

Chapter 6 Thermochemistry

Chemistry by Chang and Goldsby Chapter 6: Thermochemistry 6.1 Introduction to Thermodynamics 6.2 Energy Changes in Chemical Reactions 6.3 Introduction to Thermodynamics 6.4 Enthalpy of Chemical Reactions 6.5 Calorimetry 6.6 Standard Enthalpy of Reactions 6.7 Heat of Solution and Dilution	College textbooks include far more material than is required for the AP Chemistry exam. I have posted a condensed version of Chang's Chapter 6 on the classroom webpage that you can use with this summary. Note: Work-volume aspects of thermochemistry are not part of the AP Chemistry. So, E and w can be skipped
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6.1 The Nature of Energy and the Types of Energy – read this section over carefully as it introduces chemical potential energy.

Important points that will be used throughout the year:

“Chemical energy is stored within ... chemical substances...

When substances participate in chemical reactions, chemical energy is released, stored, or converted to other forms of energy...

Chemical energy can be considered a form of potential energy...

When one form of energy disappears, some other form of energy (of equal magnitude) must appear, and vice versa. This principle is summarized by the law of conservation of energy: the total quantity of energy in the universe is assumed constant.”

6.2 Energy Changes in Chemical Reactions

Chemical energy, H , enthalpy, is the stored potential energy within substances.

A substance's stored chemical energy is enthalpy, H , which can only be measured through changes, ΔH_{rxn}

You will never be asked for the actual stored energy of a substance H because that value cannot be determined.

Instead, you will deal with the changes in enthalpy, ΔH , of the reactants to products in a chemical reaction.

Since there can be increases or decreases the values of ΔH can be positive or negative. An analogy is that you have a secret Swiss bank account that has very large unknown balance (total enthalpy). By adding to the account, you can know the increase in the balance and by withdrawing you can know the decrease in the balance.

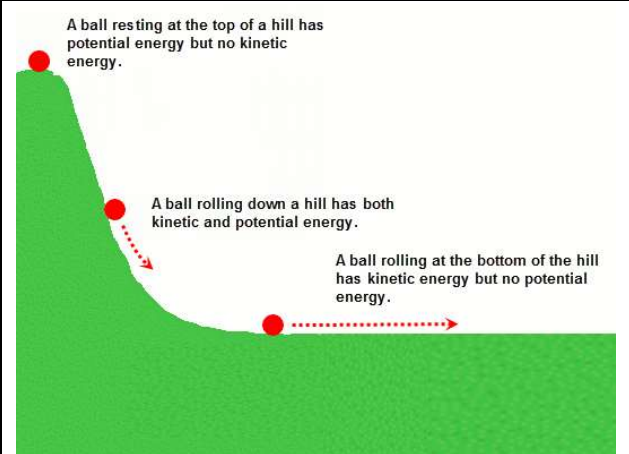
There are two types of ΔH_{rxn} reactions:

Exothermic reactions, ΔH_{rxn} = negative values (withdrawals of H)

Endothermic reactions, ΔH_{rxn} = positive values (deposits of H)

The changes in stored energy, enthalpy, ΔH_{rxn} , can be found experimentally and can be predicted theoretically. You will be expected to use both on the exam.

In an exothermic reaction, stored potential energy in the chemicals is released as kinetic energy to the surroundings.



When the ball rolls downhill, the change in Potential Energy of the ball is negative:

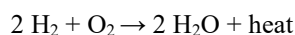
$\Delta \text{Potential Energy} = \text{negative sign}$

This is analogous to the drop in Potential Energy of chemicals in an exothermic reaction:

$\Delta H = - \text{negative value}$

Exothermic processes can be understood by comparing the enthalpies of the products to the enthalpies of the reactants in the chemical reaction.

The burning of hydrogen and oxygen to make water is exothermic, heat, kinetic energy is a product:



The reactants, $2 \text{H}_2 + \text{O}_2$, had a certain amount of enthalpy, $H_{\text{reactants}}$, (stored chemical energy in reactants).

