

Unit 9: Thermodynamics and Chemical Kinetics (Reaction Rates)

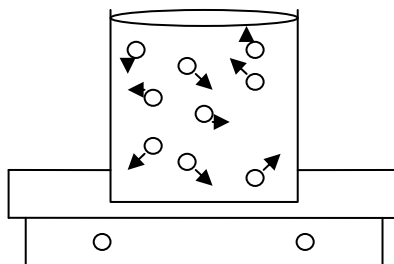
In the first part of the unit, you will learn about the energy associated with physical and chemical changes. You will also learn how to determine whether or not a reaction will occur.

In the second part of the unit, you will learn about the qualitative factors that influence the rate of a reaction and how the concentration of reactants quantitatively affects the rate of a reaction

Thermodynamics

Temperature, Heat and Energy

The study of thermodynamics is concerned with the changes in energy that accompany chemical reactions and phase changes. In order to study these changes in energy, it is first necessary to define some terms. The internal energy of matter comes in two broad categories, kinetic energy (energy of motion) and potential energy (energy of position). All substances contain kinetic energy, since their atoms and molecules are always in motion. Recall that **the temperature of a sample of matter is interpreted as a measure of the average kinetic energy of the particles.** All substances also contain potential energy, since their atoms and molecules can undergo rearrangement which may release or absorb energy.



Consider a 50.0 mL beaker of water at room temperature: The water molecules are moving, some faster, some slower than others, constantly colliding with each other, and exchanging energy in the process. Some of the water molecules at the surface of the liquid also collide with molecules in the air. In this way, the molecules of the water are constantly exchanging energy with their surroundings. Since the beaker, the water and the air are all at room temperature, on the average the water neither gains nor loses energy. There is no net transfer of energy between these samples of matter.

If we put this beaker on a warm hot plate, the situation changes. Energy begins to flow from the glass into the water and from the water into the air. This flow of energy is called heat. **Heat is the word used to describe energy which is transmitted from one substance or object to another.** Heat only exists while it is being transferred. Before it is transferred, the energy is considered part of the internal energy of the glass. After it has been transferred, it is considered part of the internal energy of the water. While it is being transferred, we call it heat. Think of music: In whatever form it is stored, we can only hear it while it is being performed. In that sense, the performance is like heat.

Why does heat flow from the glass into the water and from the water into the air? At first, the glass is warmer than the water because heat from the hot plate is conducted into the glass. Since the glass is at a higher temperature than the water, collisions between glass particles and water particles will on the average transfer energy into the water. This energy is then transferred between water molecules so that the energy is distributed throughout the water. As heat is conducted through the glass into the water, the water becomes warmer than the surrounding air. So on the average, collisions between water molecules at the surface and air molecules above it will result in a transfer of energy out of the water and into the air. In general, heat always flows from an area of higher temperature to an area of lower temperature.

Quantifying Heat and Calorimetry

If two samples of matter at different temperatures are allowed to come in contact, **heat** will flow from the higher temperature substance to the lower temperature substance until the temperatures are the same. Heat will also flow to or from the surroundings during chemical and physical changes. This transfer of energy is given a symbol, **Q**. Heat transfers indicated can be calculated by using the following relationship:

heat transferred = (mass) (specific heat*) (change in temperature)

$$Q = m s (T_f - T_i)$$

or $Q = m s \Delta T$

* The specific heat of a substance is a characteristic property of that substance.

Specific heat = energy required to raise the temperature of 1.0 g of a substance one degree Centigrade. Usually expressed in **Joules/gram·°C**. (1000 J = 1 kJ)

Notice that the heat transfer is **negative if the temperature decreases**.

A standard method of investigating the energy changes involved in chemical reactions is called **calorimetry**. The reaction is performed in insulated surroundings (usually water) and the temperature change of the water is recorded. The heat released to or absorbed from the surroundings during the experiment can then be calculated.

Problem on Calorimetry

1. How much heat is required to raise the temperature of 35.0 grams of water from 20.0°C to 35°C? (The specific heat of water is 4.184 Joules/gram·°C)

[2197 J (= 2.20 kJ)]

Enthalpy

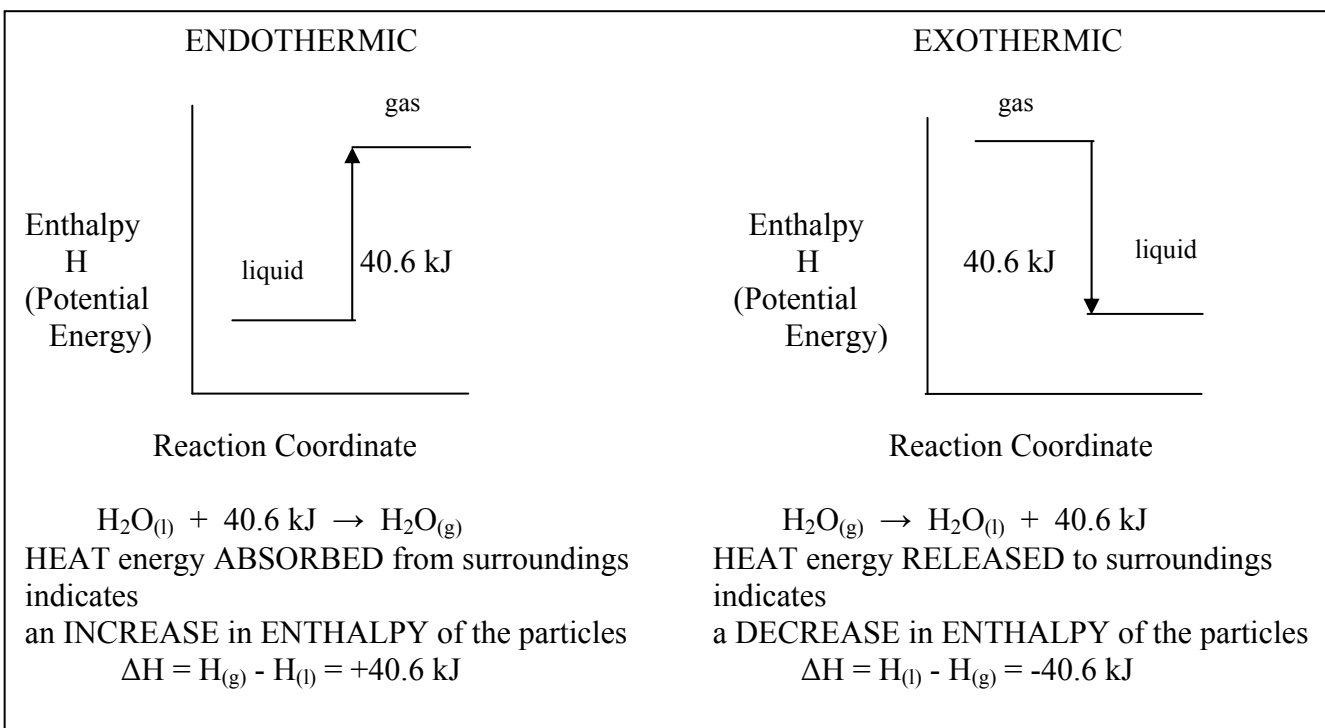
When methane gas is burned, a lot of heat energy is generated. According to the law of conservation of energy, energy is never created or destroyed. So where was the energy before it became heat? The energy was in another, less visible form we might call “chemical potential energy”. The word that chemists use to describe the total stored energy in a substance is called **enthalpy**, and is abbreviated as **H**. It is a form of potential energy related to the arrangement of the atoms in a substance, and is therefore associated with chemical bonds and intermolecular forces. It is actually impossible to directly measure the exact amount of potential energy in a substance, but *changes* in enthalpy (ΔH) for processes can be determined indirectly by measuring the amount of heat (**Q**) which is either released to or absorbed from the surroundings during the process.

