Chemistry 123 **Problem Set Solution** **Winter Term 2003**
Assignment #3 **Instructor: R. Rossi**

<u>Common Symbols</u> 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 $\tilde{E}$

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

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

sf = significant figures

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

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

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

χ_x = mole fraction of x, which is just $\%_{mol}$ expressed as a fraction

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. We'll be well-served by carefully counting up the atoms in TNT and determining its formula. It comes out to be $C_7H_5N_3O_6$.

   a. With the formula of TNT in hand, and the information given in the problem, we know TNT blows up like this:

$$C_7H_5N_3O_{6(s)} \;\rightarrow\; CO_{(g)} + C_{(s),\text{ graphite}} + H_{2(g)} + N_{2(g)}$$

Crazy Harry would be proud of us. Now we know what the unbalanced equation is, and it's pretty darn nasty, so I thought it wise to balance it systematically. I started by balancing nitrogen, then hydrogen, then oxygen. That allowed me to end with carbon, which is the most "flexible" product in that I can add them one at a time, all by themselves:

$$\begin{array}{lllllllll}
C_7H_5N_3O_{6(s)} & \rightarrow & CO_{(g)} & + & C_{(s),\text{ graphite}} & + & H_{2(g)} & + & N_{2(g)} \\
C_7H_5N_3O_{6(s)} & & CO_{(g)} & & C_{(s),\text{ graphite}} & & H_{2(g)} & & N_{2(g)} \\
 & & CO_{(g)} & & & & H_{2(g)} & & N_{2(g)} \\
 & & CO_{(g)} & & & & H_{2(g)} & & \\
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\end{array}$$

The balanced detonation reaction for TNT is therefore

$$\boxed{2\,C_7H_5N_3O_{6(s)} \;\rightarrow\; 12\,CO_{(g)} + 2\,C_{(s),\text{ graphite}} + 5\,H_{2(g)} + 3\,N_{2(g)}}$$

Note that a very small volume of solid is transformed into a huge volume of very hot gas in a very short period of time. That's what gives TNT, and other so-called high explosives, their extremely dangerous punch.

   b. Now that we have a balanced reaction, we can employ Hess' Law, just as we will in problems 2 and 3:

$$\Delta H^o_{rxn} = \sum_{\text{products}} \Delta H^o_f - \sum_{\text{reactants}} \Delta H^o_f$$

Most of the products of the detonation reaction are elements in their standard states, so this isn't too ugly. We are given $\Delta H^o{}_f$ for TNT in the text of the problem, and we can get $\Delta H^o{}_f$ for carbon monoxide from Appendix 4 of Zumdahl:

$$\begin{aligned}
\Delta H^o_{\text{detonation}} &= \Delta H^o_f\left[12\,CO_{(g)}\right] + \Delta H^o_f\left[2\,C_{(s),\text{graphite}}\right] + \Delta H^o_f\left[5\,H_{2(g)}\right] + \Delta H^o_f\left[3\,N_{2(g)}\right] - \left(\Delta H^o_f\left[2\,C_7H_5N_3O_{6(s)}\right]\right) \\
&= 12\cdot\Delta H^o_f\left[CO_{(g)}\right] + 2\cdot H^o_f\left[C_{(s),\text{graphite}}\right] + 5\cdot\Delta H^o_f\left[H_{2(g)}\right] + 3\cdot\Delta H^o_f\left[N_{2(g)}\right] - 2\cdot\Delta H^o_f\left[C_7H_5N_3O_{6(s)}\right] \\
&= 12\left[-110.5\frac{\text{kJ}}{\text{mol}}\right] + 2\cdot\left[0\frac{\text{kJ}}{\text{mol}}\right] + 5\cdot\left[0\frac{\text{kJ}}{\text{mol}}\right] + 3\cdot\left[0\frac{\text{kJ}}{\text{mol}}\right] - 2\left[-65.5\frac{\text{kJ}}{\text{mol}}\right] \\
&= -1326\frac{\text{kJ}}{\text{mol}} + 131\frac{\text{kJ}}{\text{mol}} \quad \left(\text{This is per mole of reaction!}\right)
\end{aligned}$$

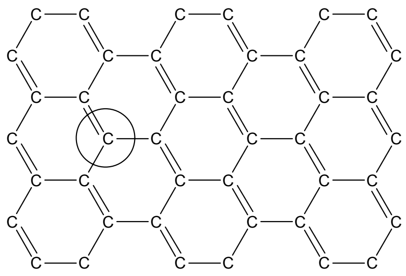
$$\Delta H^o_{\text{detonation}} = \boxed{-1195\frac{\text{kJ}}{\text{mol of detonation}} \times \frac{\text{mol of detonation}}{2\text{ mol TNT}} = \text{-}597.5\frac{\text{kJ}}{\text{mol TNT}} \text{ based on enthalpies of formation}}$$

   c. Here we carry out an imaginary process, separating (gaseous) TNT into its constituent atoms and then allowing them to combine into the (gaseous) products of the detonation reaction. We can estimate how much energy it takes to break each bond, and how much energy will be released by the formation of new bonds, based on the bond enthalpies given in Table 8.4. Looking at the structure of TNT, we see we will need to break the following bonds in order to separate a single TNT molecule into independent atoms: 3 N=O, 3 N–O, 3 C–N, 3 C=C, 4 C–C, and 5 C–H bonds.

