Chapter 6

Energy
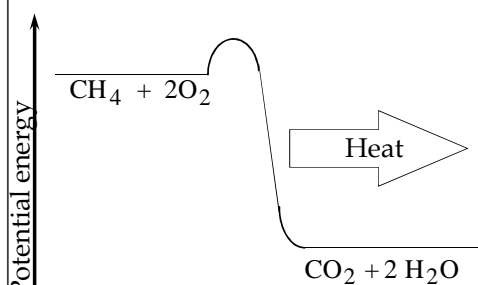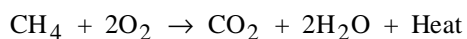**Thermodynamics**

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Energy is...

- The ability to do work.
- Conserved.
- made of heat and work.
- a state function.
- independent of the path, or how you get from point A to B.
- Work is a force acting over a distance.
- Heat is energy transferred between objects because of temperature difference.
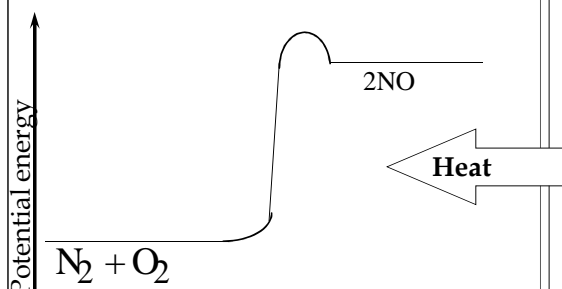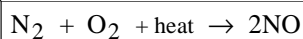
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The universe

- is divided into two halves.
- the system and the surroundings.
- The system is the part you are concerned with.
- The surroundings are the rest.
- Exothermic reactions release energy to the surroundings.
- Endothermic reactions absorb energy from the surroundings.

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$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + Heat$$

Potential energy

$CH_4 + 2O_2$

Heat

$CO_2 + 2H_2O$

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$$N_2 + O_2 + heat \rightarrow 2NO$$
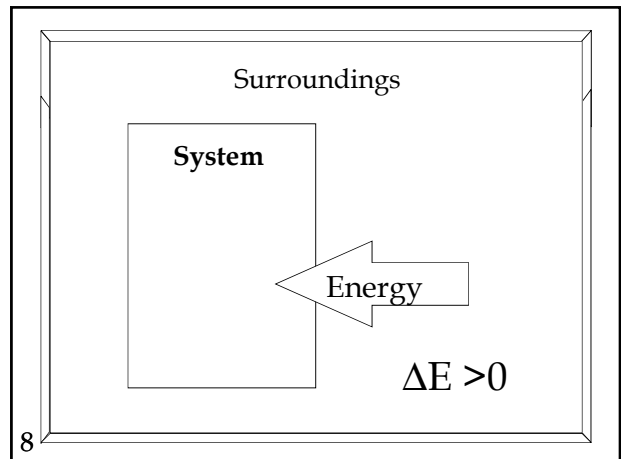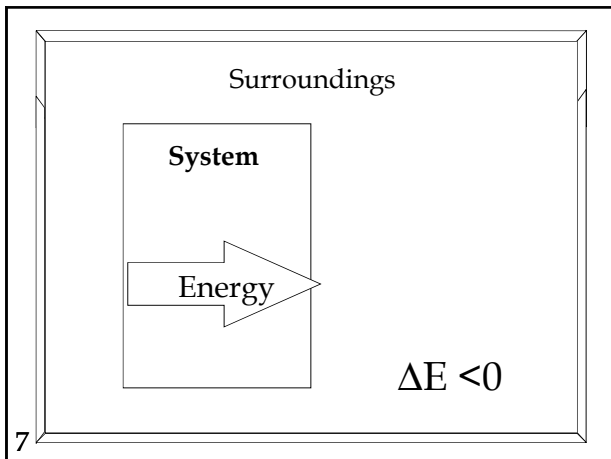
Potential energy

2NO

Heat

$N_2 + O_2$

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Direction

- Every energy measurement has three parts.
1. A unit (Joules of calories).
2. A number how many.
3. and a sign to tell direction.
- negative - exothermic
- positive- endothermic

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Slide 7

Surroundings

System

Energy →

$\Delta E < 0$

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Slide 8

Surroundings

System

← Energy

$\Delta E > 0$

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Same rules for heat and work

- Heat given off is negative.
- Heat absorbed is positive.
- Work done by system on surroundings is positive.
- Work done on system by surroundings is negative.
- Thermodynamics- The study of energy and the changes it undergoes.

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First Law of Thermodynamics

- The energy of the universe is constant.
- Law of conservation of energy.
- q = heat
- w = work
- $\Delta E = q + w$
- Take the systems point of view to decide signs.
- Energy is state function
- Heat and work are not

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What is work?