When hydrogen and oxygen rearrange their atoms to make water: $2 \text{H}_2 + \text{O}_2 \rightarrow 2 \text{H}_2\text{O}$.

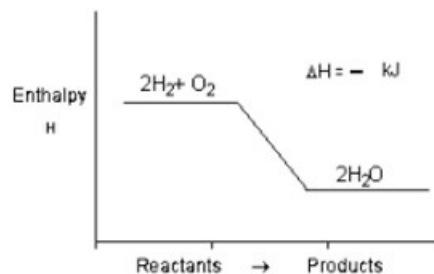
Stored chemical energy in the substances is decreased, but because energy is conserved, the stored chemical energy released as kinetic energy to the surroundings. This change in energy can be measured.

$2 \text{H}_2 + \text{O}_2$	\rightarrow	$2 \text{H}_2\text{O}$
stored energy in the reactants	=	less stored energy in the products + kinetic energy

H , enthalpy, stored potential chemical energy decreased in this chemical change because some of the enthalpy was converted to kinetic energy:

$$\Delta H_{rxn} = - , \text{ a negative value}$$

Kinetic energy of the surroundings increased by the amount of stored chemical energy the chemicals lost.



Endothermic process

It is possible to roll the rock back up the hill, that is change water back into hydrogen and oxygen, but not only must you separate the atoms in the molecule, but as this is done the kinetic energy that was released on forming the water must be changed back into potential energy. This can be done using electricity or extremely high temperatures.

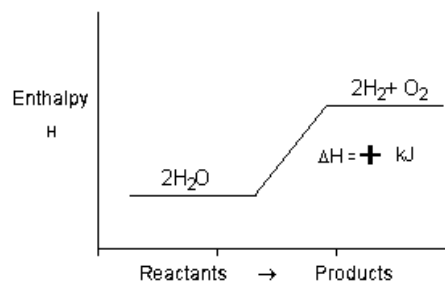
$2 \text{H}_2\text{O}$	\rightarrow	$2 \text{H}_2 + \text{O}_2$
water + kinetic energy	=	potential energy in hydrogen and oxygen is restored

The Kinetic Energy is converted into Potential Energy stored in the products increasing Enthalpy:

$$\Delta H_{\text{rxn}} = + \text{positive value}$$

Hydrogen and oxygen now have their original stored energy.

In the gravitational analogy, the ball pushed back uphill with its original potential energy.



All endothermic reactions increase in chemical potential energy as the reactants form products.

6.3 Introduction to Thermodynamics only a small part of this section is relevant.

Stored chemical energy can be described using E , internal energy, and H , enthalpy.

The differences between the E and H involve the work, w ,

Differences between E and H are not part of the AP Chem curriculum. Skip the section and equations on internal energy, E and w .

Bottom line: You will not have to deal with E

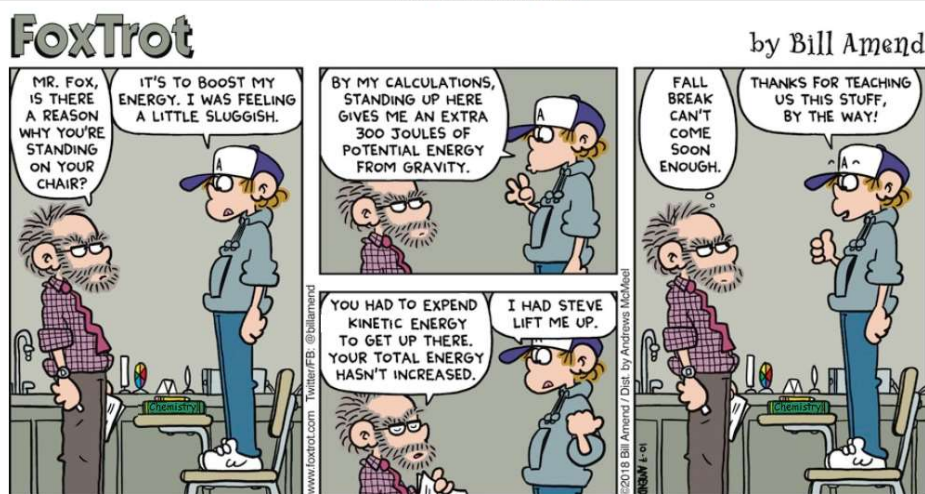
The First Law of Thermodynamics is the law of conservation of energy:

Energy can be converted from one form to another but cannot be created or destroyed.

