# AP* Chemistry
THERMOCHEMISTRY

Terms for you to learn that will make this unit understandable:

- **Energy (*E*)** – the ability to do work or produce heat ; the sum of all potential and kinetic energy in a system is known as the internal energy of the system
  - *Potential energy* – in chemistry this is usually the energy stored in bonds (i.e., when gasoline burns there are differences in the attractive forces between the nuclei and the electrons in the reactants and the products)
  - *Kinetic energy* – energy of motion, usually of particles, proportional to Kelvin temperature; kinetic energy depends on the mass and the velocity of the object: $KE = ½ mv^2$
- **Law of Conservation of Energy** – energy never created nor destroyed
  - *AKA* energy of the universe is constant
  - *AKA* **First Law of Thermodynamics**
- **Heat (*q*)** – transfer of energy in a process (flows from a warmer object to a cooler one – heat transfers because of temperature difference but, remember, temperature is not a measure of energy—it just reflects the motion of particles)
- **Enthalpy (*H*)–** heat content at constant pressure
  - **Enthalpy of reaction (ΔH_{rxn})** – heat absorbed or released by a chemical reaction
  - **Enthalpy of combustion (ΔH_{comb})** -- heat absorbed or released by burning (usually with O_2)
  - **Enthalpy of formation (ΔH_f)** – heat absorbed or released when **ONE** mole of compound is formed from elements in their standard states
  - **Enthalpy of fusion (ΔH_{fus})** -- heat absorbed to melt 1 mole of solid to liquid @MP
  - **Enthalpy of vaporization (ΔH_{vap})** -- heat absorbed to change 1 mole liquid to gas @BP
- **System** – area of the universe we are focusing on (i.e., the experiment)
- **Surroundings** – everything outside of the system
- **Endothermic** – net absorption of energy (heat) by the system; energy is a reactant; (i.e., baking soda and vinegar when mixed get very cold to the touch)
- **Exothermic** – net release of energy (heat) by the system; energy is a product; (i.e., burning methane gas in the lab burner produces heat; light sticks give off light which is also energy)
- **State Function** – A property independent of past or future behavior ; (it does not matter which road brought you to school today–you started at your house and ended here –there are probably lots of ways for that to happen)
- **Entropy (*S*)** – measure of disorder in the system (measure of chaos)
- **Gibb's Free Energy (*G*)** – criteria for spontaneity and amount of free energy to do work
- **Thermodynamics** – study of energy and its interconversions
- **Work** – force acting over distance
- **Standard Conditions**—you already know about STP, but recall that the *T* is STP is 0°C and humans are not happy lab workers when it is that cold! So, think of standard *conditions* as standard *lab* conditions which are 1 atm of pressure, 25°C (much more comfy!) and if solutions are involved, their concentration is 1.0 *M*. All of this information is communicated by adding the symbol ° to *G, H or S*. So, if you see $\Delta H°$, then you automatically know the pressure, temperature and conditions that apply to that value!
- **There has recently been a change in how enthalpy, entropy and free energy units are expressed. For example, you may see $\Delta H°$ values expressed as kJ in older printed material. Currently, they should be expressed in kJ/mol where the "mol" is "moles of reaction". See Jim Spencer's article on AP Central for additional information.**

ENERGY AND WORK

➢ See definition of energy.

➢ $\Delta E = q\text{(heat)} + w\text{(work)}$

➢ Signs of q
  - $+q$ if heat absorbed
  - $-q$ if heat released

$P = \frac{F}{A}$

$P = \frac{F}{A}$

Area = A

Δh Δh ΔV

(a) Initial state   (b) Final state
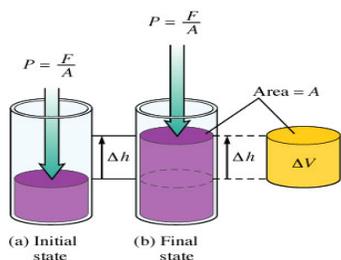
➢ Signs of w (commonly related to work done by or to gases)
  ◆ $+w$ if work done on the system (i.e., compression)
  ◆ $-w$ if work done by the system (i.e., expansion)
    ➢ When related to gases, work is a function of pressure
    ➢ (pressure is force per unit of area) and Δvolume

$$w = -P\Delta V$$

NOTE: Energy is a state function. (Work and heat are not.)
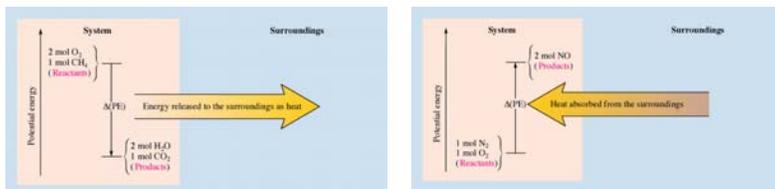
Exercise 1   **Internal Energy**

Calculate ΔE for a system undergoing an endothermic process in which 15.6 kJ of heat flows and where 1.4 kJ of work is done on the system.

