CHEM 115
Calorimetry and Hess's Law

Lecture 14
Prof. Sevian

Note: The first part of the lecture will be a continuation of Lecture 13 (which is not reprinted on the Lecture 14 notes posted online). So, please bring pages 16-22 of the Lecture 13 notes with you to class, as well as what is in this handout.

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Agenda

- Relevant chemistry in the news
- Transfer of energy and the Law of Conservation of Energy
- Calorimetry examples
  - Heat transfer (q) from a hot metal block placed in a known amount of cool water
  - Heat of reaction [$\Delta H = q$ / (moles reacted)] when two solutions, each containing one reactant, are mixed
- Hess's law
  - Enthalpy is a state function, so path doesn't matter in a change
  - Three rules of how ΔH changes correspond to algebraic manipulations of chemical equations
  - Examples of using Hess's law
  - A relevant challenge problem: maximizing energy production while minimizing carbon dioxide production

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US government action on greenhouse gases

New York Times article 3/23/09: EPA (Environmental Protection Agency) moves toward regulating greenhouse gases

http://www.nytimes.com/2009/03/24/science/earth/24epa.html?_r=1&hp

1955: Air Pollution Control Act enacted by Congress provides funding for research on air pollution

1963: Clean Air Act Establishes national program to address air pollution and funds to research techniques to minimize it

1967: Air Quality Act Establishes enforcement procedures for air pollution problems and more funding for research

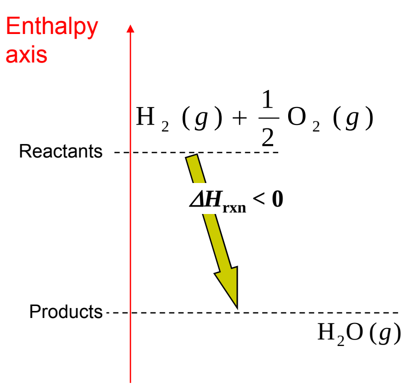
1970: Clean Air Act Establishes standards for air quality & emissions, and implementation plans and regulation

1977 and 1990: Amendments to the Clean Air Act Authorize and expand various programs

April 2, 2007: US Supreme Court orders EPA to determine whether CO_2 and other greenhouse gases are pollutants under Clean Air Act

Last Friday: EPA sent "endangerment finding" to US Office of Mgmt & Budget to request permission to regulate motor vehicle emissions

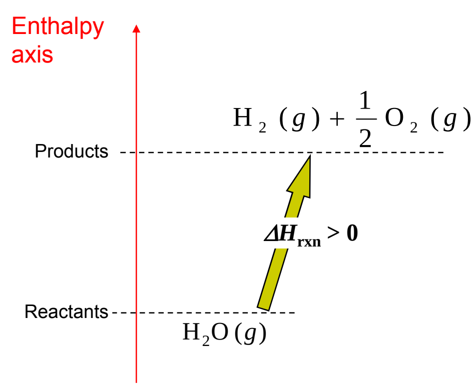
Enthalpy Changes



Two ways to write the **forward reaction** with enthalpy information

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g) + 241.8\,kJ$$

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g) \qquad \Delta H = -241.8\,kJ$$

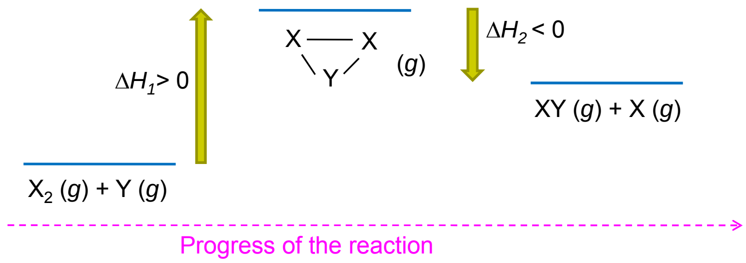


Two ways to write the **reverse reaction** with enthalpy information

$$H_2O(g) + 241.8\,kJ \rightarrow H_2(g) + \frac{1}{2}O_2(g)$$

$$H_2O(g) \rightarrow H_2(g) + \frac{1}{2}O_2(g) \qquad \Delta H = +241.8\,kJ$$

Clicker question #1 (for today)
(was labeled clicker question #3 inLecture 13)