In AP Chemistry, the application of the law:

Increases in Potential Energy (stored chemical energy) are accompanied by a decrease in Kinetic Energy.

Increases in Kinetic Energy are accompanied by decreases in Potential Energy (stored chemical energy).



6.4 Enthalpy of Chemical reactions.

Enthalpy of Chemical Reactions

H , the total or absolute amount of Enthalpy (stored energy) of a substance cannot be determined.

No one knows what hidden, uncharted, stored energy may be lurking in a compound.

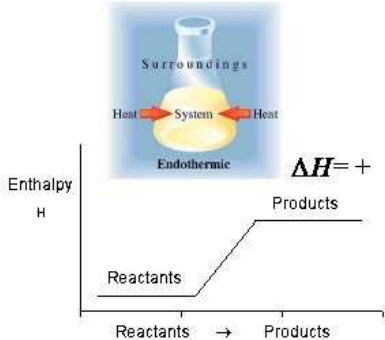
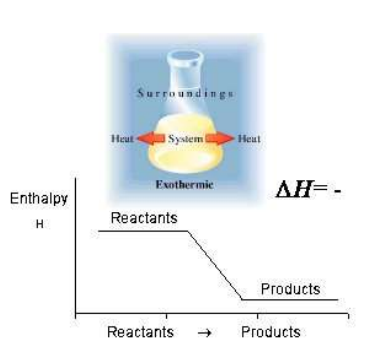
Only the ΔH_{rxn} , the CHANGE in enthalpy of a reaction can be determined.

Enthalpy measurements are **changes** of stored energy.

The change will always be stored energy of products minus stored energy of reactants¹.

$$\Delta H_{rxn} = H_{products} - H_{reactants}$$

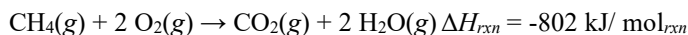
The bank checking account analogy there is a huge bank balance, but you have no way of finding the total amount in the account. However, you have a record of deposits and the withdrawals you can know the changes in the balance.

 <p>The surrounding's kinetic energy (heat) is changed into potential energy that is stored in the products.</p>	 <p>Surroundings get kinetic energy (heat) from the reaction, as the chemicals lose potential energy.</p>
<p>Energy in an endothermic reaction is stored in the substances as potential chemical energy.</p> <p style="text-align: center;">Reactants + Heat → Products</p>	<p>Energy in an exothermic reaction raises the temperature of the surroundings</p> <p style="text-align: center;">Reactants → Products + Heat</p>

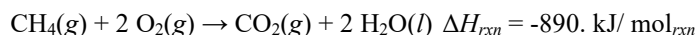
Since ΔH involves chemical reactions, the conventions of its use require a complete chemical equation.

- (1) The phase (state) of the substances in a reaction must be included in the reaction.

If methane is burned with oxygen to form carbon dioxide and steam, the reaction will release 802 kJ of energy to the surroundings:



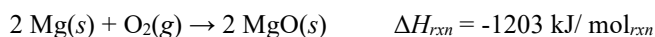
However, if the reaction is done so that the steam is condensed to water, the energy released as the water molecules condense from a gas to a liquid (-44 kJ/mol which would be -88 kJ for 2 mol) must be included².



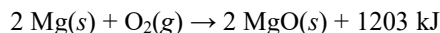
¹ The Delta, Δ , consistently represents change, as in slope, $\Delta x = x_2 - x_1$, where the first measurement is subtracted from the second measurement.