   Most of the products are simple diatomic molecules, so we can get accurate values for their bond enthalpies from Table 8.4. We are going to form 12 CO, 5 H_2, and 3 N_2. The only really tricky product is graphite, which is a solid.

Problem 1(c), continued

How do we figure out how many bonds are formed when C atoms combine to form graphite?!? This is pretty tricky, and I wouldn't expect most people to get it. The first time I gave this problem I got it wrong, and one of my students had to patiently explain it to me. (Thanks Jess!) It's tempting to focus on the effect of pulling one carbon atom out of a graphite lattice:



It looks like we would have to break one C=C bond, and two C–C bonds, to pull the circled carbon atom out of the graphite…and sure enough, we would. But if we then pulled a second carbon out from the same spot, it wouldn't require breaking as many bonds…and a third carbon would come out even easier. At the edges of a chunk of graphite, you probably only make or break a single bond when you add or remove a carbon atom. Quite the sticky wicket!!! What to do? Well, the best estimate you can make is to consider each bond to a given carbon in graphite to be in "joint custody," half owned by the carbon atom in question and half owned by the other carbon atom it is connected to. On average, if we make or break up a lot of graphite, it should require breaking ½ of a C=C bond and the equivalent of a full C–C bond (two halves) per C atom that we remove. [Even this smart little explanation misses the real mark, because graphite actually has a resonant bond structure…but we don't know a whit about that yet, so don't worry!] If you've followed me to this point, you'll see that forming "$C_{(s),\ graphite}$" requires (on average) forming 1/2 mole of C=C bonds and 1 mole of C–C bonds per mole of graphite. Ok, so using Table 8.4 we can now work this problem:

Product Bonds Formed

$$\begin{array}{lll} \text{Form } 12\ CO_{(g)} \rightarrow & 12\ C\equiv O & 12\left(1072\,\frac{kJ}{mol}\right)\\ \text{Form } 2\ C_{(s),\ graphite} \rightarrow & 1\ C=C & \left(614\,\frac{kJ}{mol}\right)\\ \rightarrow & 2\ C-C & 2\left(347\,\frac{kJ}{mol}\right)\\ \text{Form } 5\ H-H & 5\ H-H & 5\left(432\,\frac{kJ}{mol}\right)\\ \text{Form } 3\ N\equiv N & 3\ N\equiv N & 3\left(941\,\frac{kJ}{mol}\right) \end{array}$$

$$1915_5\,\frac{kJ}{mol\ detonation}\times\frac{1\ mol\ detonation}{2\ mol\ TNT}$$

$$=9577._5\,\frac{kJ}{mol\ TNT}\ \text{of bonds formed}$$

Reactant Bonds Broken

$$\left(\begin{array}{ll} 3\ N=O & 3\left(607\,\frac{kJ}{mol}\right)\\ 3\ N-O & 3\left(201\,\frac{kJ}{mol}\right)\\ 3\ C-N & 3\left(305\,\frac{kJ}{mol}\right)\\ 3\ C=C & 3\left(614\,\frac{kJ}{mol}\right)\\ 4\ C-C & 4\left(347\,\frac{kJ}{mol}\right)\\ 5\ C-H & 5\left(413\,\frac{kJ}{mol}\right) \end{array}\right)\times 2$$

↙This is per TNT molecule!

(We need to multiply this by two because we are breaking up two TNT's in the reaction)

$$1726_8\,\frac{kJ}{mol\ detonation}\times\frac{1\ mol\ detonation}{2\ mol\ TNT}$$

$$=8634\,\frac{kJ}{mol\ TNT}\ \text{bonds broken}$$

Problem 1(c), continued

Remembering that it takes energy to break bonds, and thus you have to put energy into a molecule to do it,

$$\begin{aligned}
\Delta H^{o}_{\text{detonation}} &= +\left(\text{total energy of reactant bonds broken}\right)-\left(\text{total energy of product bonds formed}\right)\\
&= +\left(3\left[607\,\frac{\text{kJ}}{\text{mol}}\right]+3\left[201\,\frac{\text{kJ}}{\text{mol}}\right]+3\left[305\,\frac{\text{kJ}}{\text{mol}}\right]+3\left[614\,\frac{\text{kJ}}{\text{mol}}\right]+4\left[347\,\frac{\text{kJ}}{\text{mol}}\right]+5\left[413\,\frac{\text{kJ}}{\text{mol}}\right]\right)\times 2\\
&\quad -\left(12\left[1072\,\frac{\text{kJ}}{\text{mol}}\right]+1\left[614\,\frac{\text{kJ}}{\text{mol}}\right]+2\left[347\,\frac{\text{kJ}}{\text{mol}}\right]+5\left[432\,\frac{\text{kJ}}{\text{mol}}\right]+3\left[941\,\frac{\text{kJ}}{\text{mol}}\right]\right)\\
&= +\left(182_{1}+603+915+184_{2}+138_{8}+206_{5}\right)\frac{\text{kJ}}{\text{mol of TNT}}\times\left[\frac{2\text{ mol TNT}}{\text{mol of detonation reaction}}\right]\\
&\quad -\left(1286_{4}+614+694+2160+282_{3}\right)\frac{\text{kJ}}{\text{mol of detonation reaction}}\\
&= \left[+863_{4}\,\frac{\text{kJ}}{\text{mol of TNT}}\right]\times\frac{2\text{ mol of TNT}}{1\text{ mol of detonation reaction}}-1915_{5}\,\frac{\text{kJ}}{\text{mol of detonation reaction}}\\
&= 172_{68}\,\frac{\text{kJ}}{\text{mol of detonation reaction}}-1915_{5}\,\frac{\text{kJ}}{\text{mol of detonation reaction}}\\
&= -18_{87}\,\frac{\text{kJ}}{\text{mol of detonation reaction}}\times\left(\frac{\text{mol of detonation reaction}}{2\text{ mol TNT}}\right)
\end{aligned}$$

