Name ________________________ **AP CHEM** __/__/__

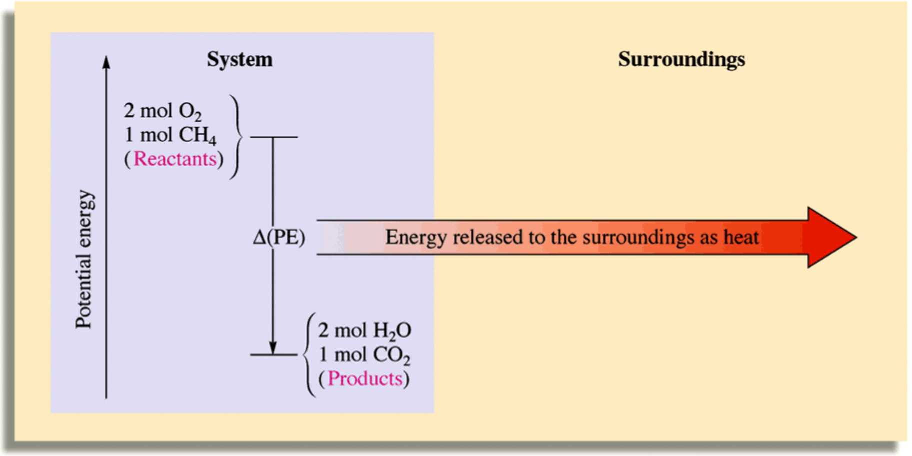
Chapter 6 Outline – Thermochemistry

The Nature of Energy

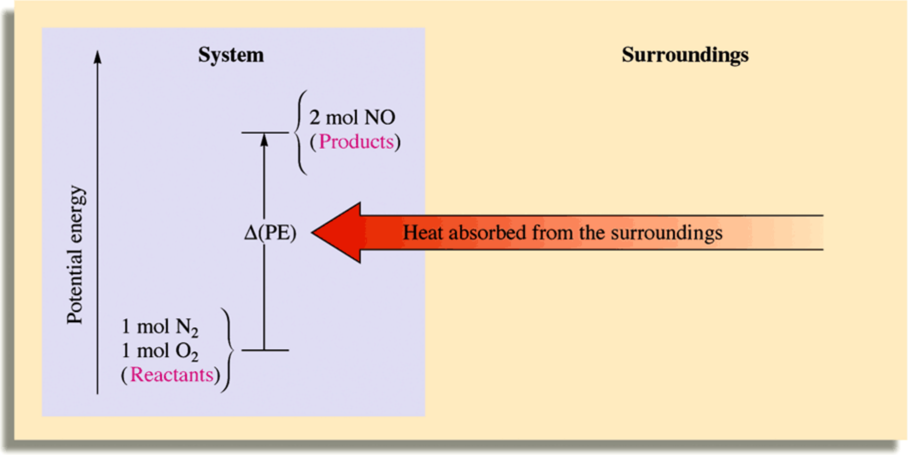
- Energy is the ability to do work or produce heat
- Energy is conserved; the law of conservation of energy states that energy can be converted from one form to another, but it cannot be destroyed
- Potential energy is energy due to position or composition; water behind a dam is an example of potential energy because the water can produce work as it passes through turbines, creating electricity. Another example of potential energy is gasoline; when gasoline is burned, energy is produced
- Kinetic energy is due to the motion of an object and depends on the mass of the object and its velocity;
- $KE = \frac{1}{2} mv^2$
- Heat & temperature are different. **Temperature** is a property that reflects the **random motions of the particles**. **Heat** involves the **transfer of energy** between two objects due to a temperature difference.
- Work is a force acting over a distance. Work & heat are two ways to transfer energy.
- The way energy transfer is divided between work & heat depends on specific conditions – the pathway
- State functions refer to the change in enthalpy, ΔH; the change in entropy, ΔS; the change in free energy, ΔG; and the change in energy, ΔE; (basically all of the delta functions) because their numerical values and mathematical signs have to do with the difference between the final state and the initial state of the system.