² High efficiency gas furnaces condense the water formed from the burning of methane rather than allowing the steam to escape out the chimney. This increases the efficiency of the furnace by about 10%.

- (2) AP Chemistry uses the units of $\text{kJ/mol}_{\text{rxn}}$ for balanced chemical equations. Whenever you see the energy in a chemical reaction in AP “X $\text{kJ/mol}_{\text{rxn}}$ ” means “X kJ per the mole amounts in the given balanced equation.”



or



The -1203 kJ/mol released to the surroundings as kinetic energy is from burning 2 mol of magnesium solid with 1 mol of oxygen gas to make 2 mol of solid magnesium oxide.

- (3) Often in thermochemical reactions, fractions are used to denote fractions of mol amounts to deal with producing 1 mole of product.



The enthalpy change for burning 1 mol of magnesium solid using a half mol (16 g) of oxygen gas to make one mole of solid magnesium oxide is the release of 601 kJ of kinetic energy to the surroundings

- (4) Sometimes the full reaction equation is not shown for certain types of enthalpy reactions. Only the products are shown as it is expected that the reader knows the reaction that makes the product by the category name of the reaction.

Here are the reaction categories that will be used throughout the year

Enthalpy of Formation, $\Delta H_{\text{formation}}$ or ΔH_f .

Enthalpy of Formation reactions are the simplest and most important type of reactions in thermodynamic problems.

An Enthalpy of Formation reaction has only one mole of product, and the product is made from its constituent elements in their most common form at room temperature.

There will be more on this later in the chapter.

e.g. $\Delta H_{\text{formation}} \text{MgO}(s) = -601.7 \text{ kJ/mol}$ stands for this reaction: $\text{Mg}(s) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{MgO}(s)$

Enthalpy of Combustion ΔH_{comb}

Enthalpy of Combustion is the change in enthalpy of one mole of the substance burned in oxygen at thermodynamic standard conditions (1 atm and 25°C).

All combustion reactions are exothermic with a negative enthalpy change.

e.g. $\Delta H_{\text{comb}} \text{C}_3\text{H}_8 = -2220 \text{ kJ/mol}_{\text{rxn}}$ stands for this reaction: $\text{C}_3\text{H}_8(g) + 5\text{O}_2(g) \rightarrow 3\text{CO}_2(g) + 4\text{H}_2\text{O}(l)$

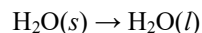
AP Chemistry exams will always show the ΔH_{comb} as negative values.

However, because all ΔH_{comb} values are exothermic, tables and reference material usually list the ΔH_{comb} as positive values because they know the chemists using these values realize that they are exothermic reactions.

Enthalpy of Fusion ΔH_{fusion}

Enthalpy of Fusion is the energy absorbed when one mole of the substance is melted (fusion). Since fusion always involves breaking intermolecular bonds, **ΔH_{fusion} values are always endothermic.**

e.g. $\Delta H_{\text{fusion}} \text{H}_2\text{O} = 6.01 \text{ kJ/mol}$ is for this reaction:

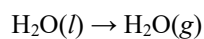


Enthalpy of Vaporization ΔH_{vap}

Enthalpy of Vaporization is the energy absorbed when one mole of the substance is vaporized (boiled). Since vaporization always involves breaking the bonds, **ΔH_{vap} values are always endothermic.**

Enthalpy of Vaporization of a substance is always greater than the enthalpy of fusion since intermolecular bonds are broken not just disrupted as in melting.

e.g. $\Delta H_{\text{vap}}^\circ \text{H}_2\text{O} = 44 \text{ kJ/mol}$ is for this reaction:

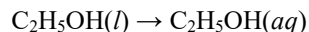


Enthalpy of Solution $\Delta H_{\text{solution}}$

Enthalpy of Solution is the enthalpy change on dissolving a solute. **$\Delta H_{\text{solution}}$ can be exothermic or endothermic.**

There will be more on this process later in the chapter.

e.g. $\Delta H_{\text{sol}} \text{C}_2\text{H}_5\text{OH} = -11 \text{ kJ/mol}$ is for this reaction:

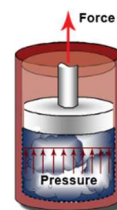


Comparison of ΔH and ΔE ...not in AP Chemistry curriculum

Chemical reactions can do work by expanding gases expanding via changes in pressure.

e.g. The expanding gases in combustion engines move pistons.

