Let’s begin with terms for you to master:

- **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** – energy by virtue of position. 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). When bonded atoms are separated, the PE is raised because energy must be added to overcome the coulombic attraction between each nucleus and the shared electrons.
  
  - When atoms bond, the above mentioned coulombic attraction results in energy being released and a subsequently lower PE.
  
  - **Kinetic energy** – energy of motion (translational, rotational & vibrational motion of particles in our case), proportional to Kelvin temperature; kinetic energy depends on the mass and the velocity of the object: $KE = \frac{1}{2} mv^2$
  
  Check out this simulation regarding the Boltzmann distribution: [http://phet.colorado.edu/en/simulation/atomic-interactions](http://phet.colorado.edu/en/simulation/atomic-interactions)

- **Law of Conservation of Energy** – You may know it as “energy is never created nor destroyed” which implies that any change in energy of a system must be balanced by the transfer of energy either into or out of the system.

  - AKA energy of the universe is constant & the **First Law of Thermodynamics**

- **Heat** ($q$) – Two systems with different temperatures that are in thermal contact will exchange thermal energy, the quantity of which is call *heat*. This transfer of energy in a process (flows from a warmer object to a cooler one, transfers heat because of temperature difference but, remember, *temperature* is not a measure of energy—it just reflects the motion of particles)

- **Temperature** ($T$)—is proportional to the average kinetic energy of the molecules, $KE_{ave}$.
  “Heat ‘em up and speed ‘em up” as you saw in the states of matter animation.

- **Enthalpy** ($H$)– flow of energy (heat exchange) at constant pressure when two systems are in contact.
  
  - **Enthalpy of reaction** ($\Delta H_{rxn}$) – amount of heat released (negative values) or absorbed (positive values) by a chemical reaction at constant pressure in kJ/mol$_{rxn}$
  
  - **Enthalpy of combustion** ($\Delta H_{comb}$)—heat absorbed or released by burning (usually with O$_2$) in kJ/mol$_{rxn}$; note that combustion reactions yield oxides of that which is combusted
  
  - **Enthalpy of formation** ($\Delta H_f$) – heat absorbed or released when ONE mole of compound is formed from elements in their standard states in kJ/mol$_{rxn}$
  
  - **Enthalpy of fusion** ($\Delta H_{fus}$)—heat absorbed to melt (overcome IMFs) 1 mole of solid to liquid @ MP expressed in kJ/mol$_{rxn}$
  
  - **Enthalpy of vaporization** ($\Delta H_{vap}$)—heat absorbed to vaporize or boil (overcome IMFs) 1 mole liquid to vapor @BP in kJ/mol$_{rxn}$

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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 exchange) by the system; energy is a reactant; (i.e., baking soda and vinegar when mixed get very cold to the touch) ; +ΔH

Exothermic – net release of energy (heat exchange) 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); −ΔH

Entropy (s) – measure of the dispersal of matter and energy; increase dispersal +ΔS; decrease dispersal −ΔS

Gibbs Free Energy (G) – criteria for determining thermodynamic favorability and calculating the theoretical amount of energy to do work

Thermodynamics – study of energy and its interconversions

Work – force acting over distance in physics often expressed as work = −PΔV where gases are involved; expressed in Joules or kJ

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 ΔH°, 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 ΔH° values expressed as kJ in older printed material. Currently, they should be expressed in kJ/mol rxn where the “mol rxn” is “moles of reaction”. See Jim Spencer’s article on AP Central for additional information.

ENERGY AND WORK

Energy is often defined as the “ability to do work”.

ΔE = q (heat) + w (work)

Signs of q

+q if heat absorbed

−q if heat released

Algebraic sign of w as it relates to work done by or work done on 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 defined as force per unit of area, so when the volume is changed work was either done on the gas or by the gas.

work = −PΔV

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.

\[-270 \text{ L} \cdot \text{atm}\]

**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 $4.00 \times 10^6$ L to $4.50 \times 10^6$ L by the addition of $1.3 \times 10^8$ J of energy as heat. Assuming that the balloon expands against a constant pressure of 1.0 atm, calculate $\Delta E$ for the process. (To convert between L $\cdot$ atm and J, use 1 L $\cdot$ atm = 101.3 J.)

\[8.0 \times 10^7 \text{ J}\]

**ENTHALPY**  
- Measure only the change in enthalpy, $\Delta H$ (the difference between the potential energies of the products and the reactants)