Chemical Energy

- When considering chemical reactions, the universe is divided into two parts, the system and the surroundings. The system is the part of the universe on which to focus attention. The surroundings include everything else in the universe
- Exothermic reactions result in the evolution of heat. Energy flows out of the system.
- Endothermic reactions absorb energy from the surroundings.
- Exothermic reactions list energy as a products: $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + \text{energy}$
- Endothermic reactions list energy as a reactant: $N_2 + O_2 + \text{energy} \rightarrow 2NO$
- You cannot have an endothermic reaction without an exothermic reaction because of the law of conservation of energy.
- In an exothermic reaction, some of the potential energy stored in the chemical bonds is being converted to thermal energy (random kinetic energy) via heat.
- The energy diagram below shows the combustion of methane. ΔPE represents the change in potential energy stored in the bonds of the products as compared to the bonds of the reactants. In an exothermic process, the bonds of the product are stronger than those of the reactants. More energy is released by forming the new bonds in the products than is consumed to break the bonds in the reactants.



- In an endothermic reaction, the situation is reversed. The products have higher potential energy (weaker bonds) than the reactants.



- The study of energy and its interconversions is called **thermodynamics**. The law of conservation of energy is often called the **first law of thermodynamics** and is stated *that the energy of the universe is constant*.
- The internal energy, E, of a system is the sum of the kinetic and potential energies of all the particles in a system. **$\Delta E = q + w$;** ΔE is the internal energy, q represents heat and w represents work.
- If q is negative, the process is exothermic; if q is positive, the process is endothermic
- If w is negative, the system is doing work on the surroundings; if w is positive, the surroundings are doing work on the system
- Example: Calculate ΔE for a system undergoing an endothermic process in which 13.6 kJ of heat flows and where 1.9 kJ of work is done on the system.

  $\Delta E = q + w$
  $\Delta E = 13.6\text{kJ} + 1.9\text{kJ}$
  $\Delta E = 15.5\text{ kJ}$
- If you really need a practice problem, you are in big trouble.
- A common type of work associated with chemical processes is work done by a gas (through expansion) or work done to a gas (through compression). The formula for these calculations is: $w = -P\Delta V$; w = work, P = pressure, ΔV is the change in volume
- Example. Calculate the work associated with the expansion of a gas from 38 L to 52 L at a constant external pressure of 11 atm.

  $w = -P\Delta V$
  $w = (-11)(52 - 38)$
  $w = (-11)(14)$
  $w = -154\text{ L atm}$
- Your turn: Calculate the work associated with the compression of a gas from 22.4 L to 7.8 L at a constant external pressure of 4.8 atm

- Now let's put the two formulas together. Example: A balloon is being inflated a volume of 2.48 L to 17.29 L by the addition of 248 J of energy as heat. Assuming that the balloon expands against a constant pressure of 0.95 atm, calculate the ΔE for the process.

$w = -P\Delta V$
$w = (-0.950)(17.29 - 2.48)$
$w = (-0.950)(14.81)$
$w = -14.1$ L atm

Convert from L atm to joules. (1 L atm = 101.3 J)

$$\frac{-14.1\text{ L atm}}{1} \times \frac{101.3\text{ J}}{1\text{ L atm}} = -1430\text{ J}$$

$\Delta E = q + w$
$\Delta E = 248 - 1430$
$\Delta E = -1180$ J

Enthalpy & Calorimetry

- $H = E + PV$, H = enthalpy, E = internal energy of the system, P = pressure, V = volume
- $\Delta H = q_p$ ΔH = change in enthalpy, q_p = heat at a constant pressure; this equation only works at constant pressure
- At constant pressure (where only PV work is allowed), the change in enthalpy, ΔH, of a system is equal to the energy flow as heat. $\Delta H = H_{\text{products}} - H_{\text{reactants}}$
- ΔH = (+) endothermic reaction; ΔH = (-) exothermic reaction
- Example: When 1 mole of methane(CH_4) is burned at a constant pressure, 890 kJ of energy is released as heat. Calculate ΔH for a process in which a 8.8-g sample of methane is burned at a constant pressure.