But E that includes this work this is not covered in AP Chemistry



6.5 Calorimetry is used in every AP Chemistry exam.

When heat energy is applied to a substance, the resulting temperature changes of the substance are not identical.

To account for this, **Specific Heat Capacity** is used when dealing with heat energy and temperature changes of pure substances and mixtures.

Specific Heat Capacity³

Specific Heat Capacity, c , is the amount of heat energy needed to change the temperature of one gram of a substance 1°C or 1 K .

The symbol for specific heat is not standardized. It is "s" in Chang and "c" on the AP Equation sheet. I will use the AP Exam abbreviation.

Molar Heat Capacity

The AP Chem exam has also used molar heat capacity which is the amount of heat needed to change one mole of a substance 1°C or 1 K .

THERMODYNAMICS / ELECTROCHEMISTRY	
$q = mc\Delta T$	q = heat m = mass c = specific heat capacity T = temperature

Substances that have small increases in temperature with the addition of heat have high specific heat capacities.

Water has one of the highest specific heat capacities.

1.0 g of water will increase in temperature 2°C on absorbing 10 J of energy.

The specific heat capacity of water = $4.18\text{ J/g }^{\circ}\text{C}$ or 4.18 J/g K

Substances that have large changes in temperature on the addition of heat have low specific heat capacities.

Metals tend to have low specific heat capacities.

1.0 g of gold will increase in temperature 78°C on absorbing 10. J of energy.

The specific heat capacity of gold = $0.128\text{ J/g }^{\circ}\text{C}$ or 0.128 J/g K

Specific heat capacity is the change per gram of a substance, and most AP Chemistry questions use specific heat capacity. However, on some occasions, another form of specific heat is used, the molar heat capacity. The important difference is that this is the amount of heat needed to change the temperature of one mole of substance rather than a gram. It is important that you keep track of units in calorimetry problems.

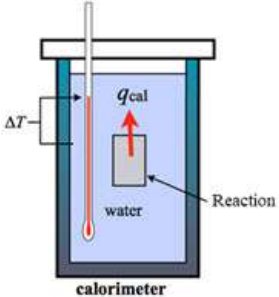
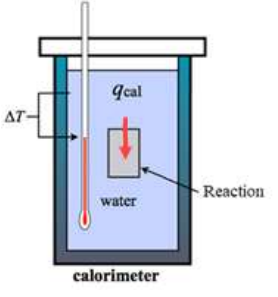
Note how the units of the specific heat capacity and molar heat capacity of water are different.

$$\text{specific heat capacity of H}_2\text{O} = \frac{4.18 \text{ J}}{\text{g K}} \quad \text{or} \quad \frac{4.18 \text{ J}}{\text{g } ^\circ\text{C}}$$

$$\text{molar heat capacity of H}_2\text{O} = \frac{75.3 \text{ J}}{\text{mol K}} \quad \text{or} \quad \frac{75.3 \text{ J}}{\text{mol } ^\circ\text{C}}$$

Calorimetry is a method of experimentally determining changes in enthalpy for reactions by using the change in energy of the reaction to change the temperature of the calorimeter.

