Chemistry 123 **DUE FRIDAY, January 31, 2003 @ 6:30 p.m.** **Winter Term 2003**
Assignment #3 **1 Double-Sided Page / 4 Problems** **SHOW YOUR WORK! Instructor: R. Rossi**

Your Name: ____

At what time and on what day was this handed in? ______________________________

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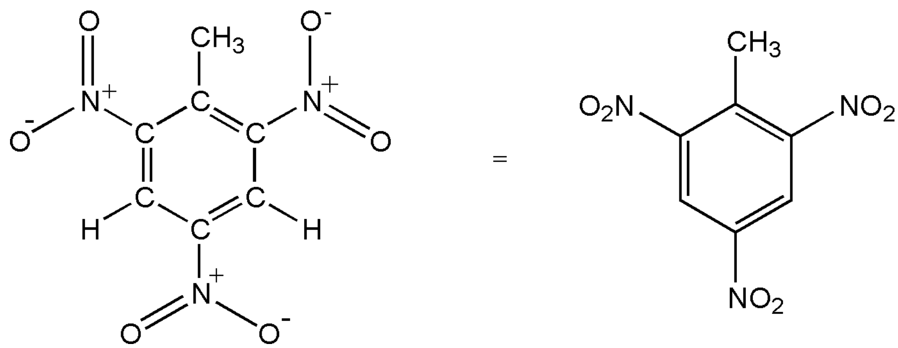
1. On October 30, 1961, in the remote Novaya Zamlya region, the former Soviet Union tested the most powerful nuclear device ever detonated on earth. This huge hydrogen bomb released the energy equivalent of the detonation of 57 megatons (57×10^6 metric tons) of TNT. "TNT" stands for 2,4,6-trinitrotoluene. The chemical structure of TNT is



The standard enthalpy of formation (ΔH°_f) of TNT is -65.5 kJ/mol. (TNT is a yellow, crystalline solid at 25°C and 1 atmosphere, but you don't want to remember that. Such knowledge can get you in trouble!)

a. TNT in its standard state at 25°C detonates to form $CO_{(g)}$, $C_{(s)}$, $H_{2(g)}$, and $N_{2(g)}$, using only the oxygen "built into" its chemical formula (viz, TNT is the only reactant). Write a balanced chemical equation for TNT's detonation reaction. Assume the carbon is formed as graphite.

b. Using the data tabulated in Appendix 4 of Zumdahl, calculate the standard enthalpy of reaction (ΔH° in kJ/mol of TNT) for the detonation of TNT in its standard state at 25°C.

c. Calculate the same quantity ($\Delta H^\circ_{\text{detonation}}$ for TNT) using bond energies from Table 8.4 in Zumdahl. Neglect the enthalpy change associated with phase transitions: assume everything is in the gas phase.

d. Which of your two ΔH° estimates do you expect should be more reliable? Why?

e. How much energy (in kJ) was released by the huge bomb tested in 1961? Base your answer on your *more reliable* $\Delta H^\circ_{\text{detonation}}$ value.

f. Imagine that the energy from this bomb had somehow been put to good use heating pots to make hot water for tea. How many 4.0 ℓ pots of hot (95°C) water could be made from cold Siberian water at 6°C using the amount of energy you determined in part (e)? (The heat capacity of liquid water is 1.0 $\text{cal} \cdot \text{g}^{-1} \cdot {}^\circ\text{C}^{-1}$.)

Helpful data: 1 metric ton = 1000 kg; 1 J = 0.239 cal; the density of $H_2O_{(\ell)}$ may be assumed to be 1.0 g/mℓ at all temperatures)

2. Derive an expression for the standard enthalpy change (ΔH°) of the following reaction:

$$2\,XNO_{(s)} + CO_{2(g)} \rightarrow X_2O_{3(s)} + CO_{(g)} + N_{2(g)} \qquad \Delta H^\circ$$

Please use the following thermochemical data:

$$X_{(s)} + CO_{2(g)} + \tfrac{1}{2} N_{2(g)} \rightarrow XNO_{(s)} + CO_{(g)} \qquad \Delta H^\circ_1 \quad \text{(Reaction 1)}$$

$$CO_{(g)} + \tfrac{1}{2} O_{2(g)} \rightarrow CO_{2(g)} \qquad \Delta H^\circ_2 \quad \text{(Reaction 2)}$$

$$2\,X_{(s)} + \tfrac{3}{2} O_{2(g)} \rightarrow X_2O_{3(s)} \qquad \Delta H^\circ_3 \quad \text{(Reaction 3)}$$

and express your answer in terms of ΔH°_1, ΔH°_2, and ΔH°_3.

Hint: Your answer will look like $\Delta H^\circ = \alpha \Delta H^\circ_1 + \beta \Delta H^\circ_2 + \gamma \Delta H^\circ_3$, where α, β, and γ are numbers you need to figure out. They can be fractions, and they can be either positive or negative.