- $\Delta H$ is a state function

- $\Delta H = q$ at constant pressure (i.e. atmospheric pressure)

- Enthalpy can be calculated from several sources including:
  - Stoichiometry
  - Calorimetry
  - From tables of standard values
  - Hess’s Law
  - Bond energies

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Thermochemistry
Stoichiometrically:

Exercise 4
Upon adding solid potassium hydroxide pellets to water the following reaction takes place:
\[ \text{KOH}(s) \rightarrow \text{KOH}(aq) + 43 \text{ kJ/mol} \]

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?

\[ q = \Delta H \] at these conditions

Answers: (a) warmer  (b) exothermic  (c) \(-10.7 \text{ kJ/mol}_{\text{rxn}}\)

Calorimetry:

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

“Coffee Cup” calorimetry:

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**

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 and the experiment is carried out at constant pressure. Constant pressure is achieved using open containers, so you will be doing experiments of that kind in lab.

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

**Molar heat capacity**—same as above but specific to one mole of substance (J/mol K or J/mol °C)
Energy released or gained at constant pressure: \( q = mC_p \Delta T \)

- **Energy** \( q \) = quantity of heat (Joules or calories)
- **mass** \( m \) = mass in grams
- **specific heat capacity** \( C_p \) = (J/g°C)
- **ΔT** = \( T_f - T_i \) (final – initial)

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! This property makes life on earth possible and regulates earth’s temperature year round!

Heat lost by substance = heat gained by water

**Units of Energy:**
- **calorie**—amount of heat needed to raise the temp. of 1.00 gram of water 1.00 °C
- **kilocalorie**—1,000 calories AND the food label calorie with a capital C.
  \[ KE = \frac{1}{2}mv^2 \] (units are \( \frac{kg \times m}{s^2} \))
- **joule**—SI unit of energy; 1 cal = 4.184 J

**Exercise 5**
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.

\(-5.6\text{ kJ/mol}_{\text{rxn}}\)

**Exercise 6**

**Enthalpy**
When 1 mole of methane (CH₄) is burned at constant pressure, 890 kJ/mol of energy is released as heat. Calculate \( \Delta H \) for a process in which a 5.8 gram sample of methane is burned at constant pressure.

\[ \Delta H = \text{heat flow} = -320\text{ kJ/mol}_{\text{rxn}} \]
Exercise 7  Constant-Pressure Calorimetry

When 1.00 L of 1.00 M Ba(NO₃)₂ solution at 25.0°C is mixed with 1.00 L of 1.00 M Na₂SO₄ solution at 25°C in a calorimeter, the white solid BaSO₄ forms and the temperature of the mixture increases to 28.1°C. Assuming that the calorimeter absorbs only a negligible quantity of heat, and 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 BaSO₄ formed.

θ Tables:

♦ $\Delta H_f^\circ$ = enthalpy of formation
  
  = Production of \textbf{ONE} mole of compound FROM its \textit{ELEMENTS} in their standard states (°)
  
  = \textbf{ZERO} (0.00) for \textit{ELEMENTS} in standard states

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

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta H_f^\circ$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₃(g)</td>
<td>-46</td>
</tr>
<tr>
<td>NO₂(g)</td>
<td>34</td>
</tr>
<tr>
<td>H₂O(l)</td>
<td>-286</td>
</tr>
<tr>
<td>Al₂O₃(s)</td>
<td>-1676</td>
</tr>
<tr>
<td>Fe₂O₃(s)</td>
<td>-826</td>
</tr>
<tr>
<td>CO₂(g)</td>
<td>-394</td>
</tr>
<tr>
<td>CH₃OH(l)</td>
<td>-239</td>
</tr>
<tr>
<td>C₅H₁₀(l)</td>
<td>-269</td>
</tr>
</tbody>
</table>

The “Big Mamma” Equation: $\Delta H_{rxn} = \Sigma \Delta H_f(\text{products}) - \Sigma \Delta H_f(\text{reactants})$

(also known as Hess’s Law)
Exercise 8

<table>
<thead>
<tr>
<th>Substance</th>
<th>$\Delta H_f^\circ$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_4$ClO$_4$(s)</td>
<td>−295</td>
</tr>
<tr>
<td>Al$_2$O$_3$(s)</td>
<td>−1676</td>
</tr>
<tr>
<td>AlCl$_3$(s)</td>
<td>−704</td>
</tr>
<tr>
<td>NO(g)</td>
<td>90.0</td>
</tr>
<tr>
<td>H$_2$O(g)</td>
<td>−242</td>
</tr>
</tbody>
</table>

