºC to base my estimate on!

$$\text{Solubility of NaCl} = \frac{35\text{ g of NaCl}}{\underline{100}\text{ g of water}}\left(\frac{\underline{1}\text{ mol NaCl}}{58.44\text{ g of NaCl}}\right)\left(\frac{\underline{1000}\text{ g of water}}{\underline{1}\text{ kg of water}}\right) = 5.9_{89}\ \frac{\text{mol NaCl}}{\text{kg of water}}$$

$$\text{Solubility of CaCl}_2 = \frac{60\text{ g of NaCl}}{\underline{100}\text{ g of water}}\left(\frac{\underline{1}\text{ mol NaCl}}{110.98\text{ g of NaCl}}\right)\left(\frac{\underline{1000}\text{ g of water}}{\underline{1}\text{ kg of water}}\right) = 5._{406}\,\frac{\text{mol CaCl}_2}{\text{kg of water}}$$

It's altogether too tempting to stop there, but it is critical that we remember that these are ionic salts, and thus they break up into ions when the dissolve in water. Each mole of NaCl yields two moles of ions, while each mole of $CaCl_2$ yields three moles of ions:

$$\text{NaCl}_{(s)} \xrightarrow{\text{water}} \text{Na}^+_{(aq)} + \text{Cl}^-_{(aq)} \text{ (two particles)} \qquad \text{CaCl}_{2(s)} \xrightarrow{\text{water}} \text{Ca}^{2+}_{(aq)} + 2\,\text{Cl}^-_{(aq)} \text{ (three particles)}$$

In reality, some ion pairing will definitely take place. Ion pairing is actually most pronounced at low temperatures and high concentrations (and I hope that makes sense to you in light of our molecular viewpoint on solutions!), so ion pairing is likely to be substantial in the situations we are considering here. But the problem asks us to neglect the effects of ion pairing, so we will!

$$m_{\text{solute particles}} \text{ in saturated NaCl}_{(aq)} = 5.9_{89}\,\frac{\text{mol NaCl}}{\text{kg of water}} \times \left(\frac{2\text{ moles of ions in solution}}{1\text{ mole of NaCl}}\right) = 11._{98}\,\frac{\text{moles of solute particles}}{\text{kg of solvent (water)}}$$

$$m_{\text{solute particles}} \text{ in saturated CaCl}_{2(aq)} = 5._{406}\,\frac{\text{mol CaCl}_2}{\text{kg of water}} \times \left(\frac{3\text{ moles of ions in solution}}{1\text{ mole of CaCl}_2}\right) = 1_{6\cdot 22}\,\frac{\text{moles of solute particles}}{\text{kg of solvent (water)}}$$

Note that it's the ionicity difference that causes $CaCl_2$ to function at lower temperatures than does NaCl! NaCl is actually more soluble than is $CaCl_2$, on a molal basis. (They're close, but $CaCl_2$ produces 1.5 times as many ions, so it's effective at lower temperatures.)

$$\Delta T_{f,\text{ saturated NaCl}} = -K_f\, m_{\text{solute particles}} = -\left(1.86\,\frac{C^\circ\cdot\text{kg}}{\text{mol}}\right)\left(11._{98}\,\frac{\text{mol}}{\text{kg}}\right) = -22._{28}\,C^\circ$$

and, since the freezing point of pure water is 0ºC, $T_{f,\text{ saturated NaCl}} = T_{f,\text{ pure water}} + \Delta T_{f,\text{ saturated NaCl}} = 0^\circ C + -22._{28}\,C^\circ = -22._{28}\,^\circ C$

$$\Delta T_{f,\text{ saturated CaCl}_2} = -K_f\, m_{\text{solute particles}} = -\left(1.86\,\frac{C^\circ\cdot\text{kg}}{\text{mol}}\right)\left(1_{6\cdot 22}\,\frac{\text{mol}}{\text{kg}}\right) = -3_{0\cdot 17}\,C^\circ$$

and, since the freezing point of pure water is 0ºC, $T_{f,\text{ saturated CaCl}_2} = T_{f,\text{ pure water}} + \Delta T_{f,\text{ saturated CaCl}_2} = 0^\circ C + -3_{0.17}\,C^\circ = -3_{0.17}\,^\circ C$

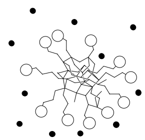
These temperatures are equivalent to -8.1ºF and -2_2ºF, respectively, so they certainly fall within the realm of possibility in our fair state of Minnesota! Note also that both these values are probably over-estimates, because we have ignored the effects of ion pairing. NaCl will actually produce less than two particles per NaCl unit (some ions will form ion pairs), and so NaCl will actually depress the freezing point of water less than 22ºC. According to the Michigan Department of Transportation, in fact, NaCl is only effective down to 12ºF/-9ºC. (Others give slightly different numbers for NaCl; effective values for $CaCl_2$ seem wildly variable and I don't trust 'em.)

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?