- Work is a force acting over a distance.
- $w = F \times \Delta d$
- $P = F/area$
- $d = V/area$
- $w = (P \times area) \times \Delta (V/area) = P\Delta V$
- Work can be calculated by multiplying pressure by the change in volume at constant pressure.
- units of liter x atm = L-atm

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Work needs a sign

- If the volume of a gas increases, the system has done work on the surroundings.
- work is negative
- $w = -P\Delta V$
- Expanding work is negative.
- Contracting, surroundings do work on the system w is positive.
- 1 L atm = 101.3 J

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Examples

- What amount of work is done when 15 L of gas is expanded to 25 L at 2.4 atm pressure?
- If 2.36 J of heat are absorbed by the gas above, what is the change in energy?
- How much heat would it take to change the gas without changing the internal energy of the gas?

Enthalpy

- abbreviated H
- $H = E + PV$ (that's the definition)
- $\Delta H = \Delta E + \Delta PV$
- at constant pressure.
- $\Delta H = \Delta E + P\Delta V$
- the heat at constant pressure q_p can be calculated from
- $\Delta E = q_p + w = q_p - P\Delta V$
- $q_p = \Delta E + P\Delta V = \Delta H$

Calorimetry

- Measuring heat.
- Use a calorimeter.
- Two kinds
- Constant pressure calorimeter (called a coffee cup calorimeter)
- heat capacity for a material, C is calculated
- $C = $ heat absorbed$/ \Delta T = \Delta H/ \Delta T$
- specific heat capacity $= C/mass$
- $Q = Cm\Delta T$

Calorimetry

- molar heat capacity $= C/moles$
- heat $=$ specific heat $\times$ m $\times \Delta T$
- heat $=$ molar heat $\times$ moles $\times \Delta T$
- Make the units work and you've done the problem right.
- A coffee cup calorimeter measures ΔH.
- An insulated cup, full of water.
- The specific heat of water is 1 cal/g^{o}C
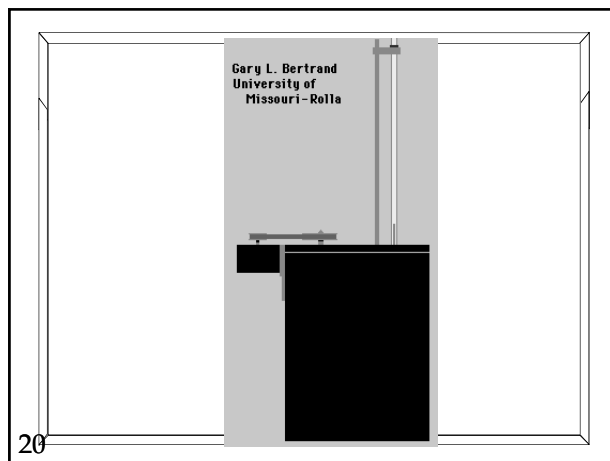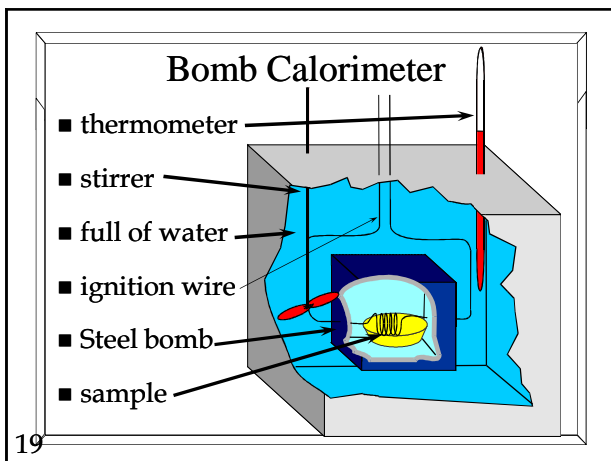- Heat of reaction $= \Delta H = C \times$ mass $\times \Delta T$

Examples

- The specific heat of graphite is 0.71 J/g^{o}C. Calculate the energy needed to raise the temperature of 75 kg of graphite from 294 K to 348 K.
- A 46.2 g sample of copper is heated to 95.4^{o}C and then placed in a calorimeter containing 75.0 g of water at 19.6^{o}C. The final temperature of both the water and the copper is 21.8^{o}C. What is the specific heat of copper?

Calorimetry

- Constant volume calorimeter is called a bomb calorimeter.
- Material is put in a container with pure oxygen. Wires are used to start the combustion. The container is put into a container of water.
- The heat capacity of the calorimeter is known and/or tested.
- Since $\Delta V = 0$, $P\Delta V = 0$, $\Delta E = q$

Bomb Calorimeter

- thermometer
- stirrer
- full of water
- ignition wire
- Steel bomb
- sample

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Properties

- intensive properties not related to the amount of substance.
- density, specific heat, temperature.
- Extensive property - does depend on the amount of stuff.
- Heat capacity, mass, heat from a reaction.