Enthalpy and Phase Changes

Melting, boiling and evaporation are all endothermic processes. Heat energy is absorbed from the **surroundings**. This heat is converted into an increase in the enthalpy of the **system** of particles. Condensation and freezing are exothermic processes. Heat energy is released to the **surroundings**. The enthalpy decrease of the **system** of particles is converted into the heat that is released.

Enthalpy Diagrams

An enthalpy diagram below shows the changes in enthalpy which take place as familiar phase changes proceed. The diagram on the **left depicts boiling and evaporation**. The enthalpy of the product (gas phase) is greater than the enthalpy of the reactant (liquid phase). The diagram on the **right depicts condensation**. The enthalpy of the product (liquid phase) is less than the enthalpy of the reactant (gas phase)



Heat of Solution

The dissolving process is often accompanied by an energy change. The energy considerations can be thought of in terms of three distinct events:

1. **Solute particles become attached to and surrounded by solvent molecules.** This action is exothermic because the solvent molecules are attracted to the solute particles. The solvent molecules and solute particles do NOT form a true chemical bond, but the energy result is analogous.
 2. **Solute particles are separated from the solid mass.** This action absorbs energy. It is endothermic because solute particles are attracted to each other, and energy is required to “pull” the solute particles apart.
 3. **Solvent molecules are moved apart to “make room” for solute particles as they disperse.** This action is also endothermic because there are also significant attractive forces between the solvent water molecules. Again, energy is required to separate the solvent molecules.
- If the exothermic action (step 1) is less than the sum of the endothermic actions (steps 2 and 3), then the **net change is endothermic**. Consequently, the **temperature of the solution decreases** as the solid dissolves. This is indicated by a **positive** heat of solution. (ΔH_{soln})
 - If the energy involved in step 1 is greater than the sum of the energies involved in steps 2 and 3, the **net change is exothermic**. As a result, the **temperature of the solution increases** as the solid dissolves. This is indicated by a **negative** heat of solution. (ΔH_{soln})
 - The MOLAR HEAT OF SOLUTION (ΔH_{soln}) is the heat released or absorbed when one mole of a substance is dissolved in a solvent (usually water).

Quantitatively, the typical calculations are based on calorimetry.

$$1) \text{ Heat released or absorbed} = (\text{mass of H}_2\text{O}) (\text{specific heat of H}_2\text{O} *) (\text{final temp} - \text{initial temp})$$

*specific heat of water = 4.18 J/g·°C

or
$$Q_{\text{expt}} = m_{\text{H}_2\text{O}} s \Delta T$$

2) The molar heat of solution (ΔH_{soln}) can then be calculated by the following relationship:

$$\Delta H_{\text{soln}} = \frac{-Q_{\text{expt}}}{\text{moles}_{\text{ solute}}}$$

Problem on Heat of solution

2. A student added 4.50 grams of KCl (MM = 74.6 g/mol) to 100.0g of water in a calorimeter. The temperature of the water in the calorimeter dropped from 24.00°C to 21.20°C.

a. How much heat (in kJ) was released to or absorbed from the water in the calorimeter?
(specific heat of water = 4.18 J/g °C)

(1.17 kJ)

b. Calculate the moles of KCl dissolved.

(0.0603 moles)

c. What is the molar heat of solution of KCl? Include the proper sign of ΔH_{soln} .

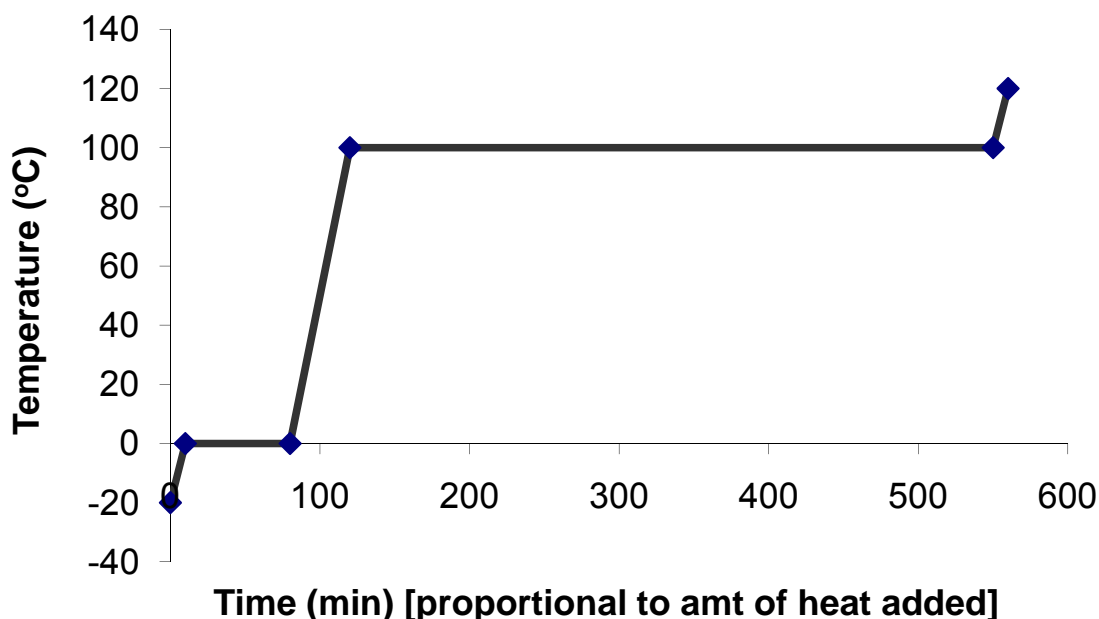
(+19.4 kJ/mol)

Energy and Phase Changes - Heating Curves Revisited

The conceptual information here is largely review. The inclusion of enthalpy and the quantitative treatment is new material

The heating curve is a temperature versus time graph which demonstrates the relationship between absorbance of heat energy, temperature and phases of matter. It is assumed that the heat is being added at a constant rate so that the measure of time on the x-axis also is a measure of heat energy absorbed. In the graph below, the curve shows what happens when one mole (18.0g) of H₂O is heated at a constant rate starting with ice at -20°C and ending with steam at 110°C.