Let's assume we **don't** do anything different when cooking at high altitudes…we keep our house and kitchen at about the same temperature as others do, and yeast, for example, grows and multiplies without much regard for altitude. So the population of yeast goes up, and they gobble up glucose and release ethanol (that's the smell of rising bread!) and CO_2 at the same molar rate as yeast in bread anywhere else. But at high altitude, the atmospheric pressure is appreciably lower, so the same number of moles of gas will expand to occupy an appreciably larger volume up in the mountains! Our bread would turn into a mushroom bloom! To make the *volume* of gas produced by our yeast about the same as it would be in the lowlands, we need to have fewer moles of CO_2 produced per unit time. Then we will end up with a normal-sized and -textured bread or cake, and be much happier. In more quantitative terms, we can assume $PV = nRT$ for CO_2, and if we want to keep V constant and lower P, we have to lower T and/or n. With most leavening agents, lowering T also effects a reduction in n, but with yeast you can freeze the yeast to death, so using less yeast is often preferred.

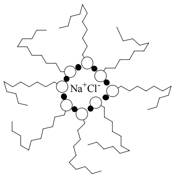
D. Zingitz lives on the planet Zorton, where the seas are full of light crude oil and the skies rain hexane. It's a highly non-polar world, where all the solvents resemble oils and fats. Zingitz is advanced in many ways, but not in the ways of laundry care. Today he has spilled some NaCl on his favorite 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.

Sure! Surfactant molecules will form micelles in non-polar environments too, they'll just be turned inside out! Their polar heads will cluster around the polar dirt (the NaCl), and they'll stick their greasy tails into the hexane. This will solubilize the polar NaCl in the hexane, allowing it to be washed away. Earth detergents will probably not be perfect for this task, because they are optimized for use in water, but earth detergent will certainly be more effective than no detergent! Note that some surfactants, like natural soap, are salts, and that these salts would probably not dissociate in hexane. The soap would still dissolve to some extent, but the Na^+ ions attached



A soap micelle in a polar environment

to the negatively charged ionic heads of the soap ions would stay right there, and the two would travel around together. In order for the micelles to be neutral, the soap molecules would have their Na^+ counterions with them in the polar center. The ionic bits would try to arrange themselves so as to minimize +/+ and -/- interactions. (See the micelle drawn at right…the black dots are the Na^+ counterions, while the white dots are the negatively-charged polar heads of the soap ions. Charge neutrality has to be maintained in polar solvents, too, but there the counterions are often only somewhat close to the charges they neutralize.)



A soap micelle in a non-polar environment

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:

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

T = 297 K today

P_{atm} = 1.032 atm today

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

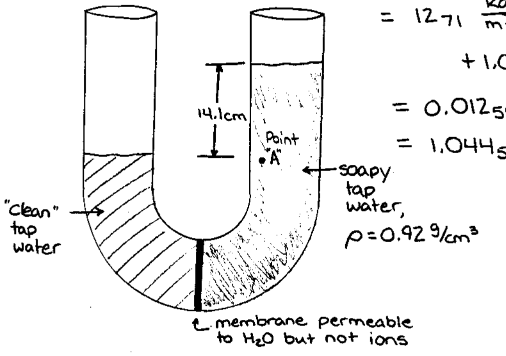
$$= 12_{71}\,\frac{\text{kg}}{\text{m}\cdot\text{s}^2}\cdot\frac{1\,\text{Pa}}{1\,\frac{\text{kg}}{\text{m}\cdot\text{s}^2}}\cdot\frac{1\,\text{atm}}{101325\,\text{Pa}} + 1.032\,\text{atm}$$

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

$$= 1.044_{55}\,\text{atm}$$

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

Device at equilibrium:



$$\text{Since } \pi = MRT,\quad M = \frac{\pi}{RT} = \frac{0.012_{55}\,\text{atm}}{0.08206\,\frac{\ell\cdot\text{atm}}{\text{mol}\cdot\text{K}}\,297\,\text{K}} = 5.1_5\times10^{-4}\,\frac{\text{mol}}{\ell}$$

so 30.0g of soap is equal to $5.1_5\times10^{-4}$ mol,

$$\text{and}\quad MW_{soap} = \frac{30.0\,\text{g}}{5.1_5\times10^{-4}\,\text{mol}} = 58_{259}\,\text{g/mol}$$

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

Golly, there are several things I did wrong here! But none of them are math errors, probably the first thing you looked for. Nope, the errors are all conceptual, and that makes them all the more serious! First, I assumed that one mole of soap leads to one mole of particles floating around in solution: I didn't devote any brain power to what particles are actually produced when soap is put in water! That's a big mistake! Soap is an ionic salt, that starts out as a neutral solid but dissociates in aqueous solution:

$$\text{Soap}_{(s)} \xrightarrow{\text{water}} \text{Soap}^-_{(aq)} + \text{Na}^+_{(aq)}$$