  $\Delta H = q_p$
  $\Delta H = -890$ kJ (the value is negative because heat is released, exothermic)

  Since less than one mole is used, you have to convert grams → moles → energy released

  $$\frac{8.8\text{ g}}{1} \times \frac{1\text{ mole CH}_4}{16.0\text{ g CH}_4} = 0.55\text{ moles} \times \frac{-890\text{ kJ}}{1\text{ mole CH}_4} = \mathbf{-490\text{ kJ}}$$
- You try: When 1 mole of ethane is burned at a constant pressure, 1020 kJ of energy is released as heat. Calculate the ΔH for a process in which a 23.5 gram sample of ethane is burned at a constant pressure.

Calorimetry

- The device used experimentally to determine the heat associated with a chemical reaction is called a calorimeter.
- Calorimetry, the science of measuring heat, is based on observing the temperature change when a body absorbs or discharges energy as heat.
- If the heat capacity is given per gram of substance, it is called the specific heat capacity and its units are J/g K or J/g °C.
- If the heat capacity is given per mole of the substance, it is called the molar heat capacity and it has the units J/mol K or J/mol °C.

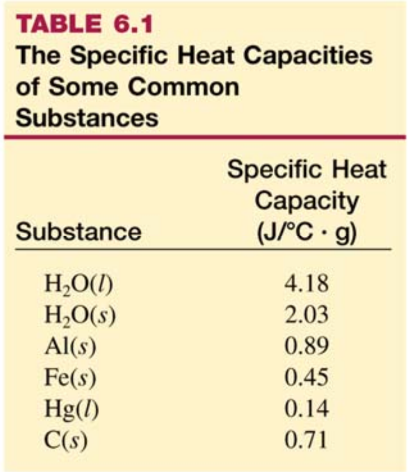
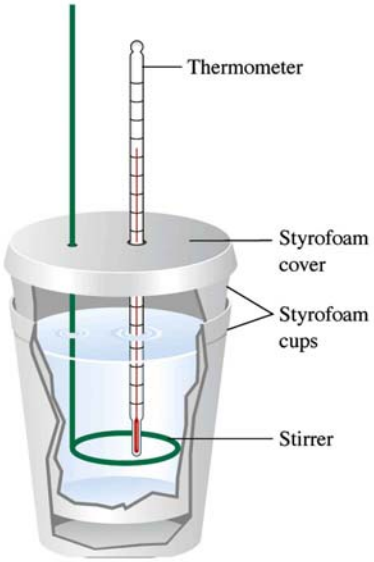


TABLE 6.1
The Specific Heat Capacities of Some Common Substances

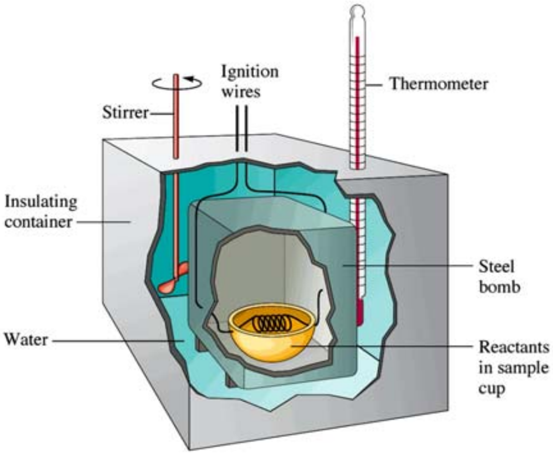
Substance	Specific Heat Capacity (J/°C · g)
$H_2O(l)$	4.18
$H_2O(s)$	2.03
$Al(s)$	0.89
$Fe(s)$	0.45
$Hg(l)$	0.14
$C(s)$	0.71



- $\Delta H = \Delta T \times m \times C_p$, ΔH = change in enthalpy, C_p = specific heat capacity, m = mass, ΔT = change in temperature
- Example: A nutritional chemist burns a saltine cracker in a calorimeter containing 250. grams of water. The temperature increases from 25.0°C to 29.8°C. What is the energy content of the cracker? The specific heat capacity of water is 4.184 J/g °C.