Finding the ΔH_{rxn} experimentally:

 <p>Exothermic rxn, $\Delta T = +$</p>	<p>A reaction is performed in an isolated, insulated container, a calorimeter. Usually, the calorimeter is filled with water or aqueous solution.</p> <p>When the reaction occurs, kinetic energy is either released to the container and water (exothermic rxn) or absorbed from the container and water (endothermic rxn).</p> <p>The temperature in the container will either increase or decrease.</p> <p>Experimental $\Delta T = +$ for an exothermic rxn</p> <p>Experimental $\Delta T = -$ for an endothermic rxn</p>	 <p>Endothermic rxn, $\Delta T = -$</p>
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Every Calorimetry experiment involves a temperature change and, as in **almost all change, Δ , calculations, the subtraction is the second value minus the first value.**

$$\Delta T = T_{\text{final}} - T_{\text{initial}} \quad \text{the sign of the change is critical!}$$

THERMODYNAMICS/ELECTROCHEMISTRY

$$q = mc\Delta T$$

q = heat
 m = mass
 c = specific heat capacity
 T = temperature

q = the experimental energy change

m = mass of substance being heated

If a solution is made in the experiment, the mass used in the equation is the mass of water plus the mass of the solute.

c = specific heat capacity

IMPORTANT!

The change in enthalpy of the chemicals in the reaction q_{rxn} will always be the opposite sign of the q in the calorimetry equation.

$$q_{rxn} = - q_{calorimeter}$$

Once the q_{rxn} is found, the enthalpy change of the reaction can be scaled to per mol of reaction by using the mol of substance that was used in the reaction.

$$\Delta H_{rxn} = \frac{q_{rxn}}{\text{moles of reaction}}$$

You **must change the sign of the $q_{calorimeter}$ value to the q_{rxn} value before** you do the ΔH_{rxn} calculation.

A calorimeter question is always on the AP Chemistry exam.

Remember:

$$\Delta T = T_{final} - T_{initial}$$

If ΔT = positive ΔH_{rxn} = exothermic

If ΔT = negative ΔH_{rxn} = endothermic

m = mass of the solution (water + solute) or substance that is heated

$$q_{rxn} = - q_{calorimeter}$$

$$\Delta H_{rxn} = q_{rxn} / \text{moles reacting (stoichiometry may be involved)}$$

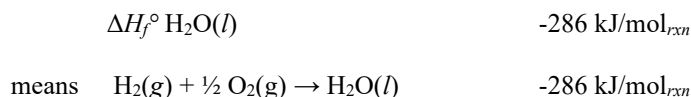
6.6 Standard Enthalpy of Formation and Reactions

ΔH_f° Standard Enthalpy of Formation can be used to predict the ΔH_{rxn}° of more complex reactions.

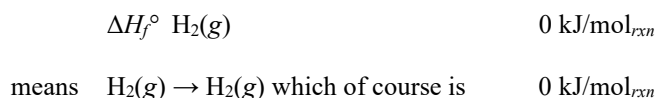
ΔH_f° is the enthalpy when 1 mole of a compound is formed from its elements (at 1 atm and 25°)

Even though only the product of the reaction is shown, it is understood that the ΔH is for a reaction.

ALL ΔH values are for reactions! You must have a reaction to have a Δ !



Elements in their most common form have standard heats of formation of 0 kJ/mol_{rxn}



There are tables of ΔH_f° reactions (Appendix 3 in Chang). The tables usually don't have ΔH_f° for elements since a student should know that elemental formation enthalpies are zero.

In AP Chemistry problems the enthalpy of formation table will be given as part of the problem. Here is a table from one of the released exams:

Substance	$\text{C}_3\text{H}_6(g)$ ΔH_f	$\text{CO}_2(g)$ ΔH_f	$\text{O}_2(g)$ ΔH_f
Standard Enthalpy of Formation	37 kJ/mol	-394 kJ/mol	----

The solution required the enthalpy of formation of oxygen which was not given. This was done on purpose since students **are expected to know that the ΔH_f of elements in their normal room temp form is zero.**

So, a student could have completed the table and solved the problem.

Substance	$\text{C}_3\text{H}_6(g)$ ΔH_f	$\text{CO}_2(g)$ ΔH_f	$\text{O}_2(g)$ ΔH_f
Standard Enthalpy of Formation	37 kJ/mol	-394 kJ/mol	0 kJ/mol

A complication: Some elements have allotropes which have a different enthalpy than the standard, common form of the element.

e.g. $\Delta H_f^\circ \text{ C (graphite)}$ 0 kJ/mol as you would expect for any element.
 $\Delta H_f^\circ \text{ C (diamond)}$ 1.9 kJ/mol because diamond is not the common form of carbon

Diamonds can be made by compressing and heating graphite. It requires 1.9 kJ of energy to change 12 g of graphite to 12 g of diamond.