17.0 kJ

Exercise 2   **PV Work**

Calculate the work associated with the expansion of a gas from 46 L to 64 L at a constant external pressure of 15 atm.

−270 L•atm


Exercise 3   **Internal Energy, Heat, and Work**

A balloon is being inflated to its full extent by heating the air inside it. In the final stages of this process, the volume of the balloon changes from 4.00×10^6 L to 4.50×10^6 L by the addition of 1.3×10^8 J of energy as heat. Assuming that the balloon expands against a constant pressure of 1.0 atm, calculate ΔE for the process. (To convert between L · atm and J, use 1 L · atm = 101.3 J.)

$$8.0 \times 10^7 \, \text{J}$$

ENTHALPY

❖ Measure only the change in enthalpy, ΔH (the difference between the potential energies of the products and the reactants)
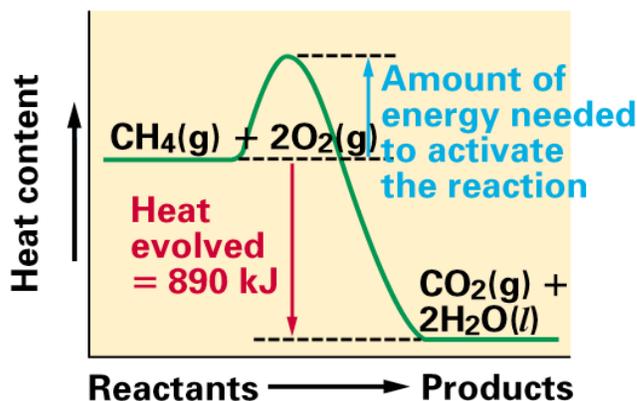
❖ ΔH is a state function
❖ $\Delta H = q$ at constant pressure (i.e. atmospheric pressure)
❖ (true most of the time for us and a very handy fact!)
❖ Enthalpy can be calculated from several sources including:
   ▪ Stoichiometry
   ▪ Calorimetry
   ▪ From tables of standard values
   ▪ Hess's Law
   ▪ Bond energies

❖ *Stoichiometrically:*

Sample Problem A: Upon adding solid potassium hydroxide pellets to water the following reaction takes place:

$$KOH(s) \rightarrow KOH(aq) + 43 \text{ kJ/mol}$$

Answer the following questions regarding the addition of 14.0 g of KOH to water:
     Does the beaker get warmer or colder?
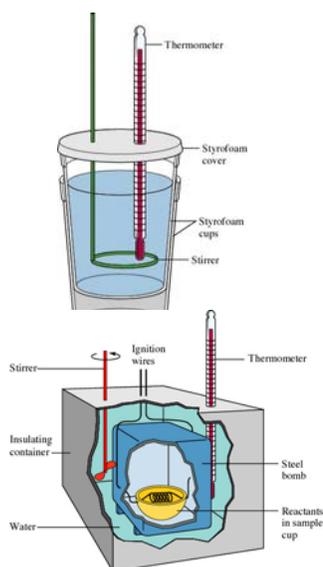   Is the reaction endothermic or exothermic?
     What is the enthalpy change for the dissolution of the 14.0 grams of KOH?

Answers: (a) warmer   (b) exothermic   (c) -10.7 kJ/mol

❖ *Calorimetry:*

The process of measuring heat based on observing the temperature change when a body absorbs or discharges energy as heat.

Types of calorimetry:

(1) Coffee-cup calorimetry – in the lab this is how we experiment to find energy of a particular system. We use a Styrofoam cup, reactants that begin at the same temperature and look for change in temperature. After all data is collected (mass or volume; initial and final temperatures) we can use the specific formula to find the energy released or absorbed. We refer to this process as constant pressure calorimetry. ** $q = \Delta H$ @ these conditions.**

(2) Bomb calorimetry – weighed reactants are placed inside a steel container and ignited. Often referred to as constant volume. This is used by industry to determine number of food calories that we consume!

Terms to know:
❖ **Heat capacity** – energy required to raise temp. by 1 degree (Joules/ °C)

❖ **Specific heat capacity (*Cp*)** – same as above but specific to 1 gram of substance

$$\text{specific heat} \ = \ \frac{\text{quantity of heat transferred}}{(g \text{ of material})(\text{degrees of temperature change})}$$

❖ **Molar heat capacity** -- same as above but specific to one mole of substance
(J/mol K   or J/mol °C)

❖ **Energy (*q*)** released or gained at constant pressure: $q = mCp\Delta T$
q = quantity of heat (Joules or calories)
m = mass **in grams**
$\Delta T = T_f$ - T_i (final – initial)
Cp = specific heat capacity (J/g°C)

❖ Specific heat of water (liquid state) = 4.184 J/g°C (or 1.00 cal/g°C)
Water has one of the highest specific heats known! That is why the earth stays at such an even temperature all year round! Cool huh?

