

A checklist of concepts to learn and skills to master in section: Thermochemistry

Learning Objectives for September Y5/MED school year 2005/2006

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Learning objectives

- Describe, distinguish, and relate the following properties. Predict whether these properties increase, decrease, or stay the same over the course of a given chemical or physical change:
Temperature, thermal energy
- Understand heat on both theoretical and experimental levels.
- Relate heat transferred to changes in thermal energy when no work is done.
- Relate heat to an object's mass and initial and final temperatures.
- Clearly distinguish heat and temperature.
- Explain how heat can be measured experimentally (calorimetry).
- Estimate the final temperature when hot and cold objects are brought into contact.
- Define heat capacity and specific heat. Describe how these quantities can be measured experimentally.
- Define enthalpy. Distinguish enthalpy from thermal energy.
- Describe how changes in enthalpy and thermal energy accompanying a chemical reaction can be measured calorimetrically.
- Define bond energy. Use tables of bond energies to estimate the enthalpy of a reaction.
- Write and manipulate thermochemical equations.
- Combine a set of step thermochemical equations to obtain a net thermochemical equation (Hess's Law)
- Write thermochemical equations for combustion and formation reactions.

Before you start...

energy, energy units, and the difference between kinetic and potential energy

review the relationship between temperature and average molecular velocity

Lecture outline

In all chemical change, chemical bonds are broken or formed. Energy is required to break a chemical bond (just as energy is required to stretch a spring until it breaks). Conversely, forming a chemical bond releases energy. Virtually all chemical reactions absorb or release energy because bond making seldom exactly balances bond breaking in the reaction. In this unit, we will learn to measure and predict the amount of heat absorbed or released by a chemical reaction.

- The concept of energy, the usual definition of energy: the ability to do work
 - work is moving an object against an opposing force
 - work = distance \times opposing force
 - SI unit of work or energy: the joule (J)
 - two basic forms of energy
 - potential energy: energy of position

- examples
 - boulder on a ledge
 - cations and anions
- chemical bonds
- kinetic energy: energy of motion
- examples
 - pool balls
 - molecules

why is the concept of energy useful?

if something is isolated from everything else, its total energy never changes
 this allows seemingly unrelated behaviors of the system to be connected
 example: the pendulum

Two things energy is NOT

- some sort of invisible fluid
- something which can be measured directly

Thermal energy

Definition: energy due to chaotic molecular motions three factors affecting thermal energy :

- *temperature*
higher temperature leads to higher thermal energy
- *sample size*
a cup of hot coffee has more energy than a teaspoon of coffee, all other things being equal.
- *composition*
E(solid) < E(liquid) < E(gas), all other things being equal
anything that changes temperature, sample size and/or composition of an object can change its thermal energy

Heat

Definition: transfer of thermal energy due to a temperature difference

- thermal energy isn't measurable, but heat is
- Three factors affect how much heat an object absorbs or loses :

- *mass of object*
- *temperature change of object*
final temperature - initial temperature
if there is no change in temperature, no heat flows
 - *composition of object*

specific heat: heat required to raise the temperature of 1 g of material by 1 K
 different materials have different specific heats material at 298 K and 1 atm specific

heat

- (J/g K)
- ice 2.09
- water 4.18
- steam .86
- sodium 1.23
- aluminum 0.9
- iron 0.45

heat capacity: heat required to raise the temperature of an object by 1 K
computing heat

heat = mass x specific heat x temperature change = heat capacity x temperature change

Examples

100.0 g of water cools from 30.10°C to 25.05 °C. How much heat is released?

100.0 g of water at 25.00 °C absorbs 100 J of heat. What is its final temperature?

A stone weighing 2.0 g absorbs 5.0 J of heat and warms by 3.0 °C. What is the specific heat of the stone? What is the heat capacity of the stone?

Enthalpy

enthalpy change: heat absorbed or released by a process running at constant pressure

symbol: **H = final enthalpy - initial enthalpy**

note: enthalpy changes depend only on initial and final states, not on the route between them!

state function: a quantity that depends only on the present state (properties) of the system, not on the process used to arrive at that state.