Were that the whole story, in the absence of ion pairing, *i* would be 2, and my molecular weight would be an under-estimate by a factor of two because the osmosis-determined molarity value would be twice the actual molarity of soap. (Recall that osmotic pressure is a colligative property, and that it depends on the concentration of non-solvent particles in solution!) But there's something else to think about, and that's the tendency of $Soap^-$ ions to form micelles! Talk about ion pairing! The formation of micelles makes the actual value of *i* open to great debate. How many $Soap^-$ ions in a micelle? Do the Na^+ ions pair with the micelles? If so, to what extent? The actual value of *i* could be anything between 2 and nearly zero! (It would be 1 if the $Soap^-$ ions formed one giant micelle and the Na^+ ions didn't pair with it at all: then my molar mass value estimate would be right on.) Well, that's all horrible and icky, but it's not all I did wrong. I also had the dim wit to use tap water! Sheesh! This is very problematic, but not for the reason some of you thought. Yeah, tap water contains ions, but in the absence of any reactivity that wouldn't matter: tap water was used on both sides of the osmotic membrane, so the concentration of ions on each side due to the tap water would be the same, and they would have no net osmotic pressure effect. (In other words, put just tap water on each side of the thingie above and the osmotic pressure will indicate zero.) Unfortunately, there *is* a pretty significant reactivity effect, in that Northfield tap water is very hard, and that hard water reacts with soap to form insoluble soap scum! That would remove $Soap^-$ ions from the solution, as well as Ca^{2+}, Mg^{2+}, and Fe^{3+} ions that were in the tap water. That would lead the ion concentration on the soapy side to be much lower than we would have expected, so that we actually would have added far more moles of soap than the osmotic pressure suggests, and thus our molar mass estimate is way too high. That does, indeed, seem to be consistent with our result! (The concentration on the soapy side might even be made lower than that on the "pure" tap water side, if just the right amount of soap were added to react with all the hardness; but we know that more than that much soap was added, because the osmotic pressure is higher on the soapy side, indicating that the concentration of solute particles on that side is higher than that on the other side.) There are two other minor mistakes, both more finicky. First, I assumed the density of the "pure" tap water was the same as that of the soapy water. In fact it is slightly above 1.0 g/mℓ, meaning that I slightly over-estimated π and under-estimated the molar mass. Second, I assumed (implicitly) that by mixing 30.0 g of soap with

1.00 ℓ of tap water, I ended up with 1.00 ℓ of solution (hence my claim that there are $5.1_5 \times 10^{-4}$ moles of soap in the solution I made up). The fact that the density of the soapy water is lower than that of tap water tells me that this is not the case: the soap must be occupying some volume in order for it to lower the density of the solution, and thus the volume of solution I ended up with must have been (slightly) more than 1.00 ℓ. Thus I actually had a few more millimoles of soap than I thought, and my molar mass is an over-estimate. You got credit on this problem for anything along the lines of what I describe in my long answer above, with full credit given to those who checked to be sure that their proposed explanation was consistent with my molar mass value being a substantial over-estimate, and a bit of extra slack if you thought about the magnitude of the error likely to result from a given explanation.

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.

As several of you observed (or asked about during the exam), the sealed container contains about

$$2.00\,\ell\left(\frac{1000\text{ m}\ell}{1\,\ell}\right)-335\text{ g solid CO}_2\left(\frac{1\text{ m}\ell\text{ solid CO}_2}{1._5\text{ g solid CO}_2}\right)=200_0\text{ m}\ell-2_{23.3}\text{ m}\ell=17_{77}\text{ m}\ell$$

of air at atmospheric temperature and pressure when it is sealed up. It turns out this doesn't make much difference to the answer to this problem, but it's worth realizing, all the same. Let's think about the scenario a bit more generally. We are told the contents of this pressure vessel will eventually end up at 25ºC, but we don't know at what pressure. The phase diagram indicates to us that at 25ºC, CO_2 exists as a liquid at pressures above about 70 atmospheres, and as a gas at pressures below that. As we don't know what the pressure in the container will be, we'll have to assume something! Suppose we assume the CO_2 will all be in the gas phase. Then there will be 335 g of gaseous CO_2, a reasonably ideal gas who's pressure can be predicted with the ideal gas law. We know the temperature will be 25ºC, but we need it in absolute units. We know there will be 335 g CO_2 gas, but we need it in moles. We know the gas will occupy 2.00ℓ, and so we can deduce the (partial) pressure (due to CO_2; the actual pressure will be a bit higher, because there are also about 72 mmol of air in the chamber that I'm ignoring down below, but could easily add in to get the total moles and total pressure):

$$T_{\text{absolute}}=25^\circ\text{C}+273.15=298._{15}\text{K}\qquad 335\text{ g CO}_2\times\left(\frac{1\text{ mol CO}_2}{12.01\text{ g C}+2\times16.00\text{ g O}}\right)=335\left(\frac{1}{44.01}\right)\text{ mol CO}_2=7.61_2\text{ mol CO}_2$$

$$P_{CO_2}=\frac{n_{CO_2}RT}{V}=\frac{(7.61_2\text{ mol})\left(0.08206\frac{\ell\cdot\text{atm}}{\text{mol}\cdot\text{K}}\right)(298._{15}\text{ K})}{2.00\,\ell}=93.1_2\text{ atm}$$

Well, shoot, if the pressure is that high at 25ºC, the CO_2 will liquefy. But wait! If *all* the CO_2 liquefies, it will occupy only slightly more volume than did the solid CO_2, and the pressure in the chamber will be about 1 atm, not high enough to have any liquid CO_2! So, we end up with both liquid and gaseous CO_2, with enough of the CO_2 in the gas phase that the pressure is about 70 atm (the exact value would come from the liquid-gas equilibrium line on a better phase diagram) and the rest present as a liquid. (If you want to get fancy and calculate it, you can: about 5.7 moles of CO_2 will be in the gas phase, leaving about 1.9 moles, or 83 grams, of $CO_{2(\ell)}$.)

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?