Heating Curve for H₂O



1) Between -20 °C and 0 °C, the H₂O is in the form of ice and steadily increases in temperature as energy is added until the ice begins to melt. The kinetic energy of the molecules is increasing (in the form of vibration) until the attractive force (hydrogen bonds) begins to partially break down at 0 °C. Any quantitative considerations would be governed by:

$$Q = m_{ice} s_{ice} \Delta T$$

2) Between 10 and 80 minutes melting occurs as additional heat energy is absorbed. During this period of time, there is a mixture of ice and water. The temperature remains constant at 0 °C. This indicates that there is no increase in the kinetic energy of the particles. Why doesn't the additional heat result in an increase in temperature during this time? This heat energy is being used to increase the enthalpy (potential energy) of the particles as they partially overcome the hydrogen bond attractions and change from the solid to the liquid phase. When sufficient energy has been added to free the molecules from their fixed position, the ice is completely melted. After all the ice has melted about 15 percent of the strength of hydrogen bonding has been disrupted. The energy required to melt 1 mole of a solid is called the **molar heat of fusion** and is **6.01 kJ/mole** for H₂O. Quantitative considerations would be governed by:

$$Q = n_{H_2O} \Delta H_{fus_{H_2O}}$$

3) Between 0 °C and 100 °C, the H₂O is in the form of liquid and steadily increases in temperature as energy is added until the water begins to boil. The kinetic energy of the molecules is increasing (in the form of vibration, rotation and translational movement) until the attractive force (hydrogen bonds) begins to completely break down at 100 °C. Any quantitative considerations would be governed by:

$$Q = m_{\text{water}} s_{\text{water}} \Delta T$$

4) Between 80 and 550 minutes boiling occurs as additional heat energy is absorbed. During this period of time, there is a mixture of water and steam. The temperature remains constant at 100 °C. This indicates that there is no increase in the kinetic energy of the particles. Why doesn't the additional heat result in an increase in temperature during this time? This heat energy is being used to increase the enthalpy (potential energy) of the particles as they completely overcome the hydrogen bond attractions and change from the liquid to the gas phase. When sufficient energy has been added to completely separate the molecules, the liquid is changed into the gas phase. After all the water has boiled the hydrogen bonding has been disrupted. The energy required to boil 1 mole of a liquid is called the **molar heat of vaporization and is 40.6 kJ/mole** for H₂O. This same amount of heat energy would be absorbed from the surroundings when 1 mole of water evaporates spontaneously. This process is called evaporative cooling. Quantitative considerations would be governed by:

$$Q = n_{\text{H}_2\text{O}} \Delta H_{\text{vapH}_2\text{O}}$$

5) Above 100 °C, the H₂O is in the form of gas and steadily increases in temperature as energy is added. The kinetic energy of the molecules is increasing (in the form of vibration, rotation and especially translational movement). Any quantitative considerations would be governed by:

$$Q = m_{\text{steam}} s_{\text{steam}} \Delta T$$

Cooling Curves

The heating curve could also be used in the opposite direction as a “cooling curve” to describe what happens when heat is continuously released by a sample of H₂O that starts as steam above H₂O.

- 1) The steam cools to 100 °C accompanied by a decrease in kinetic energy of the particles.
- 2) The steam condenses to water at 100 °C accompanied by a decrease in enthalpy of the particles.
- 3) The water cools to 0 °C accompanied by a decrease in kinetic energy of the particles.
- 4) The water freezes to ice at 0 °C accompanied by a decrease in enthalpy of the particles.
- 5) The ice continues to cool below 0 °C accompanied by a decrease in kinetic energy of the particles.

Phase Change Problems

Use the given information below to solve the following problems.

Given:

specific heat of ice = $2.03 \text{ J/g}\cdot\text{°C}$

specific heat of water = $4.18 \text{ J/g}\cdot\text{°C}$

specific heat of steam = $1.96 \text{ J/g}\cdot\text{°C}$

molar heat of fusion of H_2O = 6.01 kJ/mole

molar heat of vaporization of H_2O = 40.7 kJ/mole

3. How much energy is required to melt a 1.00 kg block of ice?

(334 kJ)

4. How much heat would be released from a 25.0 g of steam as it condenses into water?

(56.4 kJ)

5. How much energy is absorbed as 1.00 gram of water evaporates?

(2.26 kJ)

6. How much energy would be required to convert an ice cube weighing 25.0 g and having a temperature of -20.0 °C to water having a temperature of 95 °C ?

(19.3 kJ)

Enthalpy and Chemical Reactions

In an **exothermic** chemical reaction, enthalpy is essentially converted into heat that is lost to the surroundings. Therefore, the products are lower in enthalpy than the reactants. Since

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

the ΔH of the reaction is **negative**.

In an **endothermic** chemical reaction, heat that is absorbed from the surroundings is essentially converted into enthalpy. Therefore, the products are higher in enthalpy than the reactants. Since

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

the ΔH of the reaction is **positive**.

In class, draw enthalpy (or potential energy) diagrams for an exothermic and endothermic reaction. Label the enthalpy of the reactants, the enthalpy of the products and the ΔH_{rxn} .

EXOTHERMIC

ENDOTHERMIC

Determination of Heat of Reaction by Calorimetry and Heat Stoichiometry

“ ΔH_{rxn} ” has historically been interpreted as the “**heat of reaction**”. You now know “H” is an abbreviation for a enthalpy. Therefore, “ ΔH_{rxn} ” can also be translated as the “change in enthalpy for the reaction”. It represents **the enthalpy change associated with the mole amounts indicated by the coefficients in the balanced equation.** Therefore, ΔH_{rxn} can be related to the heat released or absorbed during an experiment by the following relationship:

$$\frac{\Delta H_{\text{rxn}}}{\text{coefficient}_{\text{reactant}}} = \frac{-Q_{\text{expt}}}{\text{moles}_{\text{reactant}}}$$

- If the temperature of the surroundings increases that would be characteristic of an **exothermic** reaction. Then Q will be a positive number and ΔH_{rxn} **will be a negative number** or be written on the right side of the balanced equation.
- If the temperature of the surroundings decreases that would be characteristic of an **endothermic** reaction. Then Q will be a negative number and ΔH_{rxn} **will be a positive number** or be written on the left side of the balanced equation.
- **Heat Stoichiometry:** This proportional relationship can also be used to find the heat released or absorbed (Q_{expt}) when a given amount of reactant is used or a given amount of product is formed in a reaction of known ΔH_{rxn} .

Problems on Heat of Reaction from Calorimetry and Heat Stoichiometry

7. Given the following combustion reaction for ethane (C₂H₆):



a. How much heat is produced when 5.00 moles of ethane are burned?

(Ans: 408 kJ)

b. How much heat is released when 7.00 g of ethane are burned?

(Ans: 19.0 kJ)

8. When 0.0532 g of Al metal is placed in 50.0 mL of 1.0 M HCl, a chemical reaction occurs, and all of the aluminum is consumed. The mass of the solution is 57.5 g and the temperature of the solution rises from 25.0°C to 28.6°C. (Assume the specific heat of the solution is 4.18 J/g·°C.)

a. Write a balanced molecular equation for this reaction. (Answer on p.51)

b. How much heat (Q) is evolved when this experiment takes place? Report the answer in kJ.