3. Boron and hydrogen combine to form a large number of compounds called boranes (p. 905), one of which is pentaboron nonahydride (B_5H_9), a volatile liquid at room temperature. B_5H_9 vapor ignites spontaneously in air with a green flash to produce B_2O_3 (a white solid) and $H_2O_{(\ell)}$. The molar heat of combustion of $B_5H_{9(g)}$ has been reported to be – 4507.6 kJ·mol^{-1} at 25 °C. This is the molar enthalpy change (ΔH) for the reaction

$$B_5H_{9(g)} + 6\ O_{2(g)} \rightarrow 2.5\ B_2O_{3(s)} + 4.5\ H_2O_{(\ell)} \qquad \Delta H^o_{combustion} = -4507.6\ \text{kJ·mol}^{-1}$$

   a. Write the correctly balanced chemical reaction for which the molar enthalpy change is $\Delta H^o_f\ [B_5H_{9(g)}]$.

   b. Based on the molar heat of combustion given above, the fact that $\Delta H^o_f\ [B_5H_{9(g)}] = +73.2$ kJ·mol^{-1}, and the data in Appendix 4 of Zumdahl, calculate $\Delta H^o_f[B_2O_{3(s)}]$ in kJ·mol^{-1}.

Hint: If you like, you can check your answer by looking up the accepted value in a reference book! Zumdahl has a really wimpy table of thermodynamic data…try the CRC handbook, or use the NIST Chemistry WebBook online!)

Note: $\Delta H^o_f[B_{(s)}] = 0$. This tells you something about the standard state of boron.

4. As detailed in the "Chemical Impact" box on page 108 of Zumdahl, at high altitudes you can use gasoline with a lower octane rating than your engine would normally require. Suppose you've just purchased a new Toyota Prius hybrid electric vehicle (details at http://www.toyota.com/prius), who's small, high-efficiency engine employs a remarkable 13.0:1 compression ratio. That means that the gases injected into each piston are compressed to 1/13th their original volume before the spark plug is supposed to ignite them. (Surprisingly, the Prius engine doesn't require premium-grade fuel in order to avoid knocking, that is, the air/gasoline mixture in the piston exploding independently of the spark plug setting it off, because it uses an engine cycle called the Atkinson cycle, rather than the more-common Otto cycle.) Let's assume the Prius engine employs the 14:1 air:fuel mass ratio Zumdahl mentions (14 g of air for every gram of fuel; naughty Zumdahl for not specifying if he meant on a mass or mole basis!), and that the engine's coolant system manages to keep the engine's temperature at 85°C. Further, although gasoline is actually a mixture of many different hydrocarbons, let's keep things simple and assume your gas tank is filled with 100% isooctane, C_8H_{18}, and thus your fuel has an unusually high octane rating of exactly 100, so we needn't worry that it will actually pre- or auto-ignite and make trouble for the engine under any of these conditions.

   a. Write a balanced reaction for the complete combustion of isooctane ($C_8H_{18} + O_2 \rightarrow CO_2 + H_2O$)

   b. At a 14:1 air:fuel mass ratio and using pure isooctane as the fuel, would this engine be running lean (the fuel is the limiting reagent) or rich (oxygen is the limiting reagent)?

The Prius has a 1.5 ℓ, 4-cylinder engine, so each piston has a volume before compression of 375 mℓ. If you assume the air/fuel mixture can be treated as an ideal gas, and that it reaches thermal equilibrium with the engine (85°C) by the time it is fully compressed [both shaky assumptions], what would the final pressure be in a Prius engine cylinder just before the spark plug goes off, if the engine is operating in

   c. Leadville, Colorado, where today it is 68°F and the absolute pressure is about 510 torr?

   d. Death Valley, where today the temperature is 88°F and the absolute pressure is about 770 torr?

   e. In light of what Zumdahl says about the utility of lower octane ratings at high altitudes, or based on your own experiences or the examples in this problem, what effect do you think air *temperature* has on the octane needs of gasoline combustion engines? Explain your logic, and ideally, give a concrete example!

Hints: Assume the air/fuel mixture comes into the cylinder at the temperature and pressure of the outside air. You'll need to know something about the composition of air; if you don't know what you need already, look up "Earth's Atmosphere" in Zumdahl or go back to the Mystery Gas lab and read up on it. If any of the terminology used in this question leaves you confused, check out the excellent description of how a gasoline engine works at http://www.howstuffworks.com/engine.htm For more details on octane ratings and how they relate to engine characteristics, see http://www.howstuffworks.com/question90.htm but be forewarned that the quantitative descriptions given there for what an octane rating of 100 means and how readily certain compounds preignite is very misleading, I should probably even say dead wrong. Something to think about: What can you say about the likely home address of the person who answered the octane question, given the octane ratings they cite as examples? (Answer: They don't live in the mountains!)

Units: 101325 Pa = 760 torr $\quad T(C^\circ) = \frac{5}{9}[T(F^\circ) - 32°F] \quad$ 0°C = 273.15 K $\quad$ 1 C° = 1 K° $\quad$ 1 inch = 2.54 cm *(exactly)*