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Hess's Law

- Enthalpy is a state function.
- It is independent of the path.
- We can add equations to come up with the desired final product, and add the ΔH
- Two rules
  - If the reaction is reversed the sign of ΔH is changed
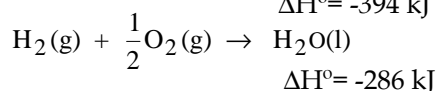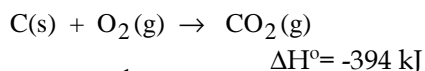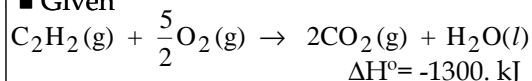 - If the reaction is multiplied, so is ΔH

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H (kJ)

O$_2$ 2NO

-112 kJ

180 kJ   NO$_2$

68 kJ

N$_2$ 2O$_2$

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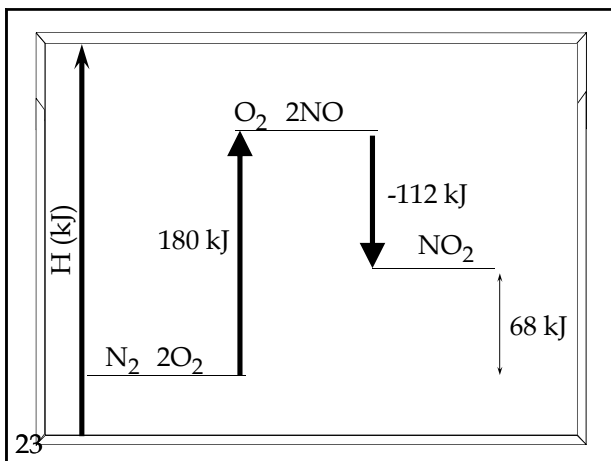
Standard Enthalpy

- The enthalpy change for a reaction at standard conditions (25ºC, 1 atm , 1 M solutions)
- Symbol ΔHº
- When using Hess's Law, work by adding the equations up to make it look like the answer.
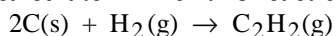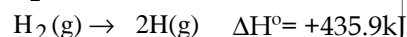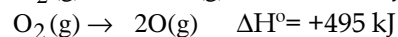- The other parts will cancel out.

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Example

- Given

$$C_2H_2(g) + \frac{5}{2}O_2(g) \rightarrow 2CO_2(g) + H_2O(l)$$
$$\Delta H^o = -1300. \text{ kJ}$$

$$C(s) + O_2(g) \rightarrow CO_2(g)$$
$$\Delta H^o = -394 \text{ kJ}$$

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$$
$$\Delta H^o = -286 \text{ kJ}$$

calculate ΔH^o for this reaction

$$2C(s) + H_2(g) \rightarrow C_2H_2(g)$$

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Example

Given

$$O_2(g) + H_2(g) \rightarrow 2OH(g) \quad \Delta H^o = +77.9 \text{kJ}$$
$$O_2(g) \rightarrow 2O(g) \quad \Delta H^o = +495 \text{ kJ}$$
$$H_2(g) \rightarrow 2H(g) \quad \Delta H^o = +435.9 \text{kJ}$$

Calculate ΔH^o for this reaction

$$O(g) + H(g) \rightarrow OH(g)$$
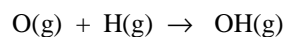
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Standard Enthalpies of Formation

- Hess's Law is much more useful if you know lots of reactions.
- Made a table of standard heats of formation. The amount of heat needed to for 1 mole of a compound from its elements in their standard states.
- Standard states are 1 atm, 1M and 25ºC
- For an element it is 0
- There is a table in Appendix 4 (pg A22)

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Standard Enthalpies of Formation

- Need to be able to write the equations.
- What is the equation that would give you the heat of formation of NO_2 ?
- ½N_2 (g) + O_2 (g) → NO_2 (g)
- Have to make one mole to meet the definition.
- Write the equation that would give you the heat of formation of methanol, CH_3OH.

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Since we can manipulate the equations

- We can use heats of formation to figure out the heat of reaction.
- Lets do it with this equation.
- $C_2H_5OH + 3O_2(g) \rightarrow 2CO_2 + 3H_2O$
- which leads us to this rule.

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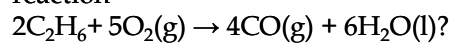## Since we can manipulate the equations

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- which leads us to this rule.

$$\sum(\Delta H_f^o \text{ products}) - \sum(\Delta H_f^o \text{ reactants}) = \Delta H^o$$

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- What is the enthalpy change for the reaction
$2C_2H_6 + 5O_2(g) \rightarrow 4CO(g) + 6H_2O(l)$?
Heats of formation are

　　　-84.7kJ/mole for C_2H_6

　　　-110.5 kJ/mole for $CO(g)$
　　　-241.8 kJ/mole for $H_2O(g)$
　　　-285.8 kJ/mole for $H_2O(l)$.)