(0.865 kJ)

c. How many moles of Al were used in the experiment?

(0.00197 mol)

d. Calculate the heat of reaction in kJ and report it with the proper sign.

(ΔH = -878 kJ)

e. Rewrite the balanced equation including the energy term in the equation. (Answer on p.51)

9. When 50.0 mL of a 1.0 M HCl solution is mixed with 50.0 mL of a 1.0 M NaOH solution, a chemical reaction occurs and the temperature of the combined solutions rises from 25.0°C to 31.9°C. (Assume the density of the combined solutions is 1.0g/mL and the specific heat is 4.18 J/g·°C.)

a. How much heat is evolved when this chemical reaction takes place? Report the answer in kJ.
(reminder: use the combined mass of the solutions)

(2.88 kJ)

b. How many moles of HCl were used in the experiment?

(0.0500 moles HCl)

c. Calculate the heat of reaction in kJ and report it with the proper sign.

($\Delta H = -57.6$ kJ)

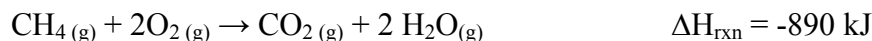
d. Write a balanced equation for this reaction that includes the heat of reaction. (Answer on p.51)

Laws of Thermochemistry

There are three fundamental laws of thermochemistry related to the enthalpy change that accompanies a chemical reaction (ΔH_{rxn}); a.k.a. the "heat of reaction".

1. The magnitude of the heat released or absorbed is directly proportional to the mole amount of reactant or product.

For example: If the combustion of one mole of methane evolves 890 kJ of heat.



The combustion of two moles of methane produces $2(890) = 1780$ kJ of heat.

2. ΔH for a given reaction is equal in magnitude but opposite in sign to ΔH for the reverse reaction.

In other words, if the heat of vaporization of liquid water is 40.7 kJ/ mole,



when a mole of gaseous water condenses, 40.7 kJ of heat is evolved or released into the environment.



3. The value of ΔH for a reaction is the same whether it occurs in one step or in a series of steps.

This means that if an overall equation can be expressed as the sum of two or more other equations:

$$\text{i.e. Equation (3) = Equation (1) + Equation (2)}$$

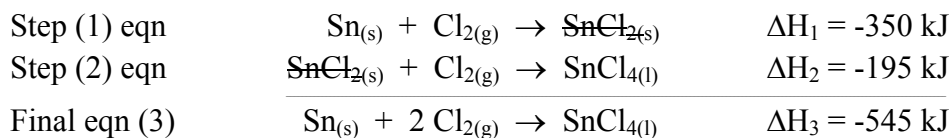
Then ΔH for the overall equation is the sum of the ΔH 's for the individual equations

$$\Delta H_3 = \Delta H_1 + \Delta H_2$$

This principle is referred to as **Hess's Law**.

As an example, consider the set of equations below:

- The final equation (3) shows the direct reaction between 1 mole of Sn and 2 moles of Cl_2 to form 1 mole of SnCl_4 .
- We can also show this overall reaction as taking place in two steps.
In the first step, 1 mole Sn reacts with 1 mole of Cl_2 to form 1 mole of SnCl_2 . Then, in a second step, 1 mole of SnCl_2 reacts with another mole of Cl_2 to form 1 mole of SnCl_4 .
- The two steps "add up" to the final equation so the ΔH for the final equation equals the sum of the enthalpy changes for the two steps.



It is NOT useful to simply memorize these laws; you will not be asked to write them on a test. Rather, you should learn how to apply them when solving thermochemistry problems. Two problem solving applications are shown on the next page.

Determination of the Heat of Reaction from Heats of Formation

DEFINITION: The standard heat of formation of a compound (ΔH_f°) is the **change in enthalpy when one mole of the compound is formed from the elements** in their stable forms at 25°C and 1 atm. (Logically then, the heat of formation of any element = 0)

- A table with Standard Heats of Formation for some compounds is on page 23.

The Laws of Thermochemistry and the heats of formation of the compounds in the equation can be used to calculate ΔH for a reaction

ΔH_{rxn} is equal to the sum of the heats of formation of the product compounds minus the sum of the heats of formation of the reactant compounds.

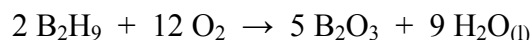
Using the symbol Σ (sigma) to represent the "sum of".

$$\Delta H_{\text{rxn}} = \Sigma \Delta H_f \text{ products} - \Sigma \Delta H_f \text{ reactants}$$

NOTE: Multiply the heat of formation of each compound by its coefficient.

In-class example

Use the standard heats of formation in the table to find the ΔH_{rxn} for the following reaction.



substance	ΔH_f° (kJ/mol)
B_2H_9	+73
O_2	(remember: all elements = 0)
B_2O_3	-1264
$\text{H}_2\text{O}_{(l)}$	-286

(-9040 kJ)

Determination of the Heat of Reaction from a Set of Chemical Equations

In this situation you are given a series of equations with known enthalpy changes ("known eqns") and a final or overall equation with an unknown ΔH ("unknown eqn").

The objective is to get the known eqns to "add up" to the final unknown eqn, and simultaneously determine its unknown ΔH .

In order to get the desired result you may need to manipulate one or more of the known eqns.

When you manipulate the known eqn you must make the corresponding change in its ΔH .

Manipulations and corresponding changes for ΔH include:

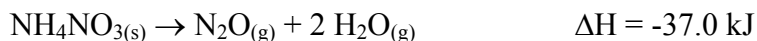
- Reversing an eqn and changing the sign of ΔH
- Multiplying the coefficients by a constant and multiplying the ΔH by the same constant
- Both reversing and multiplying
- (Of course leaving the equation in its original form is also a possibility)

When set up properly and added (like algebraic equations):

- reactants and products of the unknown eqn will remain on the proper side with the correct coefficient
- substances that are not in the unknown eqn will "cancel out"
- The sum of the enthalpy changes for the known eqns will equal the ΔH for the unknown eqn.

Thermochemistry Problems

10. Ammonium nitrate, NH_4NO_3 is commonly used as an explosive. It decomposes by the following reaction



a. What is the ΔH for the reverse reaction?

(+ 37.0 kJ)

b. Calculate ΔH when 1.00g of water is formed by this reaction.

(1.03 kJ)

11. For the reaction $\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$ $\Delta\text{H} = -286 \text{ kJ}$

Calculate the ΔH for the reaction $2 \text{H}_2\text{O}(\text{l}) \rightarrow 2 \text{H}_2(\text{g}) + \text{O}_2(\text{g})$.

(+572 kJ)

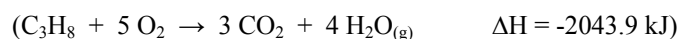
Use your table of **Standard Heats of Formation** (p.23) to answer the next two questions.

12. Calculate ΔH for the reaction $4 \text{NH}_3(\text{g}) + 5 \text{O}_2(\text{g}) \rightarrow 4 \text{NO}(\text{g}) + 6 \text{H}_2\text{O}(\text{g})$

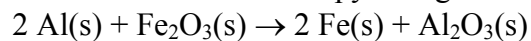
(-904 kJ)

13.a. Write a balanced equation for the combustion of propane (C_3H_8). Water is produced in the gas phase.