Which equation correctly represents the overall reaction that is represented in the diagram? (note: pick one of the two correct answers)

(A) $X_2\ (g) + Y\ (g) \rightarrow XY\ (g) + X\ (g) + \Delta H_{total}$, where $\Delta H_{total} > 0$

(B) $X_2\ (g) + Y\ (g) + \Delta H_{total} \rightarrow XY\ (g) + X\ (g)$, where $\Delta H_{total} > 0$

(C) $X_2\ (g) + Y\ (g) \rightarrow XY\ (g) + X\ (g)$ and $\Delta H_{rxn} > 0$

(D) $X_2\ (g) + Y\ (g) \rightarrow XY\ (g) + X\ (g)$ and $\Delta H_{rxn} < 0$

What $q = mC\Delta T$ means

- C depends on the material and on its phase
  - Water:
    - Liquid has C = 4.184 J/g·K (avg value to use for range of 0 to 100°C)
    - Solid has C = 2.092 J/g·K
    - Vapor (gas) has C = 1.841 J/g·K
  - Silver (solid) has C = 0.233 J/g·K
  - Marble has C = 0.880 J/g·K
  - Sand has C = 0.835 J/g·K
  - Polyethylene has C ranging from 2.3 to 2.9 J/g·K
- Within a phase of a material, C depends a little bit on temperature, but it is often ok to make the assumption that it is relatively constant over the temperature range of the experiment
  - Example: liquid water
    - C = 4.1855 J/g·K at 15°C
    - C = 4.1813 J/g·K at 25°C

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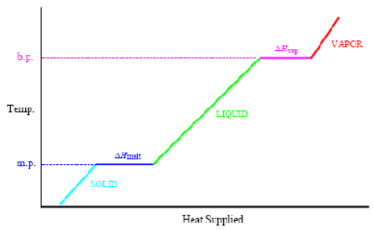
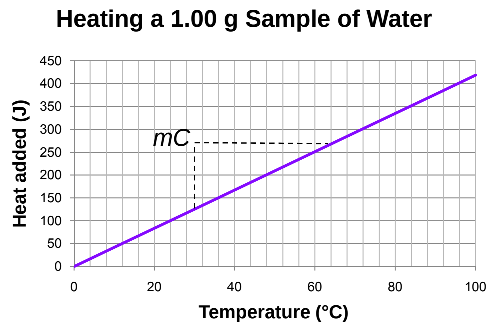
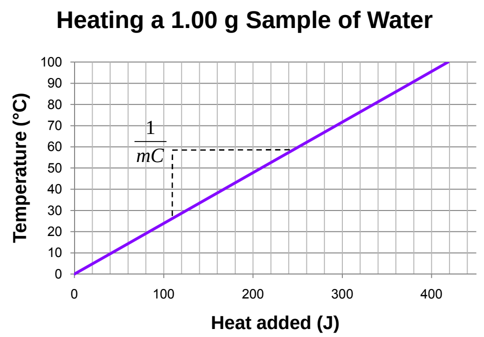
What $q = mC\Delta T$ means

- One of these is a typical "heating curve" (shown over the liquid phase)



- How is the other graph related to it?
- Slope of the *heat* vs. *T* curve is equal to *mC*





Clicker questions #2 and 3

A calorimetry experiment was set up as follows:

> One solution with a mass of 20.0 g has 1.2 moles of reactant #1 in it. A second solution of mass 30.0 g has 1.2 moles of reactant #2 in it. Both reactant solutions are at room temperature. The reactant solutions are both poured into an empty beaker at the same time. Heat is produced when the reaction occurs, and the temperature of the solution increases.