$$\Delta H^{o}_{\text{detonation}} = \boxed{-94_{3.5}\,\frac{\text{kJ}}{\text{mol of TNT}}\quad\text{based on average bond enthalpies}}$$

d. The $\Delta H^{o}_{\text{detonation}}$ value calculated from standard enthalpy of formation (ΔH^{o}_{f}) values is far more reliable than that calculated from average bond enthalpies! (The latter isn't even as reliable as its significant figures suggest – you have to be careful how you interpret the significant figures in average bond enthalpies. If we shake down every last Carleton student and determine how much cash they are packing, down to the cent, we can calculate the average sum carried by Carleton students, down to the nearest 1/100th of a cent. That doesn't mean that if we accost a random student and make them empty their pockets, we should expect them to have this exact average sum on their person! As I like to put it, "Average people are one in a million.") The main problem with the bond enthalpy estimate is that many of the bond enthalpies used in arriving at it are inherently approximate, an average over a loosely similar population, whereas ΔH^{o}_{f} values are specifically measured for the compounds they apply to, in a specific state. Bond enthalpies also fail to take into account intermolecular forces, like the forces that hold TNT and graphite together as solids. Consider this: what would a bond enthalpy calculation give you as ΔH^{o} for the reaction

$$H_2O_{(\ell)} \rightarrow H_2O_{(g)}$$

The energy required to pull TNT molecules apart from a chunk of solid TNT, and that released when sheets of graphite assemble into a chunk of solid graphite, are not included in the bond-enthalpy-based estimate. Also, for those of you who are hip to resonance, resonant bonds tend to be appreciably more stable than their resonant structure representations suggest. The ring bonds in TNT take far more energy to break that the 3 C–C and 3 C=C bonds used in our calculation suggest. The same holds true for the NO_2 groups on TNT and the bonds within graphite. [This last factor is, in fact, the main reason for the largish discrepancy between the answers to part (c) and (d).]

e. Using the reliable $\Delta H^{o}_{\text{detonation}}$ value obtained from ΔH^{o}_{f} values, this becomes an exercise in dimensional analysis:

$$57\times10^{6}\ \text{metric tons of TNT}\times\left(\frac{1000\text{ kg}}{1\text{ metric ton}}\right)\times\left(\frac{1000\text{ g}}{1\text{ kg}}\right)=5.7\times10^{13}\text{ g of TNT}$$

$$\text{Molar mass of TNT: } C_7H_5N_3O_6 = 7(12.01)+5(1.008)+3(14.01)+6(16.00)\,\frac{\text{g}}{\text{mol}} = 227.14\,\frac{\text{g of TNT}}{\text{mol of TNT}}$$

$$5.7\times10^{13}\ \text{g of TNT}\times\left(\frac{1\text{ mol TNT}}{227.13_{95}\text{ g of TNT}}\right)\times\left(\frac{-597._{5}\text{ kJ}}{\text{mol of TNT}}\right)=-1.4_{994}\times10^{14}\text{ kJ}$$

$$\boxed{1.5\times10^{14}\ \text{kJ of energy were released in the Novaya Zamlya detonation}}$$

Problem 1, continued

f. Dimensional analysis is, once again, our friend:

$$1.4_{994}\times10^{14}\,\text{kJ}\left(\frac{1000\text{ J}}{1\text{ kJ}}\right)\left(\frac{0.239\text{ calories}}{1\text{ Joule}}\right)\left(\frac{1\text{ g of water}\cdot\text{C}^\circ}{1.0\text{ calorie}}\right)\left(\frac{1}{[95^\circ\text{C}-6^\circ\text{C}]}\right)=4.0_{265}\times10^{14}\text{ g of water}$$

$$4.0_{265}\times10^{14}\text{ g of water}\left(\frac{1\text{ m}\ell\text{ water}}{1.0\text{ g water}}\right)\left(\frac{1\ \ell}{1000\text{ m}\ell}\right)\left(\frac{1\text{ pot of tea water}}{4\ \ell}\right)=1.0_{0662}\times10^{11}\text{pots of tea water...zoinks!}$$

$$\text{Hmmmmm...}10^6=\text{million, }10^9=\text{billion, }10^{12}=\text{trillion, }10^{15}=\text{quadrillion...}$$

$$\boxed{\text{They could have brewed up }10_0\text{ billion pots of Siberian tea!}}$$