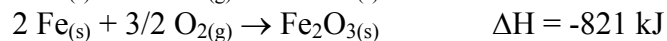
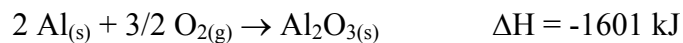
b. If the heat of formation of C_3H_8 is -103.8 kJ/mol, calculate the heat of combustion ($\Delta\text{H}_{\text{rxn}}$) of one mole of propane.



14. Calculate the standard enthalpy change for the reaction

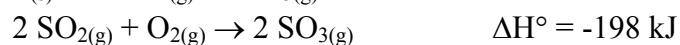


given that

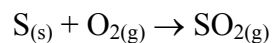


(-780 kJ)

15. Given the following data

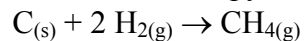


calculate the ΔH° for the reaction

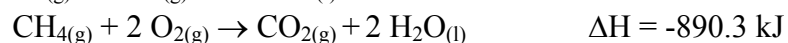


(-296 kJ)

16. Calculate the enthalpy change for the reaction



Use the following reactions



(-74.9 kJ)

Spontaneity of Chemical Reactions

In thermodynamics, the adjective **spontaneous means the reaction will eventually occur**. It does *not* indicate whether the reaction is fast or slow; only that the reactants will rearrange into the products

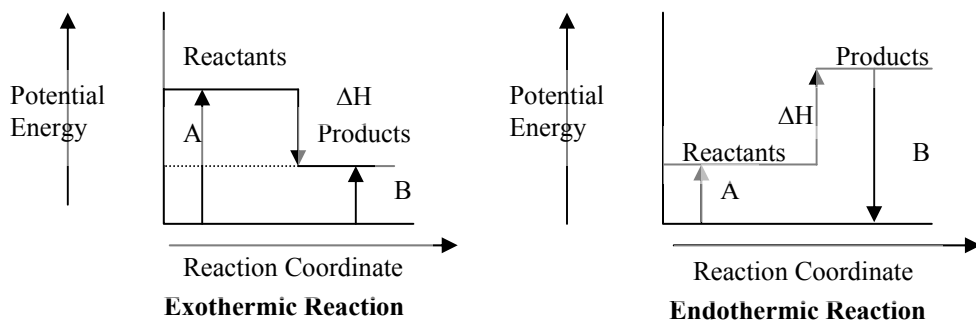
You may have asked yourself the question, Why are some chemical reactions spontaneous and others not? You know, for example, that an iron nail left outside will eventually rust. The reaction is



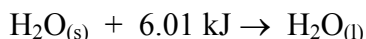
The reaction *is* **spontaneous**. On the other hand, you could isolate the rust, scrape it from the nail and it would absolutely never turn back into iron. The reverse reaction is *not* spontaneous, at least at room temperature.

Note that a process can be spontaneous and still take a very long time to occur. The oxidation of silver, for example is spontaneous but it occurs very slowly.

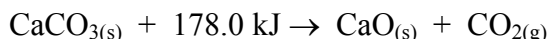
A skydiver spontaneously falls to earth because he has more potential energy in the sky and less on the ground. Water spontaneously runs downhill (and never uphill) for the same reason. Processes that result in a DECREASE IN POTENTIAL ENERGY are said to be "FAVORED BY NATURE". If a chemical reaction is exothermic, the products have less potential energy than the reactants and the reaction is often spontaneous. It turns out that *most exothermic chemical reactions are spontaneous at 25 °C and 1 atm*. Based on what we've already learned about potential energy, this makes some sense.



But it is not that simple! Saying that exothermic reactions are usually spontaneous because they are accompanied by a decrease in potential energy implies that endothermic reactions are not spontaneous. While this is often true, there are some endothermic processes which are spontaneous at room temperature. A familiar example is the melting of ice. This is an endothermic process ($\Delta H = +6.0 \text{ kJ/mole}$) yet it does occur spontaneously at room temperature:



Also, many endothermic reactions that are non-spontaneous at room temperature often become spontaneous when the temperature is raised. Consider, for example, the decomposition of limestone



At 25°C and 1 atm, this reaction is non-spontaneous. The white cliffs (calcium carbonate) of Dover, England are not decomposing nor will they be in the foreseeable future. However, if the temperature is raised to about 800°C, the limestone decomposes. In other words, this endothermic reaction becomes spontaneous at high temperatures. This is true despite the fact that ΔH remains + 178.0 kJ.

Entropy

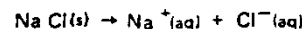
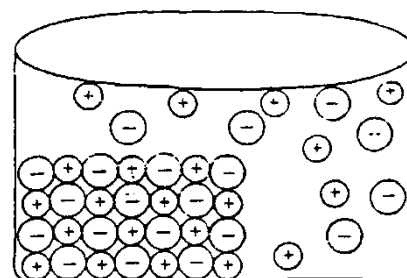
To decide whether a given reaction will be spontaneous at a given temperature, we must consider another factor in addition to ΔH . This factor is the called standard **entropy change** for the reaction, $\Delta S^\circ_{\text{rxn}}$.

$$\Delta S^\circ_{\text{rxn}} = \sum S_{\text{products}} - \sum S_{\text{reactants}}$$

Entropy has a precise mathematical definition which cannot be understood without knowledge of calculus but the entropy of a substance, like its enthalpy, is one of its characteristic properties. **Entropy is essentially a measure of the degree of randomness or disorder of the particles that make up a substance.**

Substances that are highly disordered have high entropies. Low entropy is associated with strongly ordered substances. By “order” we mean the extent to which particles of a substance are confined to a given region of space. For example:

- 1) A crystalline solid has low entropy.
- 2) When a solid **melts** its entropy increases.
- 3) Molecules of a **gas** have **more entropy** (randomness) **than** molecules of a **liquid**.
- 4) When a solid is **dissolved** in water, **entropy increases**.
- 5) When a chemical reaction produces **more particles from fewer particles**, **entropy increases**.



Processes that result in an INCREASE IN ENTROPY (OR DISORDER) are said to be "FAVORED BY NATURE".

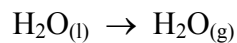
Unlike enthalpy, the absolute entropy values of substances can be determined (using calculus). And unlike enthalpies of formation, pure elements do have entropies which are not zero. Entropy values have been calculated and tabulated for all kinds of different substances and are available in tables (*See table on page 23*). The units of entropy are usually given in Joules/mol·Kelvin. What this means is that **in order to make entropy values equivalent to energy values, the entropy must be multiplied by the Kelvin temperature**. As you will see in the next section, the effects of changes in entropy become more and more important at higher temperatures.

