

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 $\text{J} / \text{g } ^\circ\text{C}$ or $\text{cal} / \text{g } ^\circ\text{C}$

e.g., **specific heat of water** = $1.00 \text{ cal} / \text{g } ^\circ\text{C}$ = $4.18 \text{ J} / \text{g } ^\circ\text{C}$

$$\begin{aligned} \text{quantity of heat} &= (\text{specific heat}) \times \text{mass} \times \Delta t \\ &= \text{J} / \text{g } ^\circ\text{C} \times \text{g} \times ^\circ\text{C} \end{aligned}$$

3. Molar Heat Capacity:

Heat Capacity per mole of a substance

e.g., molar heat capacity of water = $18.0 \text{ cal} / \text{mole } ^\circ\text{C}$

Problem:

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

$$\Delta t = 30.0 - 25.0 = 5.0 \text{ } ^\circ\text{C}$$

$$\begin{aligned} \text{amount of heat} &= (1.00 \text{ cal} / \text{g } ^\circ\text{C}) \times (250 \text{ g}) \times (5.0 \text{ } ^\circ\text{C}) \\ &= 1,250 \text{ cal} = 1.25 \text{ Kcal} \\ &= 1,250 \text{ cal} \times 4.184 \text{ J} / \text{cal} \\ &= 5,320 \text{ J} = 5.32 \text{ kJ} \end{aligned}$$

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

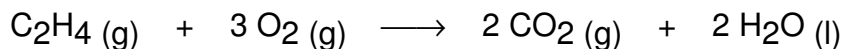
exothermic reaction: $\Delta H < 0$ (negative) -- heat is released

3. Standard Heat of Reaction (ΔH°)

ΔH° = 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:



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

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?

$$\begin{aligned} & (10.0 \text{ g}) \times (1 \text{ mole C}_2\text{H}_4 / 28.0 \text{ g}) \times (1,411 \text{ kJ / mole C}_2\text{H}_4) \\ & = 504 \text{ kJ} \end{aligned}$$

4. Manipulating Thermochemical Equations

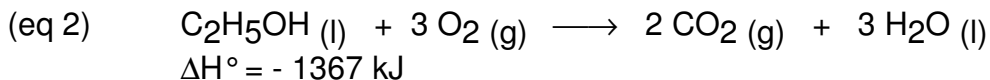
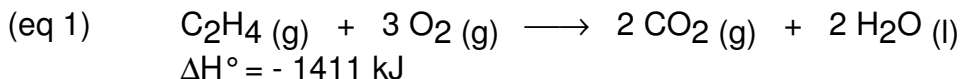
if reaction is reversed, change sign of ΔH°

if reaction is multiplied or divided by a factor, apply same factor to ΔH°

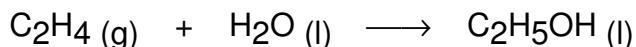
ΔH° for overall reaction = sum of ΔH° values for individual reactions

Problem:

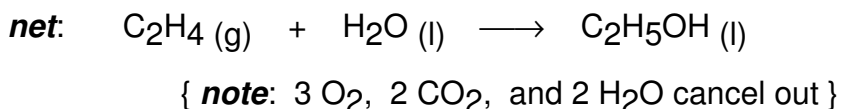
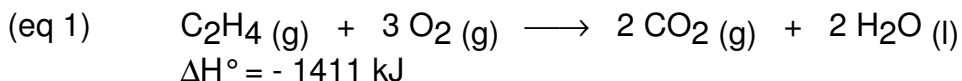
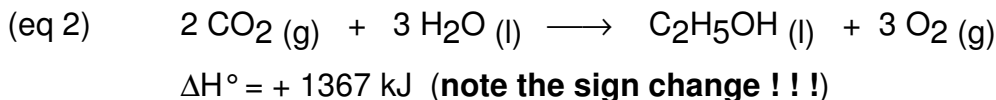
Given the following thermochemical equations,



calculate ΔH° for the following reaction:



reverse 2nd reaction to put $\text{C}_2\text{H}_5\text{OH}$ on product side
then rewrite 1st equation and add them together



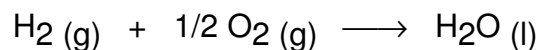
$$\Delta H^\circ = \Delta H^\circ_1 + \Delta H^\circ_2 = 1367 + (- 1411) = - 44 \text{ kJ}$$

5. Standard Heat of Formation

Standard Heat of Formation of a substance:

$$\Delta H^{\circ}_f = \Delta H^{\circ} \text{ for the formation of one mole of substance from its elements in their standard states}$$

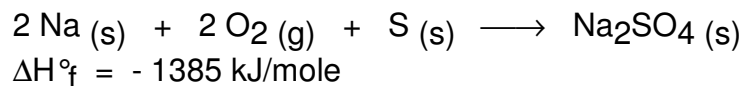
a "formation" reaction:



$$\Delta H^{\circ}_f (\text{liq water}) = -286 \text{ kJ/mole}$$

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

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



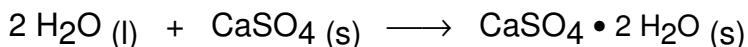
6. Hess' Law of Heat Summation

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.



$$\begin{aligned} \Delta H^{\circ} &= \Delta H^{\circ}_f [\text{CaSO}_4 \cdot 2 \text{H}_2\text{O} (\text{s})] \\ &\quad - \{ \Delta H^{\circ}_f [\text{CaSO}_4 (\text{s})] + 2 \Delta H^{\circ}_f [\text{H}_2\text{O} (\text{l})] \}^* \\ &= (-2021.1) - \{ (-1432.7) + 2(-285.9) \} \\ &= -16.6 \text{ kJ} \\ &\quad \{^* \text{units: e.g., (2 moles)} \times (285.9 \text{ kJ/mole}) = \text{kJ} \} \end{aligned}$$

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