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

This is really a pretty pedestrian problem, which I choose with the aim of balancing out what I thought was the tough problem above. (Turns out most of you did great on both these questions!) This really is a simple problem, and once you get over the shock of that, and stop looking for the trick, it's straighforward. We have 1.00 ℓ of water, and we can assume a density of 1.0 g/mℓ, so that's

$$1.00\,\ell\text{ of H}_2\text{O}_{(\ell)}\left(\frac{1.0\text{ g H}_2\text{O}_{(\ell)}}{\text{m}\ell\text{ H}_2\text{O}_{(\ell)}}\right)\left(\frac{\underline{1000}\text{ m}\ell}{\underline{1}\,\ell}\right)=10_{00}\text{ g of H}_2\text{O}_{(\ell)}\quad\text{and}\quad \tilde{m}_{H_2O}=2\times\left(1.008\frac{\text{g}}{\text{mol}}\right)+16.00\frac{\text{g}}{\text{mol}}=18.01_6\frac{\text{g}}{\text{mol}}$$

so we have $10_{00}\text{ g of H}_2\text{O}\left(\frac{\text{mol H}_2\text{O}}{18.01_6\text{ g of H}_2\text{O}}\right)=55._5$ mol of H_2O that's going to evaporate from our skin. That requires an input of

$$55._5 \text{ mol of } H_2O_{(\ell)} \times \left(\frac{44 \text{ kJ of heat energy}}{\text{mol of reaction}}\right)\left(\frac{1 \text{ mol of reaction}}{1 \text{ mol of } H_2O_{(\ell)}}\right) = 24_{42} \text{ kJ of heat energy}$$

Clearly, it's critical that the evaporating water is carrying this heat *away with it* when sweat evaporates from your body. If it were dumping this heat *into* your body (its surroundings!) then it certainly would not help to cool you off! Actually, 1.00 ℓ is about the maximum any of us could sweat out in the desert the first day we got there. But after a few weeks, most people's bodies acclimatize to the fact that they are in a hot and dry place, and that they can sweat more. They crank up the system, and a healthy desert dweller doing a triathlon can dump out as much as 3 ℓ of sweat per hour when they are really working hard! You sweat less than a liter per hour in humid climates, but it still comes out too fast to evaporate, so not only does the sweat not help you cool off as much, you also get all wet! Hence the adulation any Southwesterner will offer to the advantages of a "dry heat."

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?

The fundamental answer to this question is simply "sublimation," but I obviously expected you to explain more fully than that. Let's start with the observation that ice cream contains a substantial amount of H_2O. (Except maybe ice cream from the Chocolate Shoppe in Madison, which is just to die for, but contains over 20% milk fat!) So even though there is some fat and sugar and other stuff in there, my ice cream is basically a dirty ice cube, and thus chock full of water molecules. Well, remember the CO_2 question on the other side of this page? By logic similar to that employed there, we know that at temperatures below freezing, $H_2O_{(s)}$ and $H_2O_{(g)}$ are in equilibrium with each other. There's very little $H_2O_{(g)}$, actually, but there's some. That water vapor is more likely to come from warmer ice than from colder ice, because it forms when a water molecule picks up enough energy to break free of the ice's intermolecular forces. That requires it move with a kinetic energy greater than the average kinetic energy of its fellow molecules; how much extra kinetic it requires increases as the temperature of the ice drops. This extra kinetic energy almost always comes from a collision with a high-energy molecule already in the gas phase, often N_2 and O_2 (from air) floating around inside the ice cream container. Any given water molecule in the gas phase is going to have a limited lifetime up there, because it will eventually end up with a more "normal" kinetic energy (it'll collide with slow-moving molecules and slow down) and will go back to the solid state. This is slightly more likely to happen on cold surfaces. Water molecules are constantly going into the gas phase, and they are constantly leaving the gas phase and becoming solid again, but they are slightly more likely to become solid on and slightly less likely to sublime from a colder spot than on or from a warmer one. So, let's apply this understanding to the situation at hand! I open my fridge door to get some frozen edamame. Warm air flows in and warms the side of the ice cream container facing away from the door. A few extra water molecules leave the ice cream and go into the gas phase. These eventually settle on the exposed surfaces, with a slight preference for the colder surfaces on the inside of the container, next to the inside of the door. Repeat this process many times, and little ice crystals develop on the inside wall of the ice cream container, and the ice cream gets a little thicker! Unfortunately, if it goes to far, the ice cream develops the consistency of butter, which is nasty, even to a lipidophile like me.

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?

The cloudiness in Robin's first set of cubes was caused by bubbles of gases that were originally dissolved in the liquid water. Just like ions, neutral molecules such as N_2 and O_2 can not "fit" into the regular lattice of water molecules that comprise an ice crystal, and are forced out of the ice crystal as it grows. That leaves them all in an ever-smaller volume of liquid water, raising their concentrations until they exceed their solubilities and bubble out of solution. Those bubbles are trapped beneath the surface of the ice, because the ice freezes from the top down (recall that ice is less dense than liquid water, and think of a frozen lake!) So the trick to getting clear cubes is to remove the dissolved gases. Distillation does that, but the gases dissolve back into the water over a matter of hours after the water is distilled, so any distilled water purchased in a store is going to contain dissolved N_2, O_2, and CO_2. Because the solubility of gases in water drops with increasing temperature, heating the water to boiling will cause a lot of the dissolved gas to bubble out. (In fact, actually boiling the water for a few minutes does a *very* thorough job of removing the dissolved gases, but we didn't learn about that. That's not essential to answering this question, but hey, it might be good to know.) If that hot water is put into an ice tray and the ice tray into the freezer, the surface of the water will freeze before much air can re-dissolve into the liquid water, and there will be (almost) no bubbles in the ice cube once it freezes solid.

