

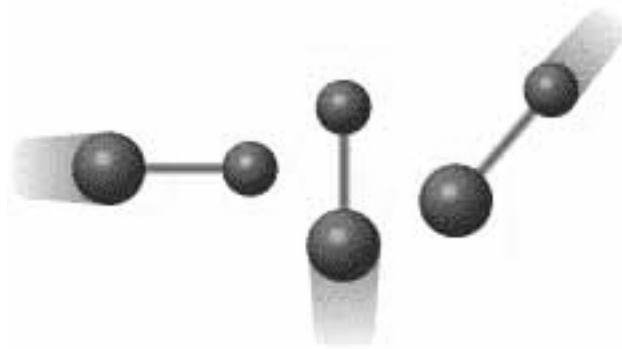
Professor K

Thermochemistry

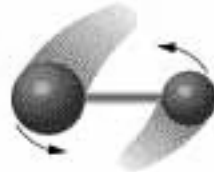
Energy

- The Universe is composed of matter and energy
- ENERGY is the capacity to do work
- POTENTIAL ENERGY is the energy of position (or composition)
- KINETIC ENERGY is the energy of an object in motion = $\frac{1}{2} mv^2$
- Units are $\text{kg (m/s)}^2 = \text{Joules}$
- Note that since work = force x distance, $\text{N x m} = (\text{kg m/s}^2) \times \text{m} = \text{J}$

Kinetic energy



(a) Translational motion



(b) Rotational motion



(c) Vibrational motion



(d) Intramolecular forces



(e) Intermolecular forces

Definitions

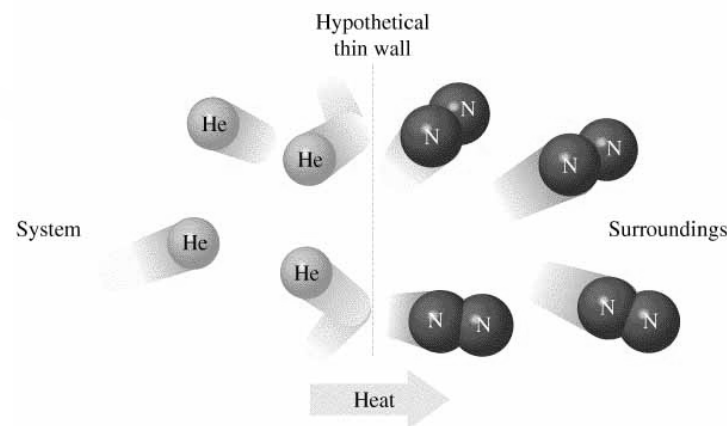
- THERMOCHEMISTRY is the study of energy changes that occur during chemical reactions
- Something loses energy; something else gains it
- The SYSTEM is the part of the Universe we are studying
- The SURROUNDINGS are the rest of the Universe

Definitions (cont'd)

- An OPEN SYSTEM exchanges matter and energy with the surroundings
- A CLOSED SYSTEM exchanges energy only with the surroundings
- An ISOLATED system exchanges neither matter nor energy with the surroundings

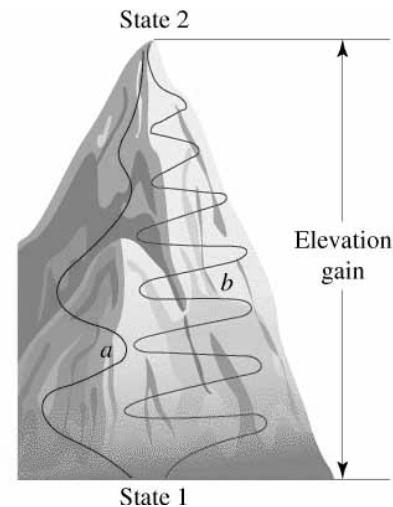
Definitions (cont'd)

- INTERNAL ENERGY (U) is the total energy of the system ($PE + KE$)
- HEAT (q) is an energy transfer between the system and surroundings



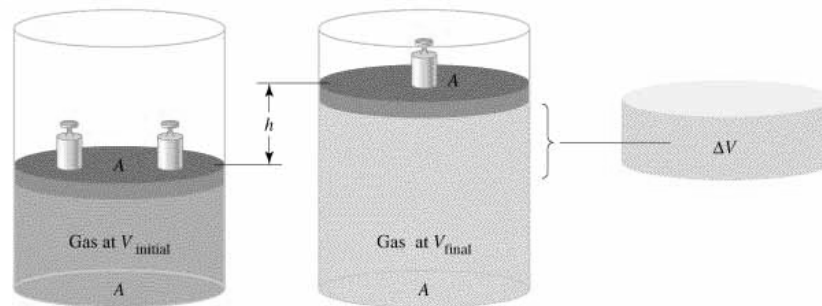
More on internal energy

- Can't be measured (too many variables)
- Can still be useful as a STATE FUNCTION
- Value depends only on current state, not path taken to get there
- q and w aren't state functions