Entropy Problems

17. Predict the sign for ΔS for
- a. salt dissolving _____
 - b. ammonia vapor condensing _____
 - c. iron rusts (see the equation on page 15) _____

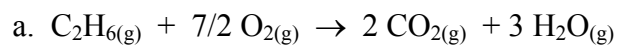
(Answers on p.51)

18. Use the table on p. 23 to calculate the entropy change for the following process:

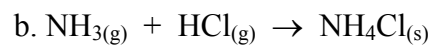


(+118.8 J/mol·K)

19. Use the table on p. 23 to calculate the entropy changes for the following processes:



(+ 46.6 J/mol·K)



(-285.4 J/mol·K)

Gibbs Free Energy

If the entropy change for a chemical reaction is positive (products have more randomness than reactants), then that reaction **may be spontaneous** even if it is an endothermic reaction. Consider for example the fact that a piece of ice left on the counter spontaneously melts.



So the question remains... How does one determine if in fact a chemical reaction will be spontaneous? The problem was first solved a century ago by J. Willard Gibbs, a Physics professor at Yale. He introduced a new quantity into thermodynamics, now called **Gibbs free energy** and given the symbol **G**.

For a reaction the change in free energy, ΔG° can be calculated directly from reference values as the difference between the standard free energies of the products and reactants.

$$\Delta G^\circ = \sum G^\circ_{\text{products}} - \sum G^\circ_{\text{reactants}}$$

Gibbs free energy of a substance is defined as the enthalpy of the substance minus the entropy of the substance multiplied by the temperature (in Kelvin)

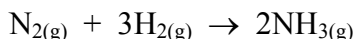
$$G = H - TS$$

The change in Gibbs free energy for a given chemical or physical process is a more useful quantity. Assuming that the temperature does not change during the process,

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$$

Gibbs was able to show that *a chemical reaction will be spontaneous if the free energy of the reactants is greater than the free energy of the products, that is, it will be spontaneous if ΔG is negative*. The equation tells us that the driving force for a reaction, ΔG , depends on two quantities. One of these is the enthalpy change (ΔH) due to the making and breaking of bonds. The other is the product of the change in entropy, ΔS , times the absolute temperature. This equation is incredibly useful because it allows us to predict (using tables) whether a reaction will be spontaneous or not at a given temperature.

EXAMPLE: A reaction equation can be written showing nitrogen and hydrogen gases reacting to form ammonia. But will the reaction actually occur at room temperature? (20 °C)



1) Checking the enthalpy of formation table (p. 23), the ΔH of this reaction can be calculated from:

$$\begin{aligned} \Delta H^\circ &= \sum H^\circ_{\text{products}} - \sum H^\circ_{\text{reactants}} \\ &= 2 \text{ mol}(-46.3 \text{ kJ/mol}) - [0 + 3(0)] = \underline{-92.6 \text{ kJ}} \end{aligned}$$

2) The change in entropy (ΔS) of the reaction can be similarly calculated:

$$\begin{aligned} \Delta S^\circ &= \sum S^\circ_{\text{products}} - \sum S^\circ_{\text{reactants}} \\ &= 2 \text{ mol} (192.8 \text{ J/ mol}\cdot\text{K}) - [1 \text{ mol} (191.6 \text{ J/ mol}\cdot\text{K}) + 3 \text{ mol}(130.7 \text{ J/ mol}\cdot\text{K})] \\ &= 385.6 \text{ J/K} - 583.7 \text{ J/K} = \underline{-198.1 \text{ J/K}} \end{aligned}$$

3) ΔG° can now be calculated using the Gibbs free energy equation, $\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$

$$\begin{aligned} \Delta G^\circ &= \Delta H^\circ - T \Delta S^\circ \\ \Delta G^\circ &= -92.6 \text{ kJ} - (293 \text{ K})(-198.1 \text{ J/K}) \\ &= -92.6 \text{ kJ} - (-58,043.3 \text{ J}) \\ &= -92.6 \text{ kJ} + 58.0 \text{ kJ} = \underline{-34.6 \text{ kJ}} \end{aligned}$$

Since $\Delta G < 0$, we conclude that the reaction *is spontaneous* at room temperature. If we mix hydrogen and nitrogen gases, they will eventually form ammonia.

Spontaneity and Equilibrium Temperature

A process which is spontaneous at one temperature is not necessarily spontaneous at all temperatures. For example, let's calculate the ΔG° for the same reaction between nitrogen and hydrogen gases but at a temperature of 500 °C (=773 K).

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T \Delta S^\circ \\ \Delta G^\circ &= -92.6 \text{ kJ} - (773 \text{ K}) (-198.1 \text{ J/K}) \\ &= -92.6 \text{ kJ} - (-153131.3 \text{ J}) \\ &= -92.6 \text{ kJ} + 153.1 \text{ kJ} = + \mathbf{60.5 \text{ kJ}}\end{aligned}$$

Since $\Delta G > 0$, the reaction is *not spontaneous* at 500 °C. So, to summarize:

- At 20 °C, nitrogen and hydrogen gases *will* spontaneously react to form ammonia.
- At 500 °C, nitrogen and hydrogen gases *will not* spontaneously react to form ammonia.

FYI - At 500 °C, the reverse process will be spontaneous since ΔG for the reverse process is now -60.5 kJ. i.e. At 500 °C, ammonia gas will spontaneously break down to form nitrogen and hydrogen gases.

Equilibrium Temperature The temperature at which certain reactions switch from being spontaneous to nonspontaneous or vice versa is called the **equilibrium temperature (T_{eq})**.

To solve for the equilibrium temperature:

Use the free energy equation and set $\Delta G^\circ = 0$

$$\Delta G^\circ = 0 = \Delta H^\circ - T_{eq} \Delta S^\circ$$

Substitute ΔH° and ΔS° into the equation and solve for T_{eq} . In general terms:

$$\boxed{\frac{\Delta H^\circ}{\Delta S^\circ} = T_{eq}}$$

Using our example from above:

$$\begin{aligned}\frac{-92.6 \text{ kJ}}{-198.1 \text{ kJ/K}} &= T_{eq} \\ \mathbf{467 \text{ K}} &= T_{eq}\end{aligned}$$

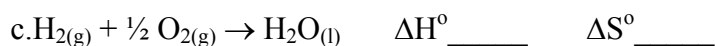
Therefore the (forward) reaction is **spontaneous at temperatures below 467 K**.

Problems and Questions on Spontaneity of Chemical Reactions,

20. The following table, when completed, will summarize the effect of temperature on reaction spontaneity. (Answers on p.51)

Case	ΔH	ΔS	Under what temperature conditions is the reaction spontaneous? i.e. Under what temperature conditions is ΔG negative? (Remember: $\Delta G = \Delta H - T\Delta S$)
1	-	+	
2	+	-	
3	+	+	
4	-	-	

21. Predict the sign of ΔH° and ΔS° for each of the following reactions. (Answers on p.51)



22. Consider the decomposition of calcium carbonate



a. Use the table of standard enthalpies of formation to determine the change in enthalpy (ΔH°).

(+179 kJ)

b. Use your table of standard entropies to determine the change in entropy (ΔS°).

(+160.3 J/mol·K)

c. Calculate the change in Gibbs Free Energy (ΔG°) for the decomposition at room temperature (20° C). Will calcium carbonate spontaneously decompose at room temperature?

