# Lecture Notes C: Thermodynamics I (cont)

Problem

How big would an asteroid have to be to evaporate the photic zone of Earth's oceans. The photic zone is the first 200m of the ocean, and is the depth which gets sufficient sunlight to support photosynthetic life.

Typical speed of an asteroid = 20 km/s

Surface area of water on the earth = 361.059 x 10^6 km^2

1) *Standard states*

Sea level acts as a "standard state"
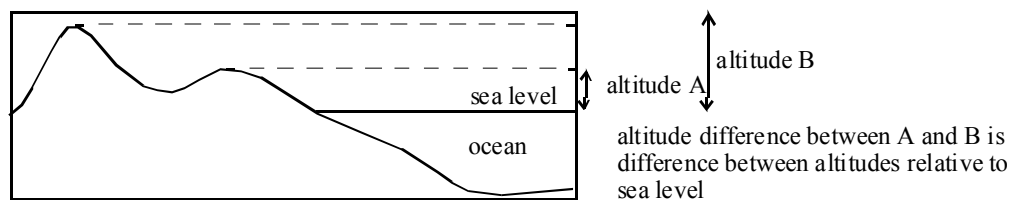
Chemical Standard States:

gas: 1 atm and 25°C.

substance in aqueous solution: 1M concentration

element or compound: most stable form at 1 atm and 25°C (O_2, H_2, graphite (C) etc.)

2) *Heats of formation (or Enthalpy's of formation)*

Enthalpy change associated with creating one mole of a chemical substance from the elements in their standard states,

$$H_2 (g) + O_2 (g) \rightarrow H_2O (l) \qquad \Delta H^o = -285.83 \text{ kJ}$$
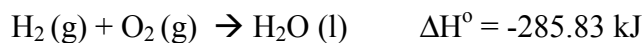
$$\Delta H_f^o (H_2O(l)) = -285.83 \text{ kJ/mole}$$

Problem

The heat of formation of $FeCO_3(s)$ is -740.57 kJ/mole. Write the corresponding reaction and give its reaction enthalpy.

3) *Calculating reaction enthalpies from heats of formation.*
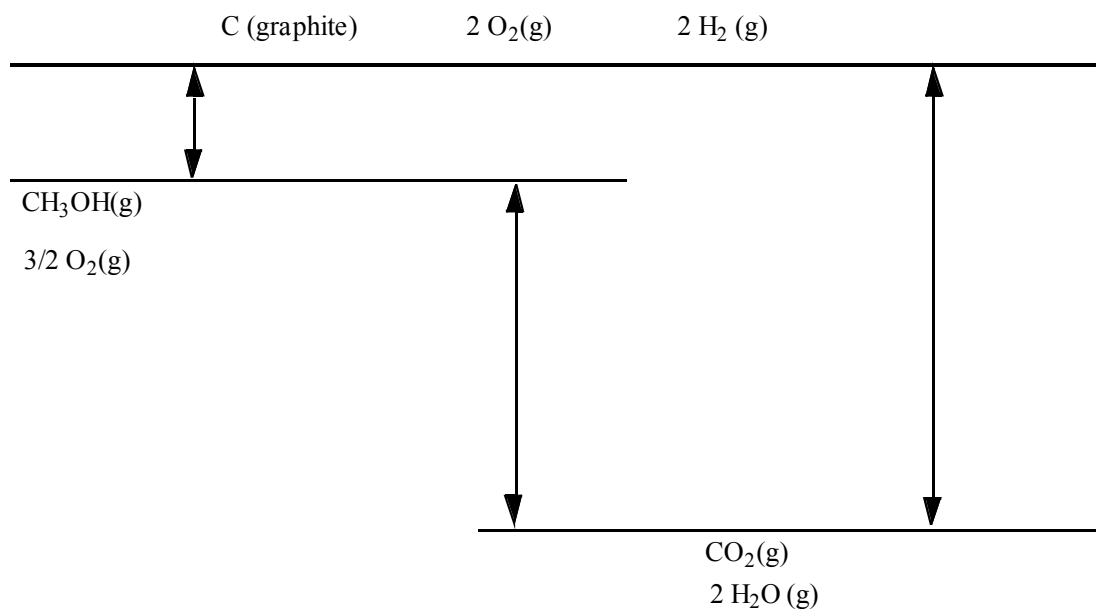
Elements in standard states