Work

- Like heat, is an energy transfer between system and surroundings
- We only focus on PV work
 - (and electrical work later)



Laws

- Law of conservation of energy
 - Energy can be exchanged, but neither created nor destroyed
- First law of thermodynamics
 - $\Delta U = q + w$
 - Heat absorbed by system, $q > 0$
 - Work done on system $w > 0$
 - Heat given off by system $q < 0$
 - Work done by system $w < 0$

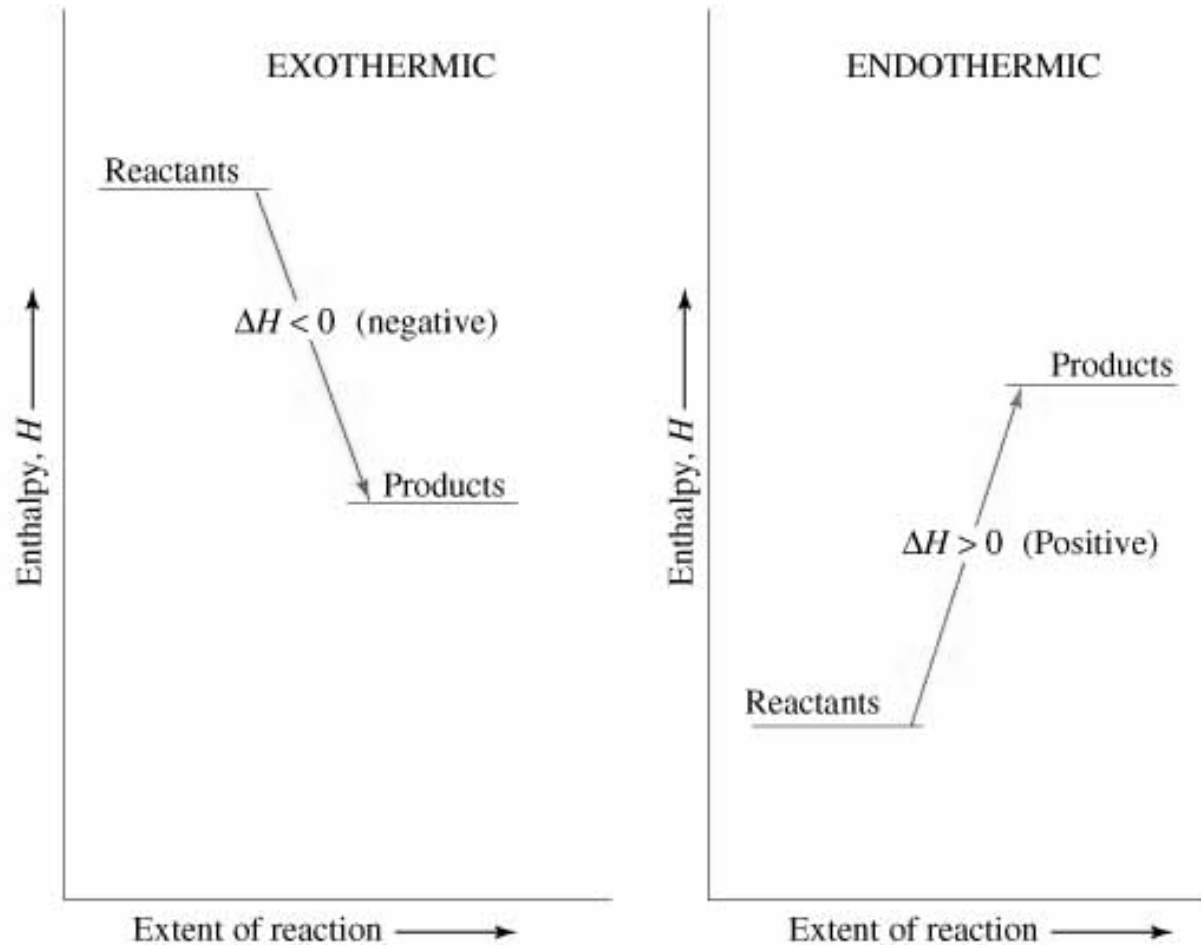
Heat of reaction

- In an EXOTHERMIC reaction, heat is given off by the system to the surroundings (q is negative)
- In an ENDOTHERMIC reaction, heat is absorbed by the system from the surroundings (q is positive)

Enthalpy (H)

- $H = U + PV$
- We will not derive it, but ΔH (enthalpy change) is the heat of reaction carried out at constant temperature and pressure with all work limited to PV work
- EXTENSIVE property – depends on how much is present
- Is a state function

Enthalpy (cont'd)