(No because $\Delta G = +132$ kJ)

d) Calculate the minimum temperature at which the decomposition of calcium carbonate will become spontaneous. (T_{eq})

(1117 K)

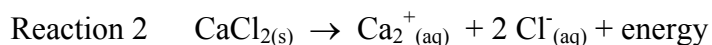
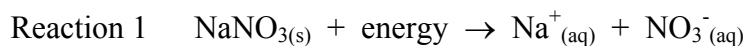
23. When water is frozen: (Answers on p.51)

a) is the enthalpy (ΔH°) positive or negative? How do you know?

b) is the change in entropy (ΔS°) positive or negative? Why?

c) use the Gibbs free energy equation to show why water freezes at low temperatures but not at high temperatures

24. Recently in the laboratory you measured the heat evolved or absorbed as two salts dissolved in water.



For each of these reactions, determine the sign of ΔG , ΔH and ΔS ?

Reaction 1 ΔG _____ ΔH _____ ΔS _____

Reaction 2 ΔG _____ ΔH _____ ΔS _____

(Answers on p.51)

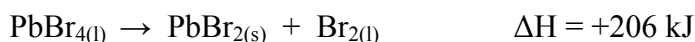
UNIT 9 THERMODYNAMICS GRADED HOMEWORK ASSIGNMENT #5

DO THIS ASSIGNMENT ON A SEPARATE SHEET OF PAPER

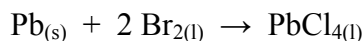
G1. 200 mL of water is in a beaker. When NaOH is dissolved in the water, the temperature of the water increases and the beaker feels warm.

- Classify the process as endothermic or exothermic.
- Identify the system and surroundings
- Does the heat flow from the system to the surroundings or from the surroundings to the system?

G2. Given the following equations:



Calculate the ΔH for the reaction.



G3.a. Define the Heat of Formation.

- Which of these equations would be associated with the heat of formation of carbon dioxide?

- $\text{C}_{(s)} + \text{O}_{2(g)} \rightarrow \text{CO}_{2(g)}$
- $\text{CO}_{(g)} + \frac{1}{2} \text{O}_{2(g)} \rightarrow \text{CO}_{2(g)}$
- $2 \text{C}_{(s)} + 2 \text{O}_{2(g)} \rightarrow 2 \text{CO}_{2(g)}$
- $\text{CaCO}_{3(s)} \rightarrow \text{CaO}_{(s)} + \text{CO}_{2(g)}$

- Write the equation for the formation of potassium chlorate, KClO_3 .

G4.a. Write the equation that shows the combustion of 1 mole of acetylene, C_2H_2 . (Assume the water is formed in a liquid state.)

- Use the values of ΔH_f° on p.23 of the Study Guide to calculate the ΔH for the combustion of 1 mole of acetylene, C_2H_2

Standard Enthalpy of Formation and Standard Entropy of Selected Substances

Formula	Name	ΔH_f° (kJ/mol)	S° (J/ mol·K)
C _(s)	diamond	+1.90	2.4
CH _{4(g)}	methane	-74.85	186.2
C ₂ H _{2(g)}	acetylene	+226.6	200.8
C ₂ H _{4(g)}	ethylene	+52.3	219.5
C ₂ H _{6(g)}	ethane	-84.7	229.5
C ₃ H ₈	propane	-103.8	270.0
C ₆ H ₁₂ O _{6(s)}	glucose	-1268	212.1
C ₁₂ H ₂₂ O _{11(s)}	sucrose	-2222	360.2
CO _(g)	carbon monoxide	-110.5	197.9
CO _{2(g)}	carbon dioxide	-393.5	213.6
CaO _(s)	calcium oxide	-635.6	39.8
CaCO _{3(s)}	calcium carbonate	-1206.9	92.9
HCl _(g)	hydrogen chloride	-92.3	187.0
H ₂ O _(g)	water (vapor or steam)	-241.8	188.7
H ₂ O _(l)	water	-285.8	69.9
H ₂ O _{2(l)}	hydrogen peroxide	-187.6	?
NH _{3(g)}	ammonia	-46.3	193.0
NH ₄ Cl _(s)	ammonium chloride	-315.4	94.6
NO _(g)	nitrogen monoxide (nitric oxide)	+90.4	210.6
NO _{2(g)}	nitrogen dioxide	+33.9	240.5
O _{2(g)}	oxygen	0	205.0
SO _{2(g)}	sulfur dioxide	-296.1	248.5
SO _{3(g)}	sulfur trioxide	-395.2	256.2

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Chemical Kinetics (Reaction Rates)

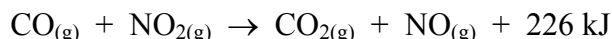
Measuring the Rate of Reaction

The rate of a reaction is expressed either in terms of the amount of product formed in a given period of time or the amount of reactant consumed in a given period of time.

Collision Theory

The Collision Theory is used to explain the factors that typically affect reaction rates. It consists of two fundamental concepts. The first seems self-evident and the second is more subtle:

- 1) In order for two molecules to react chemically, they must first come in contact or collide. Consider for example the reaction between carbon monoxide and nitrogen dioxide.



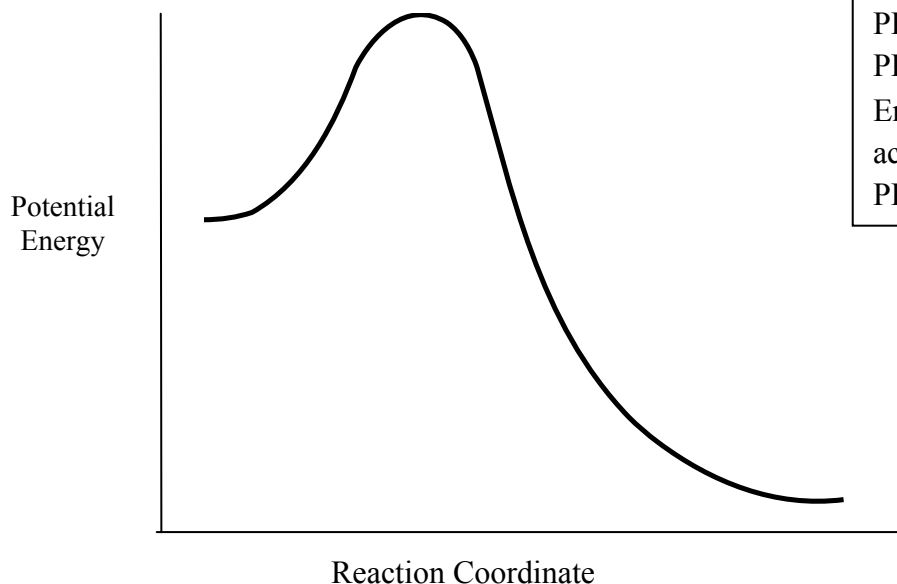
In a reaction vessel filled with these gases at room temperature, the molecules are moving fast and colliding often.

- 2) When the molecules collide, one of two things can happen.

A) If the collision is **not effective**, the reactant molecules will bounce off of each other and remain unchanged.