2. Hess' Law is again our friend and salvation. We just need to figure out what combination of the given reactions will add up to give the desired net reaction, and the sum of the respective ΔHº values will be that of the net reaction. We can't work with enthalpies of formation here, because some dirty rotten scoundrel has obscured the identities of the actual molecules we are working with. (In his defense, he's hoping to make sure we get the concept of Hess' Law forwards and backwards, ten ways to Tuesday…get the idea that this is an important concept you will see again?) The best approach to problems like this is to focus on reactants or products that appear in as few places as possible. Since $X_2O_{3(s)}$ appears as a product in both the desired reaction and Reaction 3, I start with that. Then I know I need to kill off the 2 $X_{(s)}$ on the reactant side of Reaction 3, so I'll add in two copies of the reverse of Reaction 1, which will cancel those out. That gives me:

$$\begin{array}{lcl|l}
2\,X_{(s)} + \tfrac{3}{2}\,O_{2(g)} & \rightarrow & X_2O_{3(s)} & \Delta H^\circ = +1\,(\Delta H^\circ_3)\\
+2(\ XNO_{(s)} + CO_{(g)} & \rightarrow & X_{(s)} + CO_{2(g)} + \tfrac{1}{2}\,N_{2(g)}\ ) & +\ \ \Delta H^\circ = -2\,(\Delta H^\circ_1)\\
\hline
\tfrac{3}{2}\,O_{2(g)} + 2\,XNO_{(s)} + 2\,CO_{(g)} & \rightarrow & X_2O_{3(s)} + 2\,CO_{2(g)} + N_{2(g)} & \Delta H^\circ = +\,\Delta H^\circ_3 - 2\Delta H^\circ_1
\end{array}$$

OK, well, that's not too far off. We need to kill off the $\tfrac{3}{2}\,O_{2(g)}$ because O_2 doesn't appear anywhere in the desired net reaction. Reaction 2 does that if we subtract it (add its reverse) three times:

$$\begin{array}{lcl|l}
\tfrac{3}{2}\,O_{2(g)} + 2\,XNO_{(s)} + 2\,CO_{(g)} & \rightarrow & X_2O_{3(s)} + 2\,CO_{2(g)} + N_{2(g)} & \Delta H^\circ = +\,\Delta H^\circ_3 - 2\Delta H^\circ_1\\
+3(\ CO_{2(g)} & \rightarrow & CO_{(g)} + \tfrac{1}{2}\,O_{2(g)}\ ) & +\ \ \Delta H^\circ = -3\,(\Delta H^\circ_2)\\
\hline
2\,XNO_{(s)} + CO_{2(g)} & \rightarrow & X_2O_{3(s)} + CO_{(g)} + N_{2(g)} & \Delta H^\circ = +\,\Delta H^\circ_3 - 2\Delta H^\circ_1 - 3\Delta H^\circ_2
\end{array}$$

Whaddayaknow, that also makes the other reagents in the reaction come out as desired. Yippee! So the desired ΔHº is

$$\boxed{\Delta H^\circ = \Delta H^\circ_3 - 2\,\Delta H^\circ_1 - 3\,\Delta H^\circ_2}$$

3. You can determine the standard state of an element from Appendix 4 of your book: you will find that the standard states have $\Delta H^\circ_f = 0$. (Compare $\Delta H^\circ_f\,[H_{(g)}]$ with $\Delta H^\circ_f\,[H_{2(g)}]$. $H_{(g)}$ and $H_{2(g)}$ *are not the same!!! The standard state of hydrogen is* $H_{2(g)}$.)

   a. The enthalpy of formation of a compound (here, B_5H_9) is defined as the enthalpy change associated with the formation of *one mole* of the compound in a given state (here, the gas) from elements in their standard states. Boron(B) is a solid at 25ºC and 1 atm, while hydrogen exists as $H_{2(g)}$ under these conditions. So the formation reaction for which ΔHº is $\Delta H^\circ_f[B_5H_{9(g)}]$ is
   $$5\,B_{(s)} + \tfrac{9}{2}\,H_{2(g)} \rightarrow B_5H_{9(g)} \qquad \Delta H^\circ = \Delta H^\circ_f[B_5H_{9(g)}]$$

   b. There are two ways we can do this. Either way we are using Hess' Law, but in one case it's more obvious than in the other! The first approach is to use the general rule that ΔH for any reaction may be expressed as the weighted sum of the enthalpies of formation for the products, minus the weighted sum of the enthalpies of formation for the reactants:
   $$\Delta H^\circ_{rxn} = \sum_{\text{products}} \Delta H^\circ_f - \sum_{\text{reac tan ts}} \Delta H^\circ_f$$

   Using this general rule we can write the enthalpy of combustion for $B_5H_{9(g)}$ as the sum
   $$\begin{aligned}
   \Delta H^\circ_{\text{reaction}} &= \Delta H^\circ\left[B_5H_{9(g)} + 6\,O_{2(g)} \rightarrow 2.5\,B_2O_{3(s)} + 4.5\,H_2O_{(\ell)}\right]\\
   &= \left(\Delta H^\circ_f\left[2.5\,B_2O_{3(s)}\right] + \Delta H^\circ_f\left[4.5\,H_2O_{(\ell)}\right]\right) - \left(\Delta H^\circ_f\left[B_5H_{9(g)}\right] + \Delta H^\circ_f\left[6\,O_{2(g)}\right]\right)\\
   &= \left(2.5\cdot\Delta H^\circ_f\left[B_2O_{3(s)}\right] + 4.5\cdot\Delta H^\circ_f\left[H_2O_{(\ell)}\right]\right) - \left(\Delta H^\circ_f\left[B_5H_{9(g)}\right] + 6\cdot\Delta H^\circ_f\left[O_{2(g)}\right]\right)
   \end{aligned}$$