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.)

Your first instinct might be to calculate the requested quantity from standard heat of formation ($\Delta\tilde{H}^{o}_{f}$) values, and indeed that would be ideal. Alas, the thermodynamic data tables in the back of Zumdahl blow chunks, and don't list a value for $\Delta\tilde{H}^{o}_{f}\,[N_{(g)}]$. I took advantage of that here, to force you to find the next best way: using average bond enthalpies, which are tabulated on p. 373 in Table 8.4. You need to realize that when two N atoms join together, they form a triple bond, N≡N, rather than a single or a double bond, but this is something you should have learned in doing (or correcting) Problem 1 on Assignment 3, the one about the detonation of TNT. From Table 8.4, we learn that the average bond enthalpy for an N≡N bond is 941 kJ/mol. (That's actually a really accurate value, too, because about the only N≡N bond that exists is the one in the N_2 molecule.) This means that when two moles of gas-phase N atoms combine to form one mole of N_2 molecules, and, correspondingly, form one mole of N≡N bonds, they release 941 kJ/mol. (Recall that energy is *released* when a chemical bond is formed!) Our sign convention tells us that ΔH for a change of this sort should be negative, because the reaction releases energy. Thus the requested quantity, $\Delta\tilde{H}^{o}_{rxn}$, for the reaction above should be -941 kJ/mol of reaction. Because the products and reactants in this reaction are both gases, and the bond is one found in only the molecule we are actually producing, this is actually very close to the -945.36 kJ/mol that the NIST WebBook tells us we should have gotten (based on twice the value of $-\Delta\tilde{H}^{o}_{f}\,[N_{(g)}]$).

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.

If the syringe is exposed to the earth's atmosphere when the stasis field is turned off, the syringe will experience a constant pressure equal to the local atmospheric pressure. At constant pressure, the heat flow (q) of the system will be equal to the enthalpy change: $q = \Delta H$, so both will be negative, and the system will be releasing heat energy into its surroundings. You can also justify this answer by specifying that heat energy is released when chemical bonds are formed at constant pressure.

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.

Initially, since the reaction is exothermic, the gas in the syringe will get very hot and expand. However, as heat leaves the system and the gas returns to room temperature, there will be fewer moles of gas present than at the instant the stasis field was turned off (pairs of independent N atoms will pair up to form N_2 molecules, resulting in there being less than 0.0100 moles of gas in the syringe) and so the volume of the gas will end up smaller at the end than it was at the beginning. Because the pressure in the room stayed constant throughout, the opposing pressure did too (thank you "magic" syringe!) and so the work done will be given by

$$w = -\int_{\text{initial}}^{\text{final}} P_{opp}\, dV_{sys} = -P_{opp}\int_{\text{initial}}^{\text{final}} dV_{sys} = -P_{opp}\,\Delta V_{sys}$$

As just discussed, the net volume change for the entire process, ΔV_{sys}, will be negative, and thus the work will be positive. That means the surroundings compress the system, and the surroundings do work on the magic 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?

Some of the energy released in the chemical reaction went out the window with the book! (The book carried some kinetic energy out of the window with it.) As a result, less energy remains in the room, meaning that either less heat came out of the system, or more work went into the syringe. Because the volume change of the system, ΔV_{sys}, will be the same as long as the temperature and pressure are constant, the work can't be different, and so there has to be less heat released by the system. In the more mathematical terms of the first law, with situation 1 being without the book and situation 2 being with the book:

$$\Delta E_1 = q_1 + w_1 = \Delta E_2 = q_2 + w_2 = q_2 + w_1 + KE_{\text{carried out with book}} \quad\Rightarrow\quad q_2 = q_1 + w_1 - w_1 - KE_{\text{carried out with book}} = q_1 - KE_{\text{carried out with book}}$$

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

Ideally, your intuitive understanding of entropy should suggest that when nitrogen atoms pair up, and they are required to travel together as a pair at a pretty fixed distance from each other, they are in a far more constrained situation. They have less associational and positional entropy (loosely, freedom) than they did before. So this reaction clearly leads to a decrease in entropy, and ΔSº is negative. But that intuitive understanding might still be developing, or you might still be less than confident about it, so you could consider reactions like $2\,H_{(g)} \rightarrow H_{2(g)}$ or $2\,O_{(g)} \rightarrow O_{2(g)}$, for which Appendix 4 offers Sº values:

$$2\,H_{(g)} \rightarrow H_{2(g)} \quad \Delta S^\circ = S^o_{\text{products}} - S^o_{\text{reactants}} = S^\circ[H_{2(g)}] - 2\,S^\circ[H_{(g)}] = 131 - 2(115)\frac{J}{mol\cdot K} = -99\frac{J}{mol\cdot K}$$

$$2\,O_{(g)} \rightarrow O_{2(g)} \quad \Delta S^\circ = S^o_{\text{products}} - S^o_{\text{reactants}} = S^\circ[O_{2(g)}] - 2\,S^\circ[O_{(g)}] = 205 - 2(161)\frac{J}{mol\cdot K} = -117\frac{J}{mol\cdot K}$$