Problem-solving

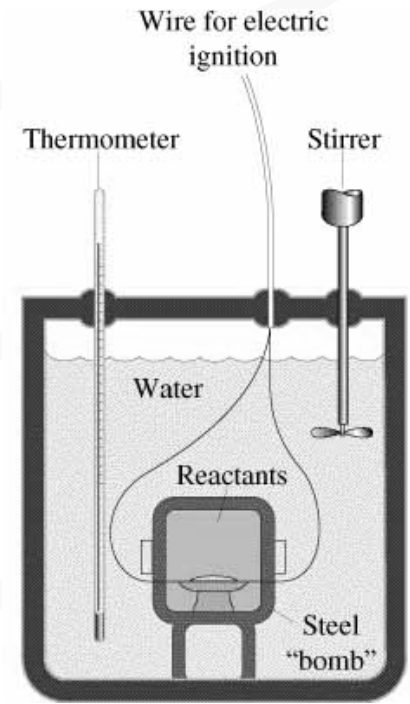
- How much heat is given off or absorbed when 5.67 mol HCl (g) is formed in the following reaction?



- $5.67 \text{ mol HCl} \times (-184.6 \text{ kJ}/2\text{mol HCl}) = -523\text{kJ}$
- (exothermic)

Calorimetry

- The measurement of heat is called CALORIMETRY (“calorie measurement”)
- $1 \text{ cal} = 4.184 \text{ J}$
- $1 \text{ Cal} = 1000 \text{ cal}$
- Lab expts make assumptions



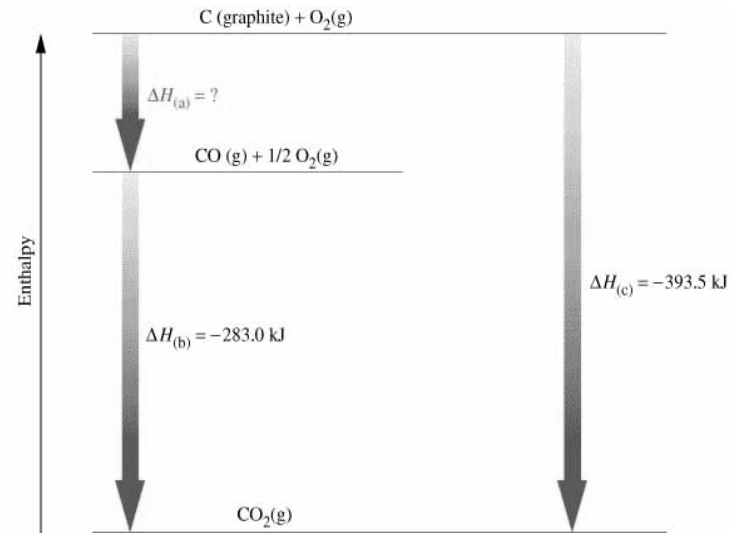
Heat capacity

- The HEAT CAPACITY of a system is the quantity of heat required to change the temperature of the system by 1°C (or 1K)
- Units are either $\text{J}/^{\circ}\text{C}$ or J/K
- MOLAR HEAT CAPACITY is the heat capacity of one mole of a substance
- SPECIFIC HEAT is the heat capacity of a 1g sample

Hess' Law

- HESS' LAW OF HEAT SUMMATION says that the heat of a reaction is constant, whether the reaction is one step or many steps
- Example:
given $\text{CO(g)} + \frac{1}{2} \text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)} \quad \Delta\text{H} = -283.0\text{kJ}$
and $\text{C (graphite)} + \text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)} \quad \Delta\text{H} = -393.5\text{kJ}$
what is ΔH for $\text{C(graphite)} + \frac{1}{2} \text{O}_2\text{(g)} \rightarrow \text{CO (g)}$?
- Reversing the first equation and adding it to the second gives us the equation we're looking for:
 $\text{CO}_2\text{(g)} \rightarrow \text{CO(g)} + \frac{1}{2} \text{O}_2\text{(g)}$
 $\text{C (graphite)} + \text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)}$
- Doing the same to the heats of reaction gives us the heat of reaction we're looking for: $-(-283.0\text{kJ}) + (-393.5\text{kJ}) = -110.5\text{kJ}$

Hess' Law (cont'd)



- Reverse the eq., reverse the ΔH
- Multiply the equation, multiply the ΔH

Standard enthalpy

- STANDARD STATE of a liquid or solid or gas is the substance at 1 atm and the T of interest
- Just like altitude is given relative to sea level, STANDARD ENTHALPY OF FORMATION ΔH_f° is the enthalpy change that occurs in the formation of 1 mol of the substance from its elements in their standard states
- STANDARD ENTHALPY OF REACTION (ΔH°) is the enthalpy change when the reactants in their standard states form products in their standard states
= ΔH_f° (products) - ΔH_f° (reactants)