  $\Delta H = C_p \times m \times \Delta T$
  $\Delta H = (29.8\text{-}25.0)\ (250.)(4.184)$
  $\Delta H = 5.0 \times 10^3$ J

- You try: How much heat energy is needed to raise the temperature of a 425.0 gram aluminum baking sheet from room temperature, 25°C, to a baking temperature of 200.°C? The specific heat capacity of aluminum is 0.89 J/g°C.



- Calorimetry can also be performed at a constant volume. To study the energy changes in reactions under conditions of constant volume, a "bomb calorimeter" is used.
- $\Delta H = C_p$ (calorimeter) $\times \Delta T$
- Example: A 0.7654 gram sample of an unknown substance is placed in a bomb calorimeter known to have a heat capacity of 12.7 kJ/°C. The unknown substance is ignited in the presence of oxygen and the temperature increase of the calorimeter is 4.67°C. The molar mass of the unknown substance is 87.6 g/mol. Calculate the energy released.

  $\Delta H = C_p$ (calorimeter) $\times \Delta T$
  $\Delta H = (12.7)(4.67)$
  $\Delta H = 59.3$ kJ

  59.3 kJ were released when 0.7654 grams of a sample is burned. Calculate kJ/mole

  $\frac{0.7654\ g}{1} \times \frac{1\ mole}{87.6\ g} = 0.00874$ moles

  $\frac{59.3\ kJ}{0.00874\ moles} = 6780$ kJ/mol → **-6780 kJ/mol (it is exothermic)**

- You try: A 0.8668 gram sample of an unknown substance is placed in a bomb calorimeter known to have a heat capacity of 8.98 kJ/°C. The unknown substance is ignited in the presence of oxygen and the temperature increase of the calorimeter is 3.71°C. The molar mass of the unknown substance is 122.7 g/mol. Calculate the energy released

Hess's Law

- Since enthalpy is a state function, the change in enthalpy in going from some initial state to some final state is independent of the pathway. Thus, in going from a particular set of reactants to a particular set of products, the change in enthalpy is the same whether the reaction takes place in one step or a series of steps. This principle is known as Hess's law.
- Example: $N_2 + 2O_2 \rightarrow 2NO_2 \quad \Delta H_1 = 68\text{ kJ}$

  This reaction can be carried out in two distinct steps:

  1. $N_2 + O_2 \rightarrow 2NO \qquad \Delta H_2 = 180\text{ kJ}$
  2. $\underline{2NO + O_2 \rightarrow 2NO_2 \qquad \Delta H_3 = -112\text{ kJ}}$

  $N_2 + 2O_2 \rightarrow 2NO_2 \qquad \Delta H_1 = 68\text{ kJ}$

  Note: $\Delta H_1 = \Delta H_2 + \Delta H_3$
- When using Hess's law, it is important to understand two characteristics of ΔH for a reaction:
  - If a reaction is reversed, the sign of ΔH is also reversed.
  - If the coefficients in a balanced equation are multiplied by an integer, the value of ΔH is multiplied by the same integer.
- You try: What is the standard enthalpy change for the reaction of lead(II) chloride with chlorine to give lead(IV) chloride?