Problem 3(b), continued

and since we know what the enthalpy of combustion is, and we can look up all the others, we can solve for the one we want, $\Delta H^{o}_{f}[B_5H_{9(g)}]$ (Being careful to pick water in the *liquid* state from the table!):

$$\Delta H^{\circ}_{\text{combustion}}\left[B_5H_{9(g)}\right] = 2.5\cdot\Delta H^{o}_{f}\left[B_2O_{3(s)}\right] + 4.5\cdot\Delta H^{o}_{f}\left[H_2O_{(\ell)}\right] - \Delta H^{o}_{f}\left[B_5H_{9(g)}\right] - 6\cdot\Delta H^{o}_{f}\left[O_{2(g)}\right]$$

$$-2.5\cdot\Delta H^{o}_{f}\left[B_2O_{3(s)}\right] = 4.5\cdot\Delta H^{o}_{f}\left[H_2O_{(\ell)}\right] - \Delta H^{o}_{f}\left[B_5H_{9(g)}\right] - 6\cdot\Delta H^{o}_{f}\left[O_{2(g)}\right] - \Delta H^{\circ}_{\text{combustion}}\left[B_5H_{9(g)}\right]$$

$$-2.5\cdot\Delta H^{o}_{f}\left[B_2O_{3(s)}\right] = 4.5\cdot\left[-286\frac{\text{kJ}}{\text{mol}}\right] - \left[+73.2\frac{\text{kJ}}{\text{mol}}\right] - 6\cdot\left[0\frac{\text{kJ}}{\text{mol}}\right] - \left[-4507.6\frac{\text{kJ}}{\text{mol}}\right]$$

$$-2.5\cdot\Delta H^{o}_{f}\left[B_2O_{3(s)}\right] = -128_7\frac{\text{kJ}}{\text{mol}} - 73.2\frac{\text{kJ}}{\text{mol}} + 4507.6\frac{\text{kJ}}{\text{mol}}$$

$$\frac{-2.5\cdot\Delta H^{o}_{f}\left[B_2O_{3(s)}\right]}{-2.5} = \frac{+314_{7.4}\frac{\text{kJ}}{\text{mol}}}{-2.5}$$

$$\Delta H^{o}_{f}\left[B_2O_{3(s)}\right] = -125_{8.96}\frac{\text{kJ}}{\text{mol}}$$

Another way to do the very same thing is to use Hess' Law more explicitly, finding a set of reactions for which we know ΔH and which sum to give the reaction in which we are interested. We start with the combustion reaction given in the problem. Then we add or subtract (in practice, add the reverse of) the formation reactions of other things for which we have data, flipping the sign on ΔH^{o}_{f} when we "un-form" a given species:

$$B_5H_{9(g)} + 6\,O_{2(g)} \rightarrow 2.5\,B_2O_{3(s)} + 4.5\,H_2O_{(\ell)} \qquad \Delta H^{\circ} = -4507.6\,\frac{\text{kJ}}{\text{mol}}$$

$$4.5\,H_2O_{(\ell)} \rightarrow 4.5\,H_{2(g)} + 2.25\,O_{2(g)} \qquad \Delta H^{\circ} = -4.5\cdot\Delta H^{o}_{f}\left[H_2O_{(\ell)}\right] = -4.5\cdot\left[-285.83\frac{\text{kJ}}{\text{mol}}\right]$$

$$5\,B_{(s)} + 4.5\,H_{2(g)} \rightarrow B_5H_{9(g)} \qquad \Delta H^{\circ} = \cdot\Delta H^{o}_{f}\left[B_5H_{9(g)}\right] = \left[+73.2\frac{\text{kJ}}{\text{mol}}\right]$$

Summing these reactions and their enthalpies gives us the result we are after:

$$B_5H_{9(g)} + 6\,O_{2(g)} + 4.5\,H_2O_{(\ell)} + 5\,B_{(s)} + 4.5\,H_{2(g)} \rightarrow 2.5\,B_2O_{3(s)} + 4.5\,H_2O_{(\ell)} + 4.5\,H_{2(g)} + 2.25\,O_{2(g)} + B_5H_{9(g)}$$

(We can cancel terms that appear on both sides of the reaction; think of it as an algebraic equation.)

$$\Rightarrow \qquad 6\,O_{2(g)} + 5\,B_{(s)} \rightarrow 2.5\,B_2O_{3(s)} + 2.25\,O_{2(g)}$$

$$\Rightarrow \qquad 3.75\,O_{2(g)} + 5\,B_{(s)} \rightarrow 2.5\,B_2O_{3(s)}$$

The enthalpy change for this reaction, in accordance with Hess' Law, is the sum of the contributing reaction enthalpies:

$$\Delta H^{o}_{\text{rxn}} = -4507.6\frac{\text{kJ}}{\text{mol}} - 4.5\left(-286\frac{\text{kJ}}{\text{mol}}\right) + \left(+73.2\frac{\text{kJ}}{\text{mol}}\right) = -4507.6\frac{\text{kJ}}{\text{mol}} + 128_7\frac{\text{kJ}}{\text{mol}} + 73.2\frac{\text{kJ}}{\text{mol}} = -314_{7.4}\frac{\text{kJ}}{\text{mol}}$$

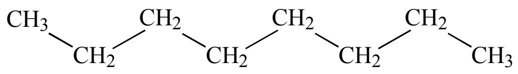
…and since this reaction is 2.5 times the formation reaction for $B_2O_{3(s)}$ we wrote down in (a), the value of the heat of formation for $B_2O_{3(s)}$, per mole of $B_2O_{3(s)}$, is simply

$$\Delta H^{o}_{f}\left[B_2O_{3(s)}\right] = \frac{\left(-314_{7.4}\frac{\text{kJ}}{\text{mol}}\right)}{2.5} = -125_{8.96}\frac{\text{kJ}}{\text{mol}}$$

