CHEM 103
Calorimetry and Hess's Law

Lecture Notes
March 23, 2006
Prof. Sevian

Announcements

- Exam #2 is next Thursday, March 30
  - Study guide, practice exam, and practice exam answer key are already posted on the course website
  - Where to take your exam:
    - Last names starting with A-H, room M-1-207
    - Last names starting with I-Z, in our regular lecture hall
- Study guide is available at the bookstore
  - The bookstore is anxious to get the books off the shelf
- Group problem #5 from Tuesday: every team got a perfect score!

Map of this chapter

- Energy in chemistry
  - Kinetic and potential energy changes as heat energy is added to a pure substance
- First law of thermodynamics
  - Transfer of energy and the Law of Conservation of Energy
  - Endothermic vs. exothermic changes
  - Enthalpy
- Measuring heat energy (enthalpy) changes (ΔH) in the laboratory
  - Heat energy and heat capacity of a material
  - Calorimetry technique
- Using laboratory measurements to calculate ΔH for reactions we can't measure in the lab

Reversing the direction of a reaction

1) Formation of water

$H_2\,(g) + \frac{1}{2}\,O_2\,(g) \rightarrow H_2O\,(l) \qquad \Delta H = -285.83\text{ kJ}$

http://jws-edcv.wiley.com/college/bcs/redesign/student/resource/0,12264,_0471150584_BKS_1907__10615_3446__,00.html

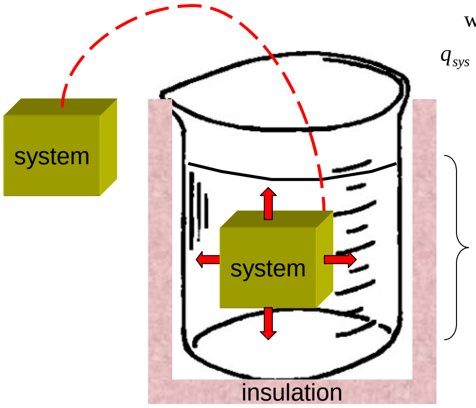
2) Electrolysis of water

$H_2O\,(l) \rightarrow H_2\,(g) + \frac{1}{2}\,O_2\,(g) \qquad \Delta H = +285.83\text{ kJ}$

http://jchemed.chem.wisc.edu/JCESoft/CCA/samples/cca3ElecW02.html

Back to Liquid Water's Capacity to Absorb Heat Energy

Measuring heat transferred
from a system



Known quantity (mass)
of water in beaker

Problem Solving Strategy

$q_w = m_w C_w \Delta T_w$

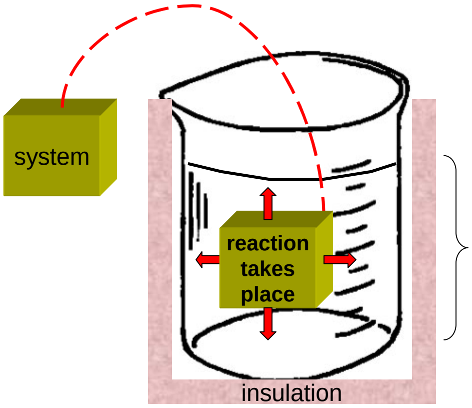
where $\Delta T_w = \textit{temp change of } \mathrm{H_2O}$

q_{sys} *is opposite of* q_w

Beaker image: core.ecu.edu/chem/chemlab/ equipment/ebeaker.htm

Calorimetry

Measuring heat transferred
from a system



100.0 g
of H_2O

Problem Solving Strategy

$q_w = m_w C_w \Delta T_w$

where $\Delta T_w = \textit{temp change of } \mathrm{H_2O}$

q_{sys} *is opposite of* q_w

Given information

Mass of water = 100.0 g

Temperature of water before = 23.3ºC

Temperature of water after = 47.3ºC

C_{water} = 4.184 J/g·K

The confusing part is that once the change takes place, the system and the water are mixed together, and the heat energy gets distributed throughout the mixture

Beaker image: core.ecu.edu/chem/chemlab/ equipment/ebeaker.htm

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)

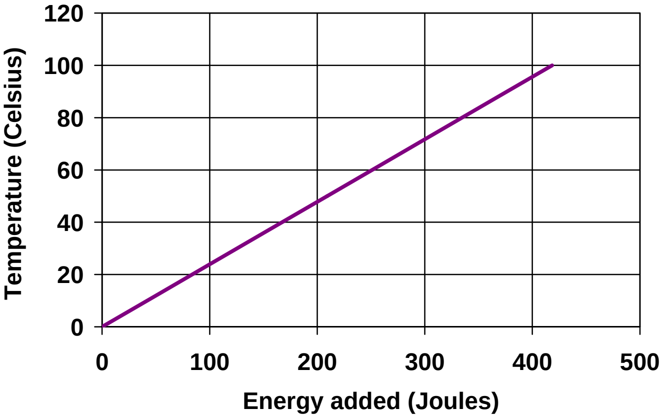
Calorimetry problems

- Water is something we know a lot of very accurate data about
- Measure heat changes that get transferred to water by a (reaction) system
- Calculate amount of heat that water received from or gave to a system
- If the calorimeter is insulated, then all heat that enters (or leaves) the water must have come from (or gone to) the system being studied
- Figure out things about the system that you didn't know before