You can find the ΔH_{rxn} for regular reactions using a Standard Enthalpy of Formation Table and Hess's Law:

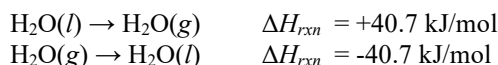
$$\Delta H_{rxn} = \sum \Delta H_{f,products} - \sum \Delta H_{f,reactants}$$

Working problems with a Standard Enthalpy of Formation Table is a simple exercise in math. Be careful with the signs, coefficients and, above all, remember **products minus reactants!**

You can also find the ΔH_{rxn} by using equations that add up to the desired reaction.

A series of equations and their ΔH_{rxn} are given. You must then manipulate the equations to add up to a new reaction. It is just like adding systems of equations in math. Just as with systems of equations, you sometimes have to reverse equations or multiply the equations so that the sum of the simpler equations produces the desired reaction.

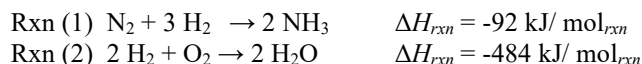
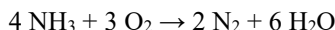
Reversing a reaction changes the sign of the enthalpy change.



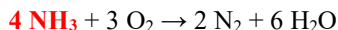
Multiplying a reaction requires multiplying enthalpy change.



Use the two given equations to find the enthalpy change for the combustion of ammonia:
All gases



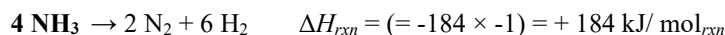
These two equations can be manipulated and added to produce the ammonia combustion reaction. In creating the desired reaction start with the ammonia reactant for the combustion reaction, 4NH_3 .



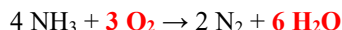
Rxn(1) must be multiplied by 2 to get 4NH_3



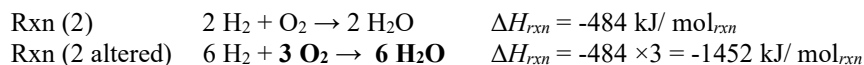
Then the rxn must be flipped to make the ammonia a reactant.



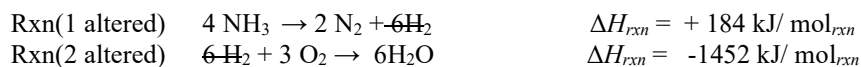
Now that the ammonia matches the desired reaction, the water or oxygen must be adjusted in Rxn (2).



Rxn(2) must be multiplied by 3. Note that the water works out since you needed 6 mol of water.



The addition of the reactions and the new enthalpies



In adding reaction problems, the given reactions will work out if you manipulate the given equations correctly.

There are three ways that allow you to determine the change in enthalpy of a reaction, ΔH_{rxn} :

1. Calorimetry (Experimental) $q = m c \Delta T$
2. Hess's Law Using ΔH_f° $\Delta H_{rxn} = \Sigma \Delta H_{f products} - \Sigma \Delta H_{f reactants}$
3. Adding several reactions to get the desired reaction

There is a fourth method using Bond Energies later in the year after you learn more about bonds.

6.7 Heat of Solution

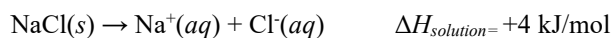
Heat of Solution is the enthalpy change on dissolving a solute. It can be exothermic or endothermic.

These two ideas are important and will be the basis for answering many questions on the AP Chemistry Exam.

BREAKING ANY BOND is ENDOTHERMIC and increases potential energy.