products

reactants

For a general reaction: aA + bB → cC + dD

Problem
Using the data in the appendix of the textbook, calculate the enthalpy of combustion for methanol vapor
(CH_3OH (g)). Assume the combustion produces CO_2 (g) and H_2O (g).

ΔH_f^o(CH_3OH (g)) = -200.66 kJ/mol ; ΔH_f^o(CO_2(g)) = -393.51 kJ/mol ; ΔH_f^o(H_2O (g)) = -241.82 kJ/mol

C (graphite)   2 O_2(g)   2 H_2 (g)

CH_3OH(g)

3/2 O_2(g)

CO_2(g)
2 H_2O (g)

Concept
Which of the following is correct?
        a) ΔH_f^o (CS_2(l)) = 89.70 kJ/mol ; ΔH_f^o (CS_2(g)) = 117.36 kJ/mol
        b) ΔH_f^o (CS_2(l)) = 117.36 kJ/mol ; ΔH_f^o (CS_2(g)) = 89.70 kJ/mol

Concept
State whether each of the following is obviously incorrect:

1) ΔH_f^o (N_2(g) at 25°C) = -100.0 kJ/mole   a) obviously incorrect   b) could be ok
2) ΔH_f^o (C_2H_4 (g) at 25°C) = 52.26 kJ/mole   a) obviously incorrect   b) could be ok
3) ΔH_f^o (Si (g) at 25°C) = 455.6 kJ/mole   a) obviously incorrect   b) could be ok
4) ΔH_f^o (As (g) at 25°C) = -302.5 kJ/mole   a) obviously incorrect   b) could be ok
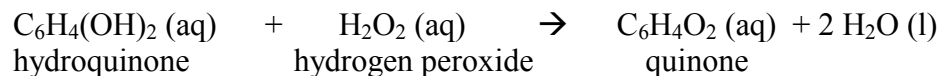
Problem
Hydrogen (perhaps produced by solar energy) would be an ideal alternative to fossil fuels, since it does not produce pollutants or green house gases when burned. The problem is that it is a gas, and hard to store and transport. What volume of hydrogen gas at 1.00 atm and 25°C would be required to produce an amount of energy equivalent to that produced by the combustion of a gallon of octane (C_8H_{18}) to form CO_2(g) and H_2O(l)?

ΔH_f^o (C_8H_{18}) = -208.6 kJ/mol ΔH_f^o (CO_2(g)) = -393.51 kJ/mol ΔH_f^o (H_2O (l)) = -285.83 kJ/mol

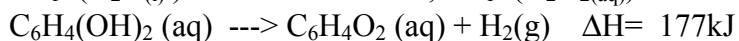Density of C_8H_{18} at 25°C is 0.7025 g/m

Problem
The Bombardier Beetle defends itself by spraying nearly boiling water on its predators. It has two glands on the tip of its abdomen. Each gland has two compartments. The inner compartment holds an aqueous solution of hydroquinone and hydrogen peroxide. The outer compartment holds a mixture of enzymes that catalyze the following reaction:

$$C_6H_4(OH)_2 \text{ (aq)} \quad + \quad H_2O_2 \text{ (aq)} \quad \rightarrow \quad C_6H_4O_2 \text{ (aq)} \; + 2 \; H_2O \text{ (l)}$$
$$\text{hydroquinone} \qquad \text{hydrogen peroxide} \qquad \text{quinone}$$

When threatened, the beetle squeezes some fluid from the inner compartment into the outer compartment, and sprays the mixture (which is near its boiling point) onto the predator.
The thermodynamic properties are:

$\Delta H_f^o \; (H_2O_{(l)}) = $ -285.83 kJ/mol ; $\Delta H_f^o \; (H_2O_{2(aq)}) = $ -191.17 kJ/mol
$C_6H_4(OH)_2 \text{ (aq)} \; \text{---> } C_6H_4O_2 \text{ (aq)} + H_2(g) \quad \Delta H= $ 177kJ

Suppose the concentration of the hydroquinone solution is 2.0M and the concentration of the H_2O_2 solution is 2.0M. What is the temperature of the solution after mixing 1ml of the hydroquinone solution with 1ml of the H_2O_2 solution?

Concept

Suppose the concentration of H_2O_2 is 2.5M, and that of hydroquinone is 2.0M. What happens to the final temperature of the solution?

    a) same as above   b) higher than above   c) lower than above

Suppose the bug mixes 0.5ml of the hydroquinone solution with 0.5ml of H_2O_2. What happens to the final temperature of the solution?

   a) same as above   b) higher than above   c) lower than above

4) Bond enthalpy

$$CH_{4\,(g)} \quad ---> \quad CH_{3(g)} + H_{(g)} \qquad \Delta H^o = 438kJ$$
$$C_2H_{6\,(g)} \quad ---> \quad C_2H_{5(g)} + H_{(g)} \qquad \Delta H^o = 410kJ$$
$$CHCl_{3\,(g)} \quad --> \quad CCl_{3(g)} + H_{(g)} \qquad \Delta H^o = 380kJ$$
$$CHBr_{3\,(g)} \quad --> \quad CBr_{3(g)} + H_{(g)} \qquad \Delta H^o = 377kJ$$
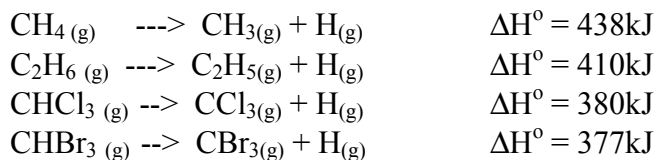
Average Bond Enthalpies in kJ/mole (Table 7.3)

	Molar Enthalpy of Atomization	H-	C-	C=	C	N-	N=	N	O-	O=
H	218.0	436	413			391			463	
C	716.7	413	348	615	812	292	615	891	351	728
N	472.2	391	292	615	891	161	418	945		
O	249.2	463	351	728					139	498
S	278.8	339	259	477						
F	79.0	563	441			270			185	
Cl	121.7	432	328			200			203	
Br	111.9	366	276							
I	106.8	299	240							

Problem

Estimate ΔH for the following reaction, using the bond enthalpy's listed above. Compare this to that obtained from the table at the end of the book.

$$H_2CCH_2 + H_2 \; --> \; H_3CCH_3$$
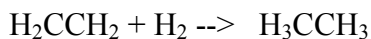
5) Molar Enthalpy of Atomization

(element in standard state)   → (single, gas-phase atom)   ΔH

Gas-phase atoms provides a convenient reference when using bond enthalpies to estimate the heat of formation of a molecule.

Problem

Estimate the heat of formation of H_2CCH_2 using the atomization energies and bond enthalpy's in the table.

6) Clarification: Sign of ΔH and conventions for ΔH_f^o vs. bond enthalpies

7) Enthalpies of Formation versus Bond Enthalpies

	2CO $_{(g)}$	+	O$_{2 (g)}$	$\rightarrow$	2CO$_{2 (g)}$
ΔH_f^o (kJ/mol)	-110.52		0		-393.51

Molar Enthalpy of Vaporization: C = 716.7kJ, O = 249.2kJ
Bond Enthalpies: CO triple bond: 1080kJ   O=O : 498kJ   C=O : 728kJ from table (really 804 in CO$_2$)

Separated Atoms   2 C, 4 O

Standard State   2C(graphite)   2 O$_2$ (g)

Reactants   2 CO (g)   O$_2$ (g)

Products   2 CO$_2$ (g)