  $PbCl_2(s) + Cl_2(g) \rightarrow PbCl_4(l)$

  The following is known:

  $Pb(s) + Cl_2(g) \rightarrow PbCl_2(s) \qquad \Delta H° = -359.4\text{ kJ}$
  $Pb(s) + 2Cl_2(g) \rightarrow PbCl_4(l) \qquad \Delta H° = -329.3\text{ kJ}$

Standard Enthalpies of Formation

- The standard enthalpy of formation($\Delta H_f°$) of a compound is defined as the change in enthalpy that accompanies the formation of one mole of a compound from its elements with all substances in their standard states
- The degree symbol (°) on a thermodynamic function indicates that the corresponding process has been carried out under standard conditions.
- Conventional Definitions of Standard States
  - For a Compound
    - The standard state for a gaseous substance is a pressure of exactly 1 atmosphere.
    - For a pure substance in a condensed state (liquid or solid), the standard state is the pure liquid or solid.
    - For a substance present in a solution, the standard state is a concentration of exactly 1M.
  - For An Element
    - The standard state of an element is the form in which the element exists under conditions of 1 atmosphere and 25°C.
- Consider this reaction:

  $\frac{1}{2} N_2(g) + O_2(g) \rightarrow NO_2(g) \qquad \Delta H_f° = 34\text{ kJ/mol}$
- Note that the reaction is written so that both elements are in their standard states and 1 mole of the product is formed. (This is why a fraction is used to balance nitrogen.) Enthalpies are always given per mole of the product with the product in standard state.
- To calculate the change in enthalpy (ΔH°) for a reaction you must find the difference between the **heats of formation** of the reactants and the products. $\mathbf{\Delta H° = \sum \Delta H_f°(products) - \sum \Delta H_f°(reactants)}$

- **For example:** Calculate the change in enthalpy for the following reaction:

  $\mathrm{Ca\ (s)\ +\ H_2O\ (l)\ \rightarrow\ Ca(OH)_2\ (s)\ +\ H_2\ (g)}$

  First balance the equation:

  $\mathrm{Ca\ (s)\ +\ 2\ H_2O\ (l)\ \rightarrow\ Ca(OH)_2\ (s)\ +\ H_2\ (g)}$

  Determine the enthalpy for the products and the reactants:

  $\mathrm{Ca\ (s)\ +\ 2\ H_2O\ (l)\ \rightarrow\ Ca(OH)_2\ (s)\ +\ H_2\ (g)}$

  $0 + 2(-286.0) \rightarrow -986.6 + 0$

  $-572.0 \rightarrow -986.6$

  Calculate the ΔH for the reaction using the formula from above:

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

  $\Delta H° = -986.6 - (-572.0)$

  $\Delta H° = -414.6$ kJ; this is an exothermic reaction

Substance	**$H_{formation}$ (kJ/mol)**
Ca (s)	0
H_2O (l)	-286.0
$Ca(OH)_2$ (s)	-986.6
H_2 (g)	0

Present Sources of Energy

- **Petroleum & Natural Gas**
  - Petroleum and natural gas were most likely formed from the remains of marine organisms that lived approximately 500 million years ago.
  - Petroleum is thick dark liquid composed mostly of hydrocarbons (C_xH_y).
  - Natural gas consists of mostly methane, but it also contains significant amounts of ethane, propane and butane.
  - Petroleum consists of hydrocarbon chain 5 – 25+ carbons in length.
  - To be used, petroleum must be separated into fractions by boiling.

Thermodynamics Formulas	
$KE = \frac{1}{2} mv^2$	KE=kinetic energy, m=mass, v=velocity
$\Delta E = q + w$	ΔE=change in internal energy, q=heat, w=work
$w = -P\Delta V$	w=work, P=pressure, V=volume
$H = E + PV$	H=heat, E=energy, P=pressure, V=volume
$\Delta H = C_p \times m \times \Delta T$	ΔH=change in enthalpy, C_p=heat capacity, m=mass, ΔT=change in temp.
$\Delta H = C_p \text{ (calorimeter)} \times \Delta T$	C_p=heat capacity of calorimeter, ΔT=change in temp.
$\Delta H° = \sum \Delta H_f°(\text{products}) - \sum \Delta H_f°(\text{reactants})$	$\sum \Delta H_f°$=sum of the heats of formation