These were the only two examples offered in Zumdahl, but to demonstrate the point, here are a few more:

$$2\,Cl_{(g)} \rightarrow Cl_{2(g)} \quad \Delta S^\circ = S^o_{\text{products}} - S^o_{\text{reactants}} = S^\circ[Cl_{2(g)}] - 2\,S^\circ[Cl_{(g)}] = 223 - 2(165)\frac{J}{mol\cdot K} = -107\frac{J}{mol\cdot K}$$

$$2\,Br_{(g)} \rightarrow Br_{2(g)} \quad \Delta S^\circ = S^o_{\text{products}} - S^o_{\text{reactants}} = S^\circ[Br_{2(g)}] - 2\,S^\circ[Br_{(g)}] = 245 - 2(175)\frac{J}{mol\cdot K} = -105\frac{J}{mol\cdot K}$$

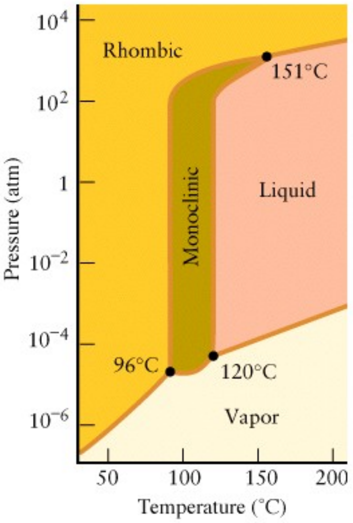
Okay, I'm willing to call that a trend! A lot of you tried to do essentially the same things I've done above, but forgot to multiply the Sº value for the atom by two! As a result, you came out with positive ΔSº values, and the wrong answer to the question. But you got credit for being on the right track. A few others forgot that it's *products - reactants,* not the other way around! By the way, the actual value of ΔSº for the formation of N_2 from N atoms, according to NIST, is -114 J/(mol·K).

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 ΔHº and ΔSº (positive and negative, negative and positive, etc.) will make a reaction a good candidate for use in emergency cold packs, and why?

Cold packs contain chemicals that become cold (and thus absorb heat from their surroundings) when they are mixed together under constant pressure conditions. This has to happen as the result of a spontaneous endothermic chemical reaction: endothermic because the pack is supposed to draw in heat, spontaneous because the packs are supposed to work on their own, without being hooked up to an air conditioner or an electrical outlet or anything like that. (Understand that the reaction that "powers" the cold pack must be spontaneous, but you don't want the cold pack as a whole to be spontaneous. To accomplish this, the reactants in a cold pack are kept from mixing with each other until the pack is "activated," by keeping one of the reactants in a sealed ampoule until the pack is needed [as with lightsticks].) The requirement that the reaction be endothermic tells us that ΔHº must be positive. The requirement that it be spontaneous can be translated to mean that ΔGº must be negative. Because ΔGº = ΔHº – T ΔSº, and because T must always be positive, ΔGº for an endothermic reaction (ΔHº>0) can only be negative if ΔSº is positive.

Useful emergency cold packs will operate on the basis of reactions that are endothermic and spontaneous.
This is only possible for reactions with both ΔH° and ΔS° positive.

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?

The denser form of any material will become ever more favored as the pressure is increased, and the material feels ever greater urge to squeeze into a smaller space and thus relieve a bit of the overwhelming pressure. We can see that for any situation in which we have monoclinic sulfur (properly spelt "sulphur" in true English, by the way), increasing the pressure (moving up vertically on the phase diagram) while keeping other things constant causes it to transform into rhombic sulfur. This is a dead giveaway that rhombic sulfur is denser than is the monoclinic allotrope. Another legitimate answer is based on Zumdahl's explanation of the water phase diagram, and specifies that the line dividing monoclinic and rhombic on the phase diagram has a positive slope. That all by itself isn't really enough, though, you also have to specify that rhombic is on top in order for that to be a complete argument!

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.

Recall that a phase diagram is a map indicating the most stable form of the material it describes as a function of some variables. The most stable state is going to be that with the most negative Gibbs Free Energy of Formation (ΔG_f) at a given point; in the case of the sulfur phase diagram, at a given temperature and pressure. So if we restrict ourselves to standard free energies (ΔG^o) by travelling along the P = 1 atm line on the phase diagram, we find that the reaction above is spontaneous at temperatures above 96ºC, but not spontaneous at lower temperatures. That means that ΔG^o for the reaction above goes from a positive value to a negative value as the temperature is increased. Since $\Delta G^o = \Delta H^o - T\Delta S^o$, and ΔH^o and ΔS^o are both weak functions of temperature, this suggests that ΔS^o must be a positive value (so that as T becomes larger, $T\Delta S^o$ becomes more positive, and ΔG^o becomes correspondingly more negative). A far less quantitative, but just as valid argument, goes like this: We can see that monoclinic sulfur becomes favored over the rhombic allotrope at high temperatures. Entropy controls spontaneity at high temperatures, whereas enthalpy controls at low temperatures. So the reaction shown above is disfavored by enthalpy, and favored by entropy. When entropy takes over at high temperatures, it becomes favorable (spontaneous). Entropy always wants to *increase*, so for entropy to favor the reaction above, ΔS for it must be positive. We can verify this using the data in Appendix 4 of Zumdahl:

$$\Delta S^o_{rxn} = S^o_{products} - S^o_{reactamts} = S^\circ[S_{(s,\ monoclinic)}] - S^\circ[S_{(s,\ rhombic)}] = (33-32)\frac{J}{mol\cdot K} = +1\frac{J}{mol\cdot K}$$

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?