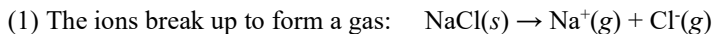
FORMING ANY BOND is EXOTHERMIC and decreases potential energy.

The equation for an ionic compound, sodium chloride, dissolving is:

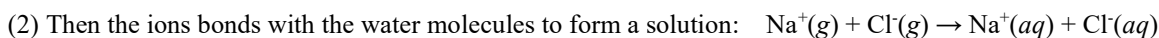


Here are the steps in forming a solution when sodium chloride dissolves:

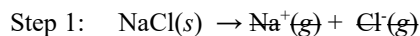
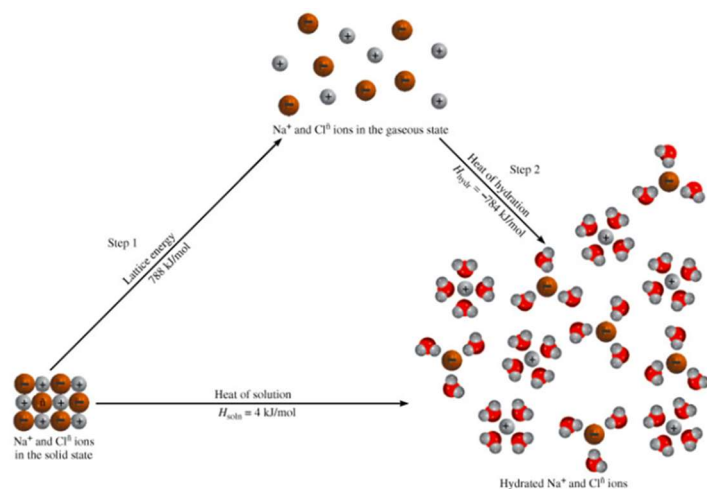
Ionic compounds have their ions separate making an electrically conductive solution. The process can be broken up into steps.



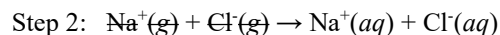
This involves the separation of ions requiring the input of a large amount of energy, 788 kJ/mol.



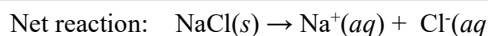
When bonds between the water molecules and ions are formed, kinetic energy is released = - 784 kJ/mol.



788 kJ/mol



-784 kJ/mol



Step 1 + Step 2 = net reaction
 $788 \text{ kJ/mol} + (-784 \text{ kJ/mol}) = +4 \text{ kJ/mol}$

Even though the process involves large changes in energy (788 kJ/mol and -784 kJ/mol) the net change in energy of dissolving salt in water is only + 4 kJ/mol, hardly noticeable.

Heat of Dilution

Heat of Dilution is taking a substance that is already dissolved and increasing its dilution. There have been no questions on this on the AP Chemistry exam.

However, you should know about this one potential hazard of dilution concerning strong acids and bases.

Sulfuric acid (a common acid) releases considerable heat when it is diluted.

Dilution done by adding water to concentrated acid is hazardous.

The less dense water when added to the concentrated acid will "float" on top of the denser acid. Mixing (exothermic dilution) will occur in a narrow layer between the water and acid. This small volume will increase the solution temperature dramatically.

The heat instantly generated by adding water to acid can cause the layer to boil and splatter or the glassware to break from thermal shock.

Instead, concentrated acid should be added to water.

Adding concentrated sulfuric acid to water slowly with constant stirring is much safer because the heat generated is spread over a larger volume as the denser sulfuric acid goes through much more water as it sinks. While the same amount of heat is generated, it is not concentrated in a narrow layer.

The lab saying is "Add acid to water as you ought-er."

Equations and symbols on the AP Equation sheet

THERMODYNAMICS/ELECTROCHEMISTRY	
$q = mc\Delta T$ $\Delta H_{\text{reaction}}^{\circ} = \sum \Delta H_f^{\circ} \text{ products} - \sum \Delta H_f^{\circ} \text{ reactants}$	q = heat m = mass c = specific heat capacity T = temperature H° = standard enthalpy