❖ Heat lost by substance = heat gained by water
(if this does not happen, calculate the heat capacity of the substance)

❖ Units of Energy:
- **calorie**--amount of heat needed to raise the temp. of 1.00 gram of water 1.00 °C
- **kilocalorie**--duh!; the food calorie with a capital C.

$$KE = \frac{1}{2}mv^2 \text{ units are } \frac{kg \times m}{s^2}$$

- **joule**--SI unit of energy; 1 cal = 4.184 J

Sample Problem B:

In a coffee cup calorimeter, 100.0 mL of 1.0 *M* NaOH and 100.0 mL of 1.0 *M* HCl are mixed. Both solutions were originally at 24.6°C. After the reaction, the final temperature is 31.3°C. Assuming that all solutions have a density of 1.0 g/cm³ and a specific heat capacity of 4.184 J/g°C, calculate the enthalpy change for the neutralization of HCl by NaOH. Assume that no heat is lost to the surroundings or the calorimeter.

–5.6 kJ/mol

Exercise 4   Enthalpy

When 1 mole of methane (CH_4) is burned at constant pressure, 890 kJ/mol of energy is released as heat. Calculate ΔH for a process in which a 5.8-g sample of methane is burned at constant pressure.

ΔH = **heat flow** = **–320 kJ/mol**

Exercise 5   **Constant-Pressure Calorimetry**

When 1.00 L of 1.00 M $Ba(NO_3)_2$ solution at 25.0°C is mixed with 1.00 L of 1.00 M Na_2SO_4 solution at 25°C in a calorimeter, the white solid $BaSO_4$ forms and the temperature of the mixture increases to 28.1°C. Assuming that the calorimeter absorbs only a negligible quantity of heat, that the specific heat capacity of the solution is 4.18 J/°C · g, and that the density of the final solution is 1.0 g/mL, calculate the enthalpy change per mole of $BaSO_4$ formed.

−26 kJ/mol

Exercise 6   **Constant-Volume Calorimetry**

It has been suggested that hydrogen gas obtained by the decomposition of water might be a substitute for natural gas (principally methane). To compare the energies of combustion of these fuels, the following experiment was carried out using a bomb calorimeter with a heat capacity of 11.3 kJ/°C. When a 1.50-g sample of methane gas was burned with excess oxygen in the calorimeter, the temperature increased by 7.3°C. When a 1.15-g sample of hydrogen gas was burned with excess oxygen, the temperature increase was 14.3°C. Calculate the energy of combustion (per gram) for hydrogen and methane.

**Methane = 55 kJ/g**
Hydrogen = 141 kJ/g

❖ **_Tables:_**

♦ ΔH_f° = enthalpy of formation.
  = Production of **ONE** mole of compound FROM
    its *ELEMENTS* in their standard states (°)
  = **ZERO** (0.00) for *ELEMENTS* in standard states

♦ Standard States: 25°C (298 K), 1 atm, 1*M*

Table 6.2 Standard Enthalpies of Formation for Several Compounds at 25°C

Compound	ΔH_f° (kJ/mol)
$NH_3(g)$	−46
$NO_2(g)$	34
$H_2O(l)$	−286
$Al_2O_3(s)$	−1676
$Fe_2O_3(s)$	−826
$CO_2(g)$	−394
$CH_3OH(l)$	−239
$C_8H_{18}(l)$	−269

The **"Big Mamma" Equation:** $\Delta H_{rxn} = \Sigma \Delta H_{f\,(products)} - \Sigma \Delta H_{f\,(reactants)}$
(also known as Hess's Law)

Sample Problem C: Calculate the ΔH°_{rxn} for the following:

$3\ Al(s)\ +\ 3\ NH_4ClO_4(s)\ \rightarrow\ Al_2O_3(s)\ +\ AlCl_3(s)\ +\ 3\ NO(g)\ +\ 6\ H_2O(g)$
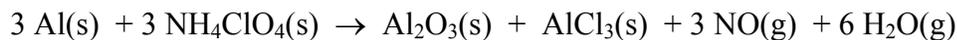
Given the following values:

Substance	ΔH_f° (kJ/mol)
$NH_4ClO_4(s)$	-295
$Al_2O_3(s)$	-1676
$AlCl_3(s)$	-704
$NO(g)$	90.0
$H_2O(g)$	-242

–2,677 kJ/mol (exo)

Thermochemistry

Sample Problem D
Sometimes all values are not found in the table of thermodynamic data. For most substances it is impossible to go into a lab and directly synthesize a compound from its free elements. The heat of formation for the substance must be found by working backwards from its heat of combustion.