It will eventually convert into rhombic sulfur, because the phase diagram indicates that rhombic sulfur is the most stable form at 25ºC and 1 atm. More rigorously, the phase diagram tells us that $\Delta\tilde{G}^o_f[S_{(s,\ rhombic)}]$ is more negative than the standard free energy of formation for any other form of sulfur at 25ºC and 1 atm, and so any reaction of the form

$$S_{(any\ form\ other\ than\ rhombic\ solid)} \rightarrow S_{(s,\ rhombic)}$$

will be spontaneous at 25ºC and 1 atm. So we know that a sample of elemental sulfur will eventually convert into rhombic sulfur if left at 25ºC and 1 atm for a long enough time. (It turns out that for sulfur, the required time is on the order of days.) [In constrast, at room temperature, the conversion of bulk diamond into bulk graphite takes millenia, good news for those of you so invested!]

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 $3.5 \pm 0.9\ \text{kJ}\cdot\text{K}^{-1}$ 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 $\Delta\tilde{H}^{\circ}_{\text{combustion}}$ for our unknown fuel. [Uncertainties are as implied by significant figures, unless specified.]

This will be perfectly analogous to what *you* did in the calorimetry lab, so if you did the calculations for this lab correctly and recorded what you were doing understandably, in your lab notebook, this should be a cake walk. We will determine the heat released from the fuel based on the temperature change of the calorimeter. To the extent that the unknown and ethanol burn in the same manner (equally completely, releasing the same amount of hot gas at the same rate), the empirically determined heat capacity takes heat loss and incomplete combustion into account, and tells us how many kilojoules of heat were actually released by combustion of the unknown fuel under the calorimeter. (It even accounts for the loss of heat due to the fact the fuel was lit before it was under the calorimeter and also pulled out from underneath before it was extinguished – because the same was done with the ethanol lamp during the calibration runs!) Paying careful heed to significant figures, here goes nothing:

$$\Delta T = 45.5°\text{C} - 24.5°\text{C} = 21.0\,\text{C}° \qquad q_{\text{fuel}} = -\left(C_{\text{P, calorimeter}}\right)\left(\Delta T\right) = -\left(3._5\,\frac{\text{kJ}}{\text{K}°}\right)\left(21.0\,\text{C}°\right)\left(\frac{1\ \text{K}°}{1\ \text{C}°}\right) = -7_{3.5}\,\text{kJ}$$

(Note that one Kelvin degree is equivalent to one Celsius degree, because we are talking about temperature *differences*.)
(Note also that with sig figs, 3.5 ± 0.9 is written as $3._5$ with one significant figure. The 5 isn't reliable to ±1 unit, but the 3 is.)

$$\text{mass}_{\text{fuel}} = 126.42\,\text{g} - 124.29\,\text{g} = 2.13\,\text{g} \qquad 2.13\ \text{g of fuel}\left(\frac{\underline{1}\ \text{mole of fuel}}{74.12\ \text{g of fuel}}\right) = 0.0287_{37}\ \text{moles of fuel}$$

$$\Delta\tilde{H}^{\text{o}}_{\text{combustion}}[\text{unknown fuel}] = \frac{q_{\text{fuel}}}{\eta_{\text{fuel}}} = \frac{-7_{3.5}\,\text{kJ}}{0.0287_{37}\ \text{mol}} = -2_{557.7}\,\frac{\text{kJ}}{\text{mol}}$$

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 suggests, so the worst case error gives a good upper bound on the uncertainty in $\Delta\tilde{H}^{\circ}_{c}$.

It's critical to remember that a worst-case analysis requires you go back to the original data, where you have it. You modify that original data by its uncertainty, simultaneously, so as to skew your end result as much as possible in a specific direction. I'm going to do everything I can to maximize my value for $\Delta\tilde{H}^{\text{o}}_{c}[\text{unknown fuel}]$. That will include modifying the molar mass of the unknown, because that too has an uncertainty associated with it! Recall that we can neglect units and sig figs in doing a worst-case error analysis, because we have already heeded them in doing the nominal case [in this case, part (a), above]

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

$$\Delta\tilde{H}^{\text{o}}_{c}[\text{unknown}]_{,\max} = \frac{-q_{\text{fuel}}}{\eta_{\text{fuel}}} = \frac{-C_p\Delta T}{m_{\text{fuel}}\left(\dfrac{1}{\tilde{m}_{\text{fuel}}}\right)} = \frac{-\left(C_p\Delta T\right)_{\max}}{\left[m_{\text{fuel}}\right]_{\min}\left(\dfrac{1}{\tilde{m}_{\text{fuel}}}\right)_{\min}}$$

$$= \frac{-(3.5+0.9)\left[(45.5+0.1)-(24.5-0.1)\right]}{\left[(126.42-0.01)-(124.29+0.01)\right]\left(\dfrac{1}{74.12+0.01}\right)}$$

$$= \frac{-(4.4)[21.2]}{[2.11]\left(\dfrac{1}{74.13}\right)} = \frac{-93.28}{0.0284635} = -3277.2\,\frac{\text{kJ}}{\text{mol}}$$