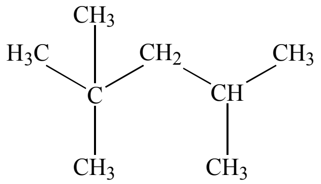
Sooooooo, either way we get the same result, $-125_{8.96}$, or -125_9, or -1260 kJ/mol. What do the smarty-pants rocket-scientist types [I'm kidding, they are really very nice people!] at NIST say we should have gotten? Well, they say -1271.94 kJ/mol, according to the most recent measurement. Given that our calculated value claims the value should be between -1248.96 and -1268.96 kJ/mol, we aren't technically in agreement. Turns out you'll find that to be the case more often than not when it comes to thermodynamic quantities. The internal consistency of most thermodynamic tables leave something to be desired, which is to say that scientists have a tendency to report their measurements of thermodynamic quantities as being more reliable than they actually are. In other words, they aren't being humble enough about the quality of their measurements, and are giving them too many significant figures! Alas, scientists are people too.

$$\boxed{\begin{array}{c}\text{Calculated value: }\Delta H^{o}_{f}\left[B_2O_{3(s)}\right] = \text{-}125_9\,\frac{\text{kJ}}{\text{mol}},\ \text{or -}1260\frac{\text{kJ}}{\text{mol}}\\ \left(\text{Tabulated value, according to NIST} = +1271.94\,\frac{\text{kJ}}{\text{mol}}\right)\end{array}}$$

4. Let me start with a quick aside here…check this out:



n-octane (C_8H_{18}) : Octane Rating = -19



isooctane (C_8H_{18}): Octane Rating = 100

As this example points out, the way atoms are connected in a chemical can make a big difference in the properties of that chemical! *n*-octane has an even lower octane rating than *n*-heptane, the "zero" octane standard, but isooctane, with the same chemical formula but a different structure, is the "gold" standard for the octane rating system! (That said, you can certainly have octane ratings *above* 100! For example, pure ethanol has an octane rating of 108, and pure MTBE has an octane rating of 116.)

a. It's not fast, but the systematic approach will work on this just as it does for anything else:

$$\begin{array}{ccccccc}
\cancel{C}_8\cancel{H}_{18} & + & \cancel{O}_2 & \rightarrow & \cancel{C}\cancel{O}_2 & + & \cancel{H}_2\cancel{O} \\
\cancel{C}_8\cancel{H}_{18} & & \cancel{O}_2 & & \cancel{C}\cancel{O}_2 & & \cancel{H}_2\cancel{O} \\
 & & \cancel{O}_2 & & \cancel{C}\cancel{O}_2 & & \cancel{H}_2\cancel{O} \\
 & & \cancel{O}_2 & & \cancel{C}\cancel{O}_2 & & \cancel{H}_2\cancel{O} \\
 & & \cancel{O}_2 & & \cancel{C}\cancel{O}_2 & & \cancel{H}_2\cancel{O} \\
 & & \cancel{O}_2 & & \cancel{C}\cancel{O}_2 & & \cancel{H}_2\cancel{O} \\
 & & \cancel{O}_2 & & \cancel{C}\cancel{O}_2 & & \cancel{H}_2\cancel{O} \\
 & & \cancel{O}_2 & & \cancel{C}\cancel{O}_2 & & \cancel{H}_2\cancel{O} \\
 & & \cancel{O}_2 & & \cancel{C}\cancel{O}_2 & & \cancel{H}_2\cancel{O} \\
 & & \cancel{O}_2 & & \cancel{C}\cancel{O}_2 & & \cancel{H}_2\cancel{O} \\
 & & \cancel{O}_2 & & \cancel{C}\cancel{O}_2 & & \cancel{H}_2\cancel{O} \\
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 & & \cancel{O}_2 & & \cancel{C}\cancel{O}_2 & & \cancel{H}_2\cancel{O} \\
 & & \cancel{O}_2 & & \cancel{C}\cancel{O}_2 & & \cancel{H}_2\cancel{O} \\
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\end{array}$$

$$2C_8H_{18} + 25O_2 \rightarrow 16CO_2 + 18H_2O$$

or

$$C_8H_{18} + 12\tfrac{1}{2}\,O_2 \rightarrow 8CO_2 + 9H_2O$$

b. The balanced equation in part (a) tells us that the stoichiometric ratio required for the complete combustion of octane is 25:2, or 12.5:1, oxygen molecules (O_2) to fuel molecules (C_8H_{18}). If we put fourteen grams of air into a piston with one gram of octane, how will the ratio of O_2 molecules to fuel molecules compare against the stoichiometric ratio? Let's find out! First, we need to know how many moles of oxygen are in fourteen grams of air. That requires, in turn, knowing the composition of air, which isn't given in the problem but is readily available from your textbook (Table 5.4 on p. 225).