- enthalpy changes are slightly different from thermal energy changes constant pressure processes must use a little energy to push back
- the atmosphere enthalpy change is thermal energy change, minus work against atmosphere, for a constant pressure process

Comparing Thermochemical Quantities

Definition SI units type

Temperature hotness/coldness property that controls direction of heat flows

K intensive property

thermal energy due to molecular motions

J extensive property

Heat transfer of thermal energy due to a temperature difference J process

Enthalpy adjusted thermal energy J extensive property

Calorimetry

- calorimetry is the experimental measurement of heat flows bomb calorimetry
- constant pressure calorimetry: heat generated by a constant pressure process
- strategy for solving calorimetry problems:
 - identify all q's by deciding which parts of the system absorb or release significant amounts of heat set up an energy conservation equation. set the sum of all heat flows to zero.
 - introduce T's. replace experimental q's with temperature changes, using $q = mcT$ or $q = CT$.
 - solve the equation for the desired quantity.

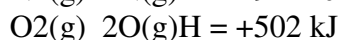
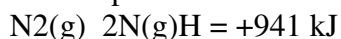
Enthalpy of Reaction

- chemical reactions usually absorb or release heat
 - energy must be absorbed to break a chemical bond
 - energy is released when a chemical bond forms
 - exothermic vs. endothermic reactions
- Reaction type: exothermic endothermic
heat is: released absorbed
reaction vessel temperature: rises falls
enthalpy change is: negative positive
net bond: formation breaking

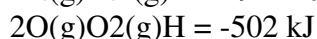
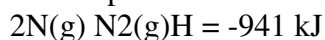
Thermochemical equations

example: spacecraft reentry

shockwave processes involve bond breaking



heat shield processes involve bond making



these are thermochemical equations: stoichiometric equations with reaction enthalpy

whatever you do to the stoichiometric equation, do also to the reaction enthalpy!

reversing the reaction reverses the sign on the reaction enthalpy

scaling the reaction scales the reaction enthalpy

adding reactions adds reaction enthalpies

How to combine 'step' thermochemical equations to get a 'target' equation:

write the step reactions.

write the target reaction.

reverse step reactions so products/reactants match the target reaction.

scale step reactions so products/reactants that don't appear in the target reaction will cancel out.

add the step reactions.

scale the resulting reaction so it matches the target reaction.

H depends on pressures, concentrations, and temperatures of reactants and products!

to keep things simple, define standard conditions:

all solution concentrations are 1 M

all gases have a partial pressure of 1 atm

all liquids and solids are under an external pressure of 1 atm

reaction occurs at 25°C

write H° when the reaction is run under standard conditions

special reaction enthalpies

the following are often tabulated for use as 'step' reactions:

definition symbol sign

enthalpy of formation: enthalpy of formation of one mole of compound from its elements in their most stable forms H_f° or -

enthalpy of combustion: enthalpy of complete combustion of one mole of compound H_c° always -

use the same procedure we outlined earlier to combine formation or combustion reactions to get a target reaction

Enthalpies of phase changes

Definition, symbol, sign

enthalpy of fusion: Heat to melt 1 mole of solid to liquid, H_{fus} , always +

enthalpy of vaporization Heat to evaporate 1 mol of liquid, H_{vap} , always +

enthalpy of sublimation Heat to vaporize 1 mol of solid, H_{sub} , always +

heating & cooling curves

obtain heat capacities from slopes of curve where temperature changes
plateaus are regions where melting or boiling is occurring
temperatures at plateaus indicate melting and boiling points
length of plateau is enthalpy of phase change
mixtures give curves without flat plateaus

Molecular view of enthalpy changes

bond enthalpy: enthalpy change per mole when a bond is broken in the gas phase for a particular substance.

average bond enthalpy: average enthalpy change per mole when the same type of bond is broken in the gas phase for many similar substances.

Average Bond Enthalpies in kJ/mol.

= denotes a double bond;

denotes a triple bond.

bond enthalpies are always positive: bond breaking is endothermic

estimating H from bond enthalpies

strategy: imagine reaction as a) dissociation of reactants into atoms,

b) recombination of atoms into products.

Add enthalpies for all product bonds

Add enthalpies for all reactant bonds

H is approximately the difference between the product and reactant bond enthalpies

limitations

procedure doesn't account for molecular attractions/repulsions, so

doesn't work well for liquid/solid phase reactions

bonds interact with each other within molecules, so bond enthalpies

really aren't additive