<u>First question</u>

If the two reactants react in a 1:1 mole ratio to produce 1 mole of a product, how many moles of product are formed?

(A) 1.0 mole of product
(B) 1.2 moles of product
(C) 2.4 moles of product

<u>Second question</u>

What is the mass of solution that absorbs the heat produced during the reaction?

(A) 20.0 g
(B) 30.0 g
(C) 50.0 g

What we've learned so far

- Systems can either lose or gain heat during a change
  - Exothermic: heat flows out to surroundings
  - Endothermic: heat flows in to system
- Heat changes can be measured using calorimetry
  - Typical calorimetry uses liquid water as the surroundings
  - Liquid water either absorbs heat from the system (T_{water} increases) or gives heat to the system (T_{water} decreases)
  - If calorimeter is well insulated then
    $q_{water} = -q_{system}$, and
    $q_{water} = m_{water} C_{water} \Delta T_{water}$ (where C_{water} is slope of line for liquid region)
- Under typical laboratory conditions (constant pressure), heat change is equal to enthalpy change
- Enthalpy change is a state function (path independent)

What's next: Because of its path independence, enthalpy change can be calculated by several methods:

- Hess's law
- Standard heats of formation
- Bond dissociation energies (second semester general chem)

Calorimetry Example

Exercise on p. 186

When 50.0 mL of 0.100 M $AgNO_3$ and 50.0 mL of 0.100 M HCl are mixed in a constant-pressure calorimeter, the temperature of the mixture increases from 22.20 ºC to 23.11 ºC. The temperature increase is caused by the following reaction:

Complete rxn: $AgNO_3\ (aq) + HCl\ (aq) \rightarrow AgCl\ (s) + HNO_3\ (aq)$

Net ionic: $Ag^+\ (aq) + Cl^-\ (aq) \rightarrow AgCl\ (s)$

Calculate ΔH for this reaction in kJ/mol $AgNO_3$, assuming that the combined solution has density and heat capacity approximately equal to that of pure water since the solution is dilute. (D = 1.00 g/mL and C = 4.184 J/g·ºC)

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State functions don't depend on path

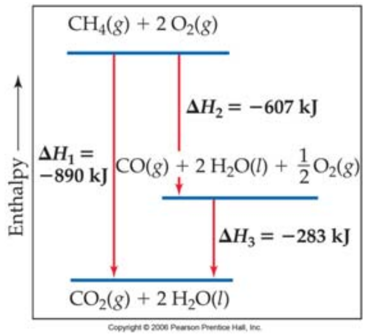
Hess's Law states that:
If a reaction is carried out in a series of steps, ΔH for the overall reaction will be equal to the sum of the ΔH values for the individual steps.

Overall reaction:
$CH_4\ (g) + 2\ O_2\ (g) \rightarrow CO_2\ (g) + 2\ H_2O\ (l)$
shown in diagram as $\Delta H_{overall} = \Delta H_1 = -890$ kJ

Sum of the individual steps:
Overall reaction can be broken up into two steps that sum to equal the Overall Reaction:
a) $CH_4\ (g) + 2\ O_2\ (g) \rightarrow CO\ (g) + 2\ H_2O\ (l) + ½\ O_2\ (g)$
b) $CO\ (g) + ½\ O_2\ (g) \rightarrow CO_2\ (g)$

Sum is $CH_4\ (g) + 2\ O_2\ (g) \rightarrow CO_2\ (g) + 2\ H_2O\ (l)$

$\Delta H_{sum} = \Delta H_2 + \Delta H_3 = (-607\text{ kJ}) + (-283\text{ kJ})$
$= -890$ kJ

