Thermochemistry (Chapter 6)

General Concepts and Terminology

1. Kinetic and Potential Energy -- review

2. Chemical Energy:

   Potential energy associated with chemical bonds:

   bond breaking: energy is required
   bond making: energy is liberated

3. Kinetic Theory:

   A simple model that "explains" the heat energy content of a substance in terms of atomic and molecular motions

4. Heat Changes in Chemical Reactions:

   exothermic *reaction*: heat is a product of the reaction
   reaction gives off heat to the surroundings
   system warms up

   endothermic *reaction*: heat is essentially a reactant
   reaction absorbs heat from the surroundings
   system cools off

Calorimetry -- measurement of heat changes

1. Heat Capacity:

   amount of heat energy required to raise the temp of substance by 1 °C

   units: energy / temp { J / °C or kJ / °C or cal / °C }

   1.00 cal = 4.184 joule

   quantity of heat = (heat capacity) x Δt

2. Specific Heat:

Heat Capacity of specified mass of substance (1 gram)

units: usually J / g ℃ or cal / g ℃

e.g., **specific heat of water = 1.00 cal / g ℃ = 4.18 J / g ℃**

quantity of heat = (specific heat) x mass x Δt
= J / g ℃ x g x ℃

3. Molar Heat Capacity:

Heat Capacity per mole of a substance

e.g., molar heat capacity of water = 18.0 cal / mole ℃

Problem:

The temp of 250 g H_2O is raised from 25.0℃ to 30.0℃. How much heat energy is required?

Δt = 30.0 - 25.0 = 5.0 ℃

amount of heat = (1.00 cal / g ℃) x (250 g) x (5.0 ℃)
= 1,250 cal = 1.25 Kcal

= 1,250 cal x 4.184 J / cal
= 5,320 J = 5.32 kJ

Enthalpy Changes (ΔH) in Chemical Reactions

1. Energy is a ***state function***

the energy change (ΔE) of a reaction depends only on the initial and final states of the system -- not on the specific pathway

OMIT (until 2nd semester):
Section 6.3 – First Law of Thermodynamics ($\Delta E = q + w$)

2. Enthalpy (H) -- "Heat Content"

the total energy of a chemical system at constant pressure

$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$

endothermic *reaction*: $\Delta H > 0$ (positive) -- heat is absorbed
exothermic *reaction*: $\Delta H < 0$ (negative) -- heat is released

3. Standard Heat of Reaction ($\Delta H°$)

$\Delta H°$ = the value of ΔH for a reaction:

- under standard conditions (temp = 25°C, pressure = 1.00 atm)
- with actual # moles specified by coefficients in balanced equation

e.g., reaction for the combustion of ethylene:

$$C_2H_4\ (g) + 3\ O_2\ (g) \longrightarrow 2\ CO_2\ (g) + 2\ H_2O\ (l)$$

$\Delta H° = -1{,}411$ kJ (very exothermic)

i.e., 1,411 kJ of heat energy are released in the reaction of 1 mole of C_2H_4 with 3 moles of O_2

If 10.0 g of C_2H_4 are burned, how much heat is produced?

$(10.0\ \text{g}) \times (1\ \text{mole}\ C_2H_4 / 28.0\ \text{g}) \times (1{,}411\ \text{kJ} / \text{mole}\ C_2H_4)$
$= 504$ kJ

4. Manipulating Thermochemical Equations

if reaction is reversed, change sign of $\Delta H°$

if reaction is multiplied or divided by a factor, apply same factor to $\Delta H°$

$\Delta H°$ for overall reaction = sum of $\Delta H°$ values for individual reactions

Problem:

Given the following thermochemical equations,

(eq 1) $C_2H_4\ (g) + 3\ O_2\ (g) \longrightarrow 2\ CO_2\ (g) + 2\ H_2O\ (l)$
$\Delta H° = -\ 1411$ kJ

(eq 2) $C_2H_5OH\ (l) + 3\ O_2\ (g) \longrightarrow 2\ CO_2\ (g) + 3\ H_2O\ (l)$
$\Delta H° = -\ 1367$ kJ

calculate $\Delta H°$ for the following reaction:

$$C_2H_4\ (g) + H_2O\ (l) \longrightarrow C_2H_5OH\ (l)$$

reverse 2nd reaction to put C_2H_5OH on product side
then rewrite 1st equation and add them together

(eq 2) $2\ CO_2\ (g) + 3\ H_2O\ (l) \longrightarrow C_2H_5OH\ (l) + 3\ O_2\ (g)$

$\Delta H° = +\ 1367$ kJ (**note the sign change ! ! !**)

(eq 1) $C_2H_4\ (g) + 3\ O_2\ (g) \longrightarrow 2\ CO_2\ (g) + 2\ H_2O\ (l)$
$\Delta H° = -\ 1411$ kJ

net: $C_2H_4\ (g) + H_2O\ (l) \longrightarrow C_2H_5OH\ (l)$

{ ***note***: $3\ O_2$, $2\ CO_2$, and $2\ H_2O$ cancel out }

$$\Delta H° = \Delta H°_1 + \Delta H°_2 = 1367 + (-\ 1411) = -\ 44 \text{ kJ}$$

5. Standard Heat of Formation

Standard Heat of Formation of a substance:

ΔH°_f = ΔH° *for the formation of one mole of substance from its elements in their standard states*

a "formation" reaction:

$$H_2\,(g) \;+\; 1/2\ O_2\,(g) \longrightarrow H_2O\,(l)$$

ΔH°_f (liq water) = - 286 kJ/mole

ΔH°_f is a property of a substance -- see text for examples

practice writing formation reactions -- e.g., Na_2SO_4

$$2\ Na\,(s) \;+\; 2\ O_2\,(g) \;+\; S\,(s) \longrightarrow Na_2SO_4\,(s)$$

ΔH°_f = - 1385 kJ/mole

6. Hess' Law of Heat Summation

calculate ΔH° for a reaction from tabulated ΔH°_f values

$$\Delta H^\circ = \sum \Delta H^\circ_f\ (\text{products}) - \sum \Delta H^\circ_f\ (\text{reactants})$$

Problem:

Determine ΔH° for the following reaction from ΔH°_f values.

$$2\ H_2O\,(l) \;+\; CaSO_4\,(s) \longrightarrow CaSO_4 \bullet 2\ H_2O\,(s)$$

$$\begin{aligned}\Delta H^\circ &= \Delta H^\circ_f\,[CaSO_4 \bullet 2\ H_2O\,(s)] \\ &\quad - \{\, \Delta H^\circ_f\,[CaSO_4\,(s)] + 2\ \Delta H^\circ_f\,[H_2O\,(l)]\,\}^* \\ &= (-\ 2021.1) - \{\, (-\ 1432.7) + 2\,(-285.9)\,\} \\ &= -\ 16.6\ \text{kJ}\end{aligned}$$

{ *units: e.g., (2 moles) x (285.9 kJ/mole) = kJ }

***Summary*: two ways to get ΔH° for a reaction**:

- by manipulating 2 or more given equations, then adding their ΔH°'s
- from tabulated ΔH°_f values using Hess' Law