So, according to the worst-case error method, our experimental result is

$$\Delta\tilde{H}^{\text{o}}_{c}[\text{unknown}] = \text{nominal} \pm \left|\,\text{nominal} - \text{worst}\,\right| = -2557.7\,\frac{\text{kJ}}{\text{mol}} \pm \left| -2557.7\,\frac{\text{kJ}}{\text{mol}} - \left(-3277.2\,\frac{\text{kJ}}{\text{mol}}\right)\right| = -2557.7 \pm 719.5\,\frac{\text{kJ}}{\text{mol}}$$

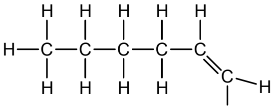
This would be properly written as -2600 ± 700 kJ/mol, but here we are interested in the range of possible values it indicates, specifically, anything between -1838 and -3277 kJ/mol. That eliminates methyl acetate, isopentane, *n*-pentane, and *n*-hexane.

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 big pot containing 10.0 ℓ of 20.0ºC water on a giant ring stand, opens a can of Steno, wafts it in front of 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.

I came up with five plausible explanations, that is, five *systematic* errors that Wally is not accounting for and which would act to *reduce* the temperature of the water below the expected temperature. I present them here in likely decreasing order of importance:

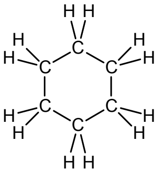
1. Wally has done nothing to compensate for (or even ameliorate) the fact that a lot of the heat released by the fuel is lost to the air. Put another way, the hot gases produced in the vicinity of the flame are quite surely going to move past the pot and into the room still hot, at a temperature well above ambient. As a result, much of the released heat ends up in the room rather than in the pot.
2. The pot itself is going to absorb some heat, so not even all of the heat absorbed by the pot will go into actually heating up the water.
3. Burning out of a can, like it does, and having several waxy components in it (to make it a gel) make it a near-certainty that Wally's Steno will not undergo complete combustion, and thus release less heat than the 31.4 kJ/g that Wally assumed.
4. Getting as warm as it did, it is very likely that some of the water in the pot evaporated. Being a highly endothermic process, this evaporation stole heat from the water that was left behind. (The most energetic water molecules are the ones that escape into the gas phase, leaving behind the sluggish ones: this is why it takes appreciably longer to boil an uncovered pot of water than a covered one!)
5. Wally wafted the can in front of you for a while, giving some of the fuel a chance to evaporate. So he actually burned < 100. grams.

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



1-hexene$_{(g)}$

$+ 9\ O_{2(g)} \rightarrow 6\ CO_{2(g)} + 6\ H_2O_{(\ell)}$ $\Delta\tilde{H}^{\circ}_{rxn} = \Delta\tilde{H}^{\circ}_{c}[\text{1-hexene}] = -4010 \pm 20$ kJ/mol



cyclohexane$_{(g)}$

$+ 9\ O_{2(g)} \rightarrow 6\ CO_{2(g)} + 6\ H_2O_{(\ell)}$ $\Delta\tilde{H}^{\circ}_{rxn} = \Delta\tilde{H}^{\circ}_{c}[\text{cyclohexane}] = -3930 \pm 20$ 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 more of cyclohexane. Your answer to this question need not be quantitative, but it's OK if it is.

These two reactions involve breaking and forming the exact same bonds, save for a small difference in the bonds broken in disconnecting the atoms comprising the two fuels. Specifically, instead of the one C=C bond in 1-hexene, two C–C bonds are broken in cyclohexane. (The same number of C–H and O=O bonds are broken in each case, and the same number of H–O and C=O bonds are formed in each case. The difference is that 6 C–C bonds are broken in disassembling cyclohexane, whereas 4 C–C and 1 C=C bond are broken in disassembling 1-hexene.) According to Table 8.4, it takes 614 kJ/mol to break C=C bonds, and 347 kJ/mol to break C–C bonds. We would therefore expect it to take slightly more energy to break two C–C bonds than it does to break one C=C bond, and therefore that the complete combustion of 1-hexene will release slightly more net energy than the complete combustion of cyclohexane. Quantitatively,

$$\begin{aligned}\Delta\tilde{H}_c^\circ[1-\text{hexene}] &= \Delta\tilde{H}_c^o[\text{cyclohexane}] + \text{break one mole of C=C bonds} + \text{form two moles of C-C bonds}\\ &= \Delta\tilde{H}_c^o[\text{cyclohexane}] + 614\text{ kJ} + (2\times -347\text{kJ}) = \Delta\tilde{H}_c^o[\text{cyclohexane}] - 80\text{ kJ}\ \text{(per mole)}\end{aligned}$$

Remarkably, that agrees really well with the given $\Delta\tilde{H}_c^\circ$ values for the two fuels; $\Delta\tilde{H}_c^\circ$ [1-hexene] is indeed 80 kJ/mol more negative.