Given the information above, calculate the $\Delta H_{rxn}^\circ$ for the following chemical reaction.

$$3 \text{Al}(s) + 3 \text{NH}_4\text{ClO}_4(s) \rightarrow \text{Al}_2\text{O}_3(s) + \text{AlCl}_3(s) + 3 \text{NO}(g) + 6 \text{H}_2\text{O}(g)$$

$\Delta H_{rxn}^\circ = -2,677 \text{ kJ/mol}_{rxn}$ (exo)

Exercise 9

$$\text{C}_6\text{H}_12\text{O}_6(s) + 6 \text{O}_2(g) \rightarrow 6 \text{CO}_2(g) + 6 \text{H}_2\text{O}(l) + 2800 \text{ kJ}$$

Occasionally, not all values are 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 calculated by working backwards from its heat of combustion. Calculate the $\Delta H_f^\circ$ of C$_6$H$_{12}$O$_6$(s) given the combustion reaction above along with the following information.

<table>
<thead>
<tr>
<th>Substance</th>
<th>$\Delta H_f^\circ$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$(g)</td>
<td>−393.5</td>
</tr>
<tr>
<td>H$_2$O(l)</td>
<td>−285.8</td>
</tr>
</tbody>
</table>

$\Delta H_f^\circ$ for glucose = $-1276 \text{ kJ/mol}$
Exercise 10
The thermite reaction occurs when a mixture of powdered aluminum and iron(III) oxide is ignited with a magnesium fuse. Using enthalpies of formation, calculate the standard change in enthalpy for the thermite reaction:

$$2\text{Al (s)} + \text{Fe}_2\text{O}_3\text{(s)} \rightarrow \text{Al}_2\text{O}_3\text{(s)} + 2\text{Fe (s)}$$

Enthalpy is independent of 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 $\Delta H$’s for the individual reactions to get the overall $\Delta H_{rxn}$.

- First, decide how to rearrange equations such that the reactants and products are on appropriate sides of the arrows in the chemical equation. It is often helpful to begin by working backwards from the final or summary chemical equation.
- If an equation had to be reversed, also reverse the sign of $\Delta H_{rxn}$
- If an equation had to be multiplied by a given factor to obtain correct coefficients, also multiply the $\Delta H_{rxn}$ by this factor since $\Delta H_{rxn}$’s are in kJ/MOLE_{rxn} (division applies similarly)
- Double check to ensure that everything cancels out to give you the exact summary chemical equation you desire.

Exercise 11
Calculate the $\Delta H$ for this overall reaction $2\text{H}_3\text{BO}_3\text{(aq)} \rightarrow \text{B}_2\text{O}_3\text{(s)} + 3\text{H}_2\text{O}\text{(l)}$ given the following equations:

- $\text{H}_3\text{BO}_3\text{(aq)} \rightarrow \text{HBO}_2\text{(aq)} + \text{H}_2\text{O}\text{(l)}$ $\Delta H = -0.02$ kJ/mol_{rxn}
- $\text{H}_2\text{B}_4\text{O}_7\text{(aq)} + \text{H}_2\text{O}\text{(l)} \rightarrow 4 \text{HBO}_2\text{(aq)}$ $\Delta H = -11.3$ kJ/mol_{rxn}
- $\text{H}_2\text{B}_4\text{O}_7\text{(aq)} \rightarrow 2 \text{B}_2\text{O}_3\text{(s)} + \text{H}_2\text{O}\text{(l)}$ $\Delta H = 17.5$ kJ/mol_{rxn}

14.4 kJ/mol_{rxn} endothermic
Exercise 12
Calculate the change in energy that accompanies the following reaction given the data below.

\[
\text{H}_2(g) + \text{F}_2(g) \rightarrow 2 \text{HF}(g)
\]

<table>
<thead>
<tr>
<th>Bond Type</th>
<th>Bond Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>H−H</td>
<td>432 kJ/mol</td>
</tr>
<tr>
<td>F−F</td>
<td>154 kJ/mol</td>
</tr>
<tr>
<td>H−F</td>
<td>565 kJ/mol</td>
</tr>
</tbody>
</table>

\[\Delta H = \text{Σ Bond Energies broken} - \text{Σ Bond Energies formed}\]

\[-544 \text{kJ/mol}_{\text{rxn}}\]

SUMMARY FOR ENTHALPY: What does it really tell you about the changes in energy regarding a
chemical reaction?

\[\Delta H = +\] reaction is endothermic and heat energy is added into the system

\[\Delta H = -\] reaction is exothermic and heat energy is lost from the system

(Nature tends toward the lowest energy state!)
Speaking of bond energies, allow us to clear up some common misconceptions AND make some dazzling connections.