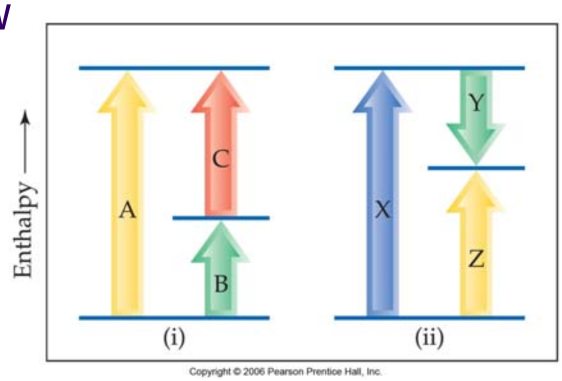


More on Hess's Law

- Concept is simple, mathematics seems more complicated

  How is ΔH_A related to ΔH_B and ΔH_C?

  How is ΔH_X related to other enthalpy changes in the diagram?



$$\Delta H_A = \Delta H_B + \Delta H_C$$
$$\Delta H_X = \Delta H_Z + (-\Delta H_Y) = \Delta H_Z - \Delta H_Y$$

- Hess's law says that ΔH_{rxn} for a given reaction is equal to products minus reactants of the heats of formation for the chemicals involved in the reaction

Summary of Hess's law

- A reaction and its reverse have equal magnitude, opposite sign ΔH values
  - If A → B has ΔH = 100 kJ, then B → A has ΔH = –100 kJ
- If you multiply a reaction by a factor, then you multiply the ΔH by the same factor
  - If A → B has ΔH = 100 kJ, then 2A → 2B has ΔH = 200 kJ
- When you add two reactions, you add the ΔH values
  - If A → B has ΔH = 100 kJ, and C → D has ΔH = 50 kJ, then A + C → B + D has ΔH = 100 + 50 kJ = 150 kJ

What is a heat of formation?
What is a formation reaction?

- Standard heat (or enthalpy) of formation, ΔH_f^o, is the enthalpy of reaction associated with a formation reaction
- A formation reaction for a compound is a reaction that produces one mole of that compound from the pure elements in their standard states (p=1 atm, T=25ºC)

Examples of formation reactions and their heats of formation:

Formation of sodium bicarbonate, $NaHCO_3$ (*s*):

$$\mathrm{Na}\,(s) + \frac{1}{2}\mathrm{H_2}\,(g) + \mathrm{C}\,(s) + \frac{3}{2}\mathrm{O_2}\,(s) \rightarrow \mathrm{NaHCO_3}\,(s) \qquad \Delta H_f^o = -947.7\, {}^{kJ}\!/_{mol}$$

Formation of ethylene, C_2H_4 (*g*):

$$2\,\mathrm{C}\,(s) + 2\,\mathrm{H_2}\,(g) \rightarrow \mathrm{C_2H_4}\,(g) \qquad \Delta H_f^o = +52.30\, {}^{kJ}\!/_{mol}$$

Using Heats of Formation to Calculate Enthalpies of Reaction

Standard enthalpies of formation

$\Delta H_f^o[H_2O(l)] = -285.83\ ^{kJ}/_{mol}$

$\Delta H_f^o[CO_2(g)] = -393.5\ ^{kJ}/_{mol}$

$\Delta H_f^o[C_2H_5OH(l)] = -277.7\ ^{kJ}/_{mol}$

Example problem: Use standard enthalpies of formation to calculate the enthalpy of reaction for the combustion of ethanol, C_2H_5OH (l).

Solution: Start by writing the reaction

$$C_2H_5OH\ (l) + 3O_2\ (g) \rightarrow 2\ CO_2\ (g) + 3\ H_2O(l) \qquad \Delta H_f^o = ?$$

Method 1: Write all the formation reactions for any non-elements at standard state. Then figure out how to arrange those reactions to sum to the overall reaction and do the same to the ΔH's.

Method 2: Use the equation $\Delta H_{rxn}^o = \sum_{products} \Delta H_f^o - \sum_{reactants} \Delta H_f^o$