Problem 4(b), continued

The mole fraction of oxygen in dry air is 0.20948, according to this dandy table. That actually doesn't do us a great deal of good all by itself, because we don't know how many moles of air the engine is pulling in, only the mass of the air. If we remembered it from the Mystery Gas lab, we could use the average molar mass of air, 29.3 g/mol. But suppose we didn't remember that? Out of luck? Hardly! We could also figure out the average molar mass of air from the data in Table 5.4 and the methodology we used to determine average molar mass in problem 4d on Assignment 1:

$$\begin{aligned}\tilde{m}_{\text{air}} &= (\chi_{N_2})(\tilde{m}_{N_2})+(\chi_{O_2})(\tilde{m}_{O_2})+(\chi_{\text{Ar}})(\tilde{m}_{\text{Ar}})+(\chi_{CO_2})(\tilde{m}_{CO_2})+\text{other gases (who's contribution is negligible)}\\ &=(0.78084)\left(28.02\frac{\text{g}}{\text{mol}}\right)+(0.20948)\left(32.00\frac{\text{g}}{\text{mol}}\right)+(0.00934)\left(39.95\frac{\text{g}}{\text{mol}}\right)+(0.000345)\left(44.01\frac{\text{g}}{\text{mol}}\right)+\begin{matrix}\text{negligible}\\ \text{terms}\end{matrix}\\ &= 21.87_{9}\,\frac{\text{g}}{\text{mol}}+6.703_{36}\,\frac{\text{g}}{\text{mol}}+0.3731_{33}\,\frac{\text{g}}{\text{mol}}+0.01518_{345}\,\frac{\text{g}}{\text{mol}}+\text{negligible terms}\\ &= 28.97_{1}\,\frac{\text{g}}{\text{mol}}\end{aligned}$$

Oooh, golly. That's not 29.3 g/mol, now is it? Criminy! Looking back at how I came up with that number, I realize I added the average mole fraction of water in air multiplied by the molar mass of water to the value above, which is for dry air…which isn't right! The more water there is in the air, the *lower* the average molar mass of the stuff will get, because water vapor is less dense than air's majority components, at least to the extent that the water vapor acts as an ideal gas. Ooops, color me embarrassed. NEway…I'll get that fixed for the next go-round. Let's see if it makes a difference, yes? Let's figure out how many moles of oxygen we would have in fourteen grams of air assuming each molar mass:

$$\underline{14}\text{ g of air}\left(\frac{\underline{1}\text{ mole of air}}{29.0\text{ g of air}}\right)\left(\frac{0.20948\text{ mol }O_2}{\underline{1}\text{ mole of air}}\right)=0.101_{13}\text{ mol }O_2\text{ using }\tilde{m}_{\text{air}}=29.0\frac{\text{g}}{\text{mol}}$$

$$\underline{14}\text{ g of air}\left(\frac{\underline{1}\text{ mole of air}}{29.3\text{ g of air}}\right)\left(\frac{0.20948\text{ mol }O_2}{\underline{1}\text{ mole of air}}\right)=0.100_{09}\text{ mol }O_2\text{ using }\tilde{m}_{\text{air}}=29.3\frac{\text{g}}{\text{mol}}$$

Ok, that's going to be in the piston with one gram of fuel, which is C_8H_{18}:

$$\tilde{m}_{C_8H_{18}}=8(\tilde{m}_C)+18(\tilde{m}_H)=8\left(12.01\frac{\text{g}}{\text{mol}}\right)+18\left(1.008\frac{\text{g}}{\text{mol}}\right)=(96.08+18.14_4)\frac{\text{g}}{\text{mol}}=114.22_4\,\frac{\text{g}}{\text{mol}}$$

$$\underline{1}\text{ g }C_8H_{18}\left(\frac{\underline{1}\text{ mol }C_8H_{18}}{114.22_4\text{ g }C_8H_{18}}\right)=0.0087547_{27}\text{ mol }C_8H_{18}$$

So the mole ratio of oxygen to fuel will be

$$\text{either}\quad\frac{0.101_{13}\text{ mol of }O_2}{0.0087547_{27}\text{ mol of }C_8H_{18}}=11.5_5\qquad\text{or}\qquad\frac{0.100_{09}\text{ mol of }O_2}{0.0087547_{27}\text{ mol of }C_8H_{18}}=11.4_{33}$$

Whew! Either way, that's less than the ideal ratio of 12.5 to one, and so we don't have enough oxygen to burn all the fuel and oxygen will be the limiting reagent. In engine terminology that means the engine is running rich, which would be bad. Turns out the actual "ideal" air:fuel ratio is 14.7:1 by mass, and that you still wouldn't be able to figure that out from this scenario, because gasoline is actually a mixture of many different hydrocarbons, not just octane.

$$\boxed{\text{Oxygen would be the limiting reagent. The engine would be running rich.}}$$

By the by, does it make sense that air intake metering systems in engines operate on a mass rather than a volume basis? While the ideal ratio of air mass to fuel mass stays constant with temperature and altitude, the same can not be said for a volume-based ratio! Using a mass airflow sensor avoids having to make a more complex calculation of the ideal airflow volume, based on many other variables, and thus makes engines both more reliable and cleaner-burning.

c. The hints tell us to assume that the air/fuel mixture comes into the cylinder at the temperature and pressure of the outside air. So the piston starts out with a 375 mℓ gulp of air and fuel at 68°F and 510 torr (absolute). We just need to convert the temperature into more sensible units, in particular, to an absolute scale:

$$T_{\text{initial}}=T_i=68^\circ\text{ F}=\frac{5}{9}[68-32]^\circ\text{ C}=20.^\circ\text{ C}=293\text{ K}\qquad P_{\text{initial}}=510\text{ torr}$$

As specified in the problem, the initial volume (V_i) would be 375mℓ. Assuming the fuel/air mixture doesn't preignite (a pretty good bet, even in Death Valley, given our fuel has an octane rating of 100!) the moles of gas in the piston before and after the compression stroke would be the same. We don't know what it is, but we know it is constant, that is, $\eta_i = \eta_f$. The volume and temperature are going to change, though, as is the pressure (which we need to determine).