Water: A Useful Substance

- Liquid water’s capacity to absorb heat (C) is enormous compared to most materials
- Heat capacity of water is very accurately known: 4.184 Joules per gram per degree Kelvin
- What this means:
  - If you have one gram of liquid water
  - To raise its temperature by 1 Kelvin (equal to 1ºC)
  - Takes 4.184 Joules of energy (equal to 1 calorie)
- Since $q = m\,C\,\Delta T$, if you are working with water then you know C. Therefore, if you have a specific quantity of water, and you measure the temperature it changes by, you can calculate the heat that transferred.

For a 1.00-gram sample of liquid water



What happens if you add more heat energy to liquid water at 100ºC?

- It boils
- What is boiling?
  - There is a statistical range of kinetic energies (velocities) of particles in the liquid
  - Some particles will always have enough energy to break away from attractive forces that keep them in liquid → evaporation
  - As temperature rises, eventually it is high enough that so many particles can break away that their gas pressure (vapor pressure) equals the pressure of the surroundings → boiling
- Boiling continues with no change in temperature until all liquid particles have converted to gas phase

Heating Curve of 1.00-gram Sample of Some Substance (not H_2O) at Standard Pressure

A = solid below melting*

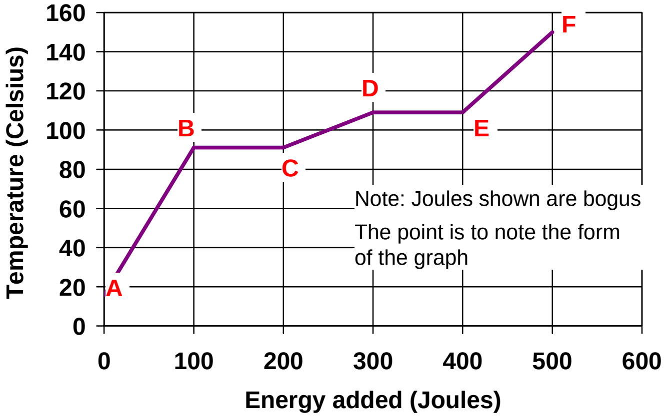
B = solid has reached melting temperature, and is beginning to melt*

C = liquid at melting temperature, has just completed melting

D = liquid has reached boiling temperature, and is beginning to boil*

E = gas at boiling temperature, has just completed boiling*

F = gas above boiling temperature

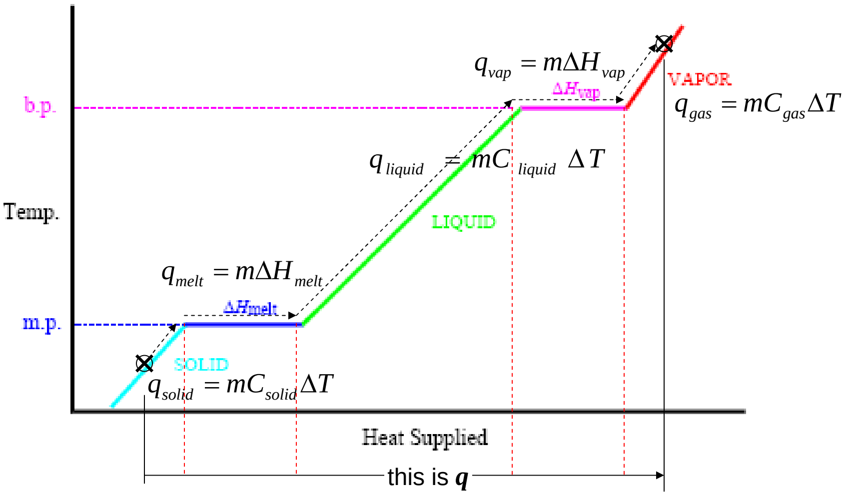


Note: Joules shown are bogus

The point is to note the form of the graph

See http://www.chemistry.wustl.edu/~gelb/gchem/materials/phases/

Heat Changes More Generally

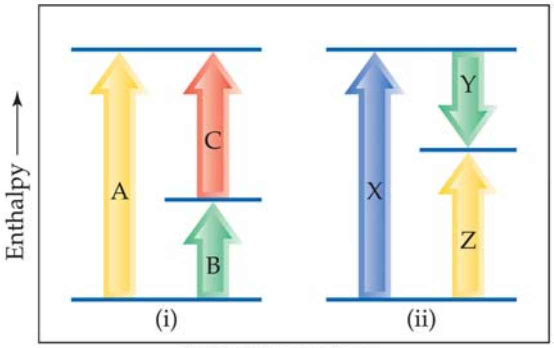


More on Hess's Law

- 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?



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- 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

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:

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

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

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

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 Δ*H*'s.

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