Let’s start with the vocabulary used to describe phase changes. First, you must realize that the vocabulary is “directional” (hence the arrows on this diagram) as well as very specific. You’ll have to mean what you say and say what you mean when answering a free response question!

Phase transitions involving overcoming intermolecular attractions or IMFs which should never be confused with ionic or covalent chemical bonds.

Fusion (melting), vaporization, and sublimation require an input of energy to overcome the attractive forces between the particles of the substance. NOTICE we did not speak of “breaking bonds”.

Freezing, condensation, and deposition (opposite of sublimation) release energy as IMFs form since the particles achieve a lower energy state mainly due to a decrease in temperature.

Is there a difference between a vapor and a gas? Yes, it’s primarily semantics. A gas is a gas at room temperature, we don’t speak of “oxygen vapor”. However, we do use the term “vapor” when the substance is normally a liquid or solid at room temperature. We say “water vapor”, “carbon dioxide vapor”, “iodine vapor”, etc.

Be very, very clear that changes in the phases of matter involve altering IMFs, not altering chemical bonds.*

The strength of the intermolecular attractions between molecules, and therefore the amount of energy required to overcome these attractive forces (as well as the amount of energy released when the attractions are formed) depends on the molecular properties of the substance, ionic, polar, nonpolar, etc.

Generally, the more polar a molecule is, the stronger the attractive forces between molecules are. Hence, more polar molecules typically require more energy to overcome the intermolecular attractions in an endothermic phase transition, and release more energy by forming intermolecular attractions during an exothermic phase transition.

Phase transitions involve the “breaking” or forming of intermolecular forces (attractive interactions between molecules). Hence, as with other chemical reactions, it is necessary to discuss the energy that is absorbed or given off during the breaking or forming of intermolecular interactions in a phase transition.

*UNLESS you have a network solid or covalent network solid which is a chemical compound in which the atoms are bonded by covalent bonds in a continuous network. In a network solid there are no individual molecules and the entire crystal may be considered a macromolecule. Examples of network solids include diamond with a continuous network of carbon atoms and silicon dioxide or quartz with a continuous three dimensional network of SiO₂ units. Graphite and the mica group of silicate minerals structurally consist of continuous two-dimensional layers covalently bonded within the layer with other bond types holding the layers together. That means they essentially slide in sheets the way your pencil “lead” (actually graphite) glides across the page leaving a trail.
You have probably seen a graph like this before arriving in AP Chemistry. Let’s make some additional dazzling connections!

Suppose this heating curve is for water (it isn’t because the horizontal line for boiling \( \Leftrightarrow \) condensing is too short. Why? (It takes WAY more energy to boil water than what is shown here due to having to overcome all those IMFs called hydrogen bonds).

Take a moment and ponder the differences in molecular structure and molecular motion among the different states of water represented above, the kinetic energy changes, and the potential energy changes.

1. Does the process above represent a collection of chemical changes, physical changes or both? Physical changes.

2. What type of force is involved in the changes you identified in question 1? Intermolecular forces as opposed to intramolecular forces (chemical bonds). Students may also specify exact IMFs such as H-bonding.

3. Define temperature: Temperature is defined as the average kinetic energy of the molecules.

4. Which conversions involve temperature changes? warming and cooling

5. Which mathematical formula is appropriate for calculating the energy associated with the processes you identified in question 4? \( q = mc\Delta T \)

6. Which conversions involve potential energy changes? freezing, melting, condensing, boiling, vaporizing

7. Which mathematical formula is appropriate for calculating the energy associated with the processes you identified in question 4? \( q = m\Delta H_{vap} \)

8. How do you calculate \( q \) for the processes identified in number 6 if you are given only the mass of the water sample? Simply divide the mass given by the molar mass of water to determine the number of moles involved, then multiply by the enthalpy of vaporization or fusion.

9. Which portions of this graph represent equilibrium conditions? Phase changes: ice \( \Leftrightarrow \) water, water \( \Leftrightarrow \) steam, the plateaus where temperature is not changing :: only potential energy is changing as system is absorbing or releasing heat. PE is added to overcome IMFs (melting or boiling) or released to when IMFs form (condensing or freezing).