$T_{\text{final}} = T_f = 85°\ C = 358\ K$ because the air is purported to be in thermal equilibrium with the cylinder after compression. The compression ratio of 13:1 tells us that V_f will be

$$V_{final} = V_f = \frac{1}{13}V_i = \frac{1}{13}(375\ \text{m}\ell) = 28.8_{46}\ \text{m}\ell$$

So now we can plug all these goodies into the ideal gas law. Initially, before the piston compresses:

$$P_i V_i = \eta_i R T_i \quad \Rightarrow \quad \frac{P_i V_i}{\eta_i T_i} = \frac{\eta_i R T_i}{\eta_i T_i} \quad \Rightarrow \quad \frac{P_i V_i}{\eta_i T_i} = R$$

Similarly, after the compression is complete the ideal gas law must still hold, and so

$$P_f V_f = \eta_f R T_f \quad \Rightarrow \quad \frac{P_f V_f}{\eta_f T_f} = \frac{\eta_f R T_f}{\eta_f T_f} \quad \Rightarrow \quad \frac{P_f V_f}{\eta_f T_f} = R$$

Combining these the two rightmost equations, which are both equal to R, gives us

$$\frac{P_f V_f}{\eta_f T_f} = R = \frac{P_i V_i}{\eta_i T_i} \quad \Rightarrow \quad \frac{P_f V_f}{\eta_f T_f} \times \frac{\eta_f T_f}{V_f} = \frac{P_i V_i}{\eta_i T_i} \times \frac{\eta_f T_f}{V_f} \quad \Rightarrow \quad P_f = \frac{\eta_f P_i V_i T_f}{\eta_i V_f T_i} = \frac{P_i V_i T_f}{V_f T_i}$$

(The last transformation drops η_i and η_f from the fraction because $\eta_i = \eta_f$, as discussed above.)

Plugging everything in, we get our answer:

$$\boxed{P_f = \frac{P_i V_i T_f}{V_f T_i} = \frac{(510\ \text{torr})(375\ \text{m}\ell)(358\ \text{K})}{(28.8_{46}\ \text{m}\ell)(293\ \text{K})} = 81_{01}\ \text{torr} = 8100\ \text{torr}\ \ (\text{or } 10._{66}\ \text{atmospheres!!!})}$$

d. Everything will be as in part (c), save the initial pressure and temperature.

Converting the temperature in Death Valley from 88°F to the Kelvin scale, which is absolute:

$$T_{\text{initial}} = T_i = 88°\ F = \frac{5}{9}[88 - 32]°\ C = 31._{11}°\ C = 304._{26}\ K \qquad P_{\text{initial}} = 770\ \text{torr}$$

and so, again employing the ideal gas law [simplified as for part (c)],

$$\boxed{P_f = \frac{P_i V_i T_f}{V_f T_i} = \frac{(770\ \text{torr})(375\ \text{m}\ell)(358\ \text{K})}{(28.8_{46}\ \text{m}\ell)(304._{26}\ \text{K})} = 11_{778}\ \text{torr} = 12000\ \text{torr}\ \ (\text{or } 15._5\ \text{atmospheres})}$$

e. Things that lower the final absolute pressure in an engine cylinder, after the fuel/air mixture is compressed, make it possible to use fuel with a lower octane rating. Lower ambient pressure is one such factor. What effect would colder air coming into the piston have on the equation for P_f, above? Well, the initial temperature is in the denominator of the equation above, so if it gets smaller, P_f will get larger. If T_f doesn't change, then colder incoming air means a higher pressure in the cylinder after compression, and a greater risk of preignition. So a higher octane rating might be required in cold weather. Is it fair to assume T_f does not change? Probably not. Car radiators don't get as hot in the winter as they do in the summer. But they still get hot, and the key thing to realize is that the drop in outside temperature (more specifically the % drop in the absolute outside temperature) will be much larger than the drop in the temperature of the engine (more specifically the % drop in the absolute temperature of the engine). Given that, we can be confident that

$\frac{T_f}{T_i} \approx \frac{T_{\text{engine}}}{T_{\text{outside air}}}$ will be greater in cold weather than in warm weather, as will P_f. As a result,

$$\boxed{\text{Fuel with a high octane rating will be more important in when it is cold than when it is hot.}}$$

[Which brings up this point: You are more likely to encounter "knocking," or "pinging," caused by pre-flame-front explosions and/or preignition in your engine when driving on a cold day in the low plains than you are under just about any other conditions. If you notice your engine hesitates or bucks when you accelerate on a day like that, or that a common hesitation grows worse, one of the first things to try is a higher octane fuel.. If that solves the problem, avoid going back to low octane fuel while it is cold, because knocking and preignition really hurt your engine!]

[The actual impact of temperature on knock is small, because your engine will pre-heat the air when it is cold. It does so by passing the intake air through part of the hot exhaust manifold. When you first start your car, though, the exhaust manifold isn't hot…and so stomping on the gas with a cold engine amounts to begging for trouble – and not just because of knock!]