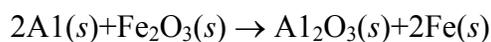Find the ΔH_f of $C_6H_{12}O_6(s)$ from the following information:
$C_6H_{12}O_6(s) + 6 O_2(g) \rightarrow 6 CO_2(g) + 6 H_2O(l) + 2800$ kJ

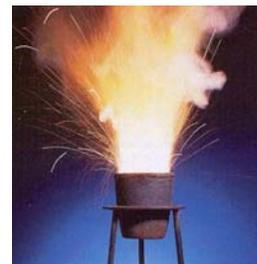| Substance	ΔH_f° (kJ/mol)
$CO_2(g)$	-393.5
$H_2O(l)$	-285.8

$$\Delta H_f^\circ = -1276 \text{ kJ/mol for glucose}$$

Exercise 10
Using enthalpies of formation, calculate the standard change in enthalpy for the thermite reaction:
$$2Al(s)+Fe_2O_3(s) \rightarrow Al_2O_3(s)+2Fe(s)$$

This reaction occurs when a mixture of powdered aluminum and iron(III) oxide is ignited with a magnesium fuse.

The thermite reaction is one of the most energetic chemical reactions known.
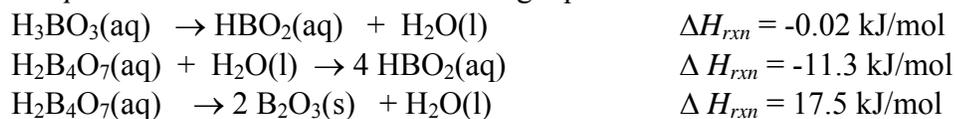
–850. kJ/mol

❖ *Hess's Law*

Enthalpy is not dependent on the reaction pathway. If you can find a combination of chemical equations that add up to give you the desired overall equation, you can also sum up the ΔH's for the individual reactions to get the overall ΔH_{rxn}.
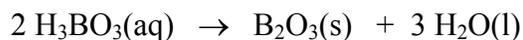
Remember this:

♦ First decide how to rearrange equations so reactants and products are on appropriate sides of the arrows.

♦ If equations had to be reversed, reverse the sign of ΔH

♦ If equations had be multiplied to get a correct coefficient, multiply the ΔH by this coefficient since ΔH's are in kJ/**MOLE** (division applies similarly)

♦ Check to ensure that everything cancels out to give you the exact equation you want.

♦ Hint** It is often helpful to begin your work backwards from the answer that you want!

Sample Problem F: Given the following equations

$H_3BO_3(aq) \rightarrow HBO_2(aq) + H_2O(l)$	$\Delta H_{rxn} = $ -0.02 kJ/mol
$H_2B_4O_7(aq) + H_2O(l) \rightarrow 4\ HBO_2(aq)$	$\Delta H_{rxn} = $ -11.3 kJ/mol
$H_2B_4O_7(aq) \rightarrow 2\ B_2O_3(s) + H_2O(l)$	$\Delta H_{rxn} = $ 17.5 kJ/mol

find the ΔH for this overall reaction

$2\ H_3BO_3(aq) \rightarrow B_2O_3(s) + 3\ H_2O(l)$

14.4 kJ/mol endothermic

❖ *Bond Energies*
- Energy must be added/absorbed to BREAK bonds (endothermic). Energy is released when bonds are FORMED (exothermic). This is a giant misconception among students! Once again, it "takes" energy to break bonds and energy is released when a bond forms.

- ΔH = sum (Σ) of the energies required to break old bonds (positive signs since energy is added to the system) plus the sum of the energies released in the formation of new bonds (negative signs since energy is lost from the system).

$\Delta H = \Sigma$ Bond Energies $_{broken} - \Sigma$ Bond Energies $_{formed}$

Sample Problem G:
Using bond energies, calculate the change in energy that accompanies the following reaction:
$$H_{2(g)} + F_{2(g)} \rightarrow 2\,HF_{(g)}$$
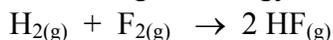
Bond Type	Bond Energy
H−H	432 kJ/mol
F−F	154 kJ/mol
H−F	565 kJ/mol

−544 kJ/mol

❖ **SUMMARY FOR ENTHALPY: What does it really tell you about an equation?**
❖ $\Delta H = +$ **reaction is endothermic and heat energy is *added* into the system**
❖ $\Delta H = -$ **reaction is exothermic and heat energy is *lost* from the system (favored – nature tends toward the lowest energy state)**