B) If the collision is an **effective collision**, a nitrogen-oxygen bond in NO_2 will be broken and a carbon-oxygen bond in CO_2 will be formed (i.e. a reaction will occur). *Why are some collisions effective while others are not?* As a CO molecule approaches an NO_2 molecule, repulsions between colliding molecules increase. The kinetic energy of the molecules decreases and the potential energy of the molecules increases. The **activation energy (E_a)** of a reaction is the minimum KE (total KE of both molecules) that the reactant molecules must bring to the collision for a chemical reaction to occur (i.e. for a collision to be effective). The E_a can also be thought of as a PE "barrier" which must be overcome. The **activated complex** is the combination of colliding reactant molecules. It has a high potential energy and represents the unstable transition state that must be formed in order for reactant bonds to be broken and product bonds to be formed. (It is hypothetical - no one has ever detected the presence of an activated complex)

The shape of the potential energy diagram below is consistent the energy changes that take place during this chemical reaction. Label the diagram in class.



Label the following:

PE of the reactants ($\text{CO} + \text{NO}_2$)

PE of the products ($\text{CO}_2 + \text{NO}$)

Enthalpy change (ΔH_{rxn})

activation energy (E_a)

PE of the activated complex (AC)

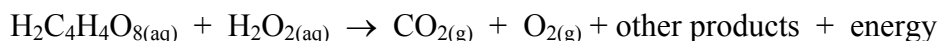
The activation energy is different for every chemical reaction. Generally:

- if a chemical reaction has a high activation energy, the rate of reaction is slow
- if the activation energy is low, the rate of reaction is fast.

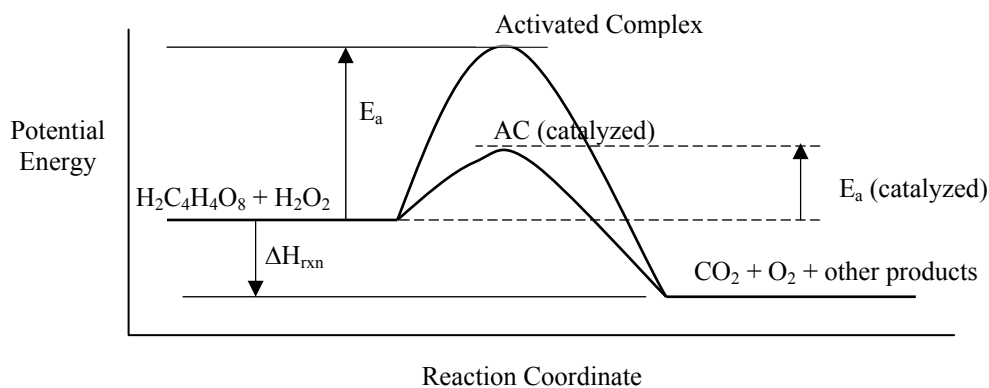
Catalysts, Enzymes and Inhibitors

One way to speed up a reaction is to add a catalyst. A **catalyst** is an atom, a molecule or an ion that increases the rate of a reaction without undergoing permanent change itself. A catalyst provides an alternate reaction pathway of LOWER ACTIVATION ENERGY. The mechanism by which a catalyst lowers the energy of the activated complex is not well understood and probably unique to each set of reactants.

Consider the reaction below:

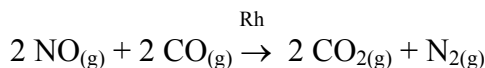


The reaction is very slow at room temperature because the activation energy for the reaction is high. But if some **COCl₂** is added to the mixture, the reaction rate increases dramatically. The potential energy diagram would appear as:



Notice the ΔH_{rxn} is not affected by the presence of a catalyst.

Many reactions can be catalyzed by allowing them to occur on an appropriate metal surface - the metal atoms catalyze the reaction. Every automobile driven in California is equipped with a **catalytic converter** which is simply a rhodium surface (Rh is a transition metal) on which the following reaction takes place.



This is a useful reaction since NO and CO are poisonous gases produced in the combustion of gasoline. CO₂ is a problematic greenhouse gas, but N₂ is relatively harmless.

Biological catalysts are called **enzymes**. These tend to be large molecules that increase the rate of the thousands of biochemical reactions occurring in all living things. For many chemical reactions, the **orientation** of the colliding molecules is important. For these reactions a molecular collision will only be an **effective collision** if the orientation of the molecules is correct. Enzymes usually work by arranging the reactant molecules in the correct orientation so that they are able to react. The net effect is a lowering of the activation energy for that reaction.

An **inhibitor** reduces a reaction rate by preventing the reaction from occurring in the usual way. The inhibitor may combine with a reactant to form a complex that is relatively stable so that a reaction will not proceed characteristically. Food preservatives are inhibitors. Vitamin C (ascorbic acid) is routinely added to cured meats to prevent the formation of cancer causing nitrosamines.

Factors that Affect the Rate of Reactions

Understanding that collisions must occur, but that only a certain fraction of collisions will result in a reaction allows us to propose some particle level explanations for experimental observations. At the particle level the rate of a reaction depends on two things:

- 1) The **frequency** of collisions (i.e. the number of collisions per second)
- 2) The **fraction** (or percentage) of collisions which are effective

These two quantities are independent. The rate of a reaction can be altered by changing either or both of these quantities.

Listed below are four factors that typically affect the rate of a reaction. All of them are phrased in the in terms that result in an increase in the rate. As part of a class discussion you will determine whether the **frequency** of collisions or **fraction** of effective collisions or **both** are increasing.

Increasing the temperature

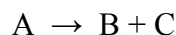
Increasing the concentration (or increasing the pressure on reactant gases)

Increasing the surface area (when reactants are in different phases)

Adding a Catalyst

Rate Laws

For any given reaction, one of the most important controlling influences is the concentration of the reactants. Generally, if we follow a chemical reaction over a period of time, we find that its rate gradually decreases as the reactants are consumed. From this we conclude that the rate is related, in some way, to the concentrations of the reactants. Algebraically, the rate depends on each concentration raised to some power. This means that for the general reaction:



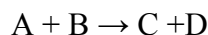
The relationship between the rate and the [A] can be expressed as:

$$\text{Rate} \propto [A]^x \quad (1)$$

Where the exponent, x , is called the **order of the reaction**. When $x = 1$, we say that the reaction is **first order** with respect to A. In our course, Second order ($x = 2$), and zero order reactions are also possible.

One very important fact is that there is not necessarily any direct relationship between the coefficients in the balanced equation for a reaction and the order of the reaction. The value of x can *only* be determined from experimentation.

If we consider a slightly more complex reaction, for example,



The rate usually depends on the concentration of both A and B. Normally, increasing the concentrations of either A or B will increase the reaction rate, and the rate is proportional to the product of the concentrations of A and B, each raised to some power

$$\text{Rate} \propto [A]^x[B]^y \quad (2)$$

In this case we can say that the order of the reaction with respect to A is x and the order with respect to B is y . We can also describe the overall order of this reaction, which is the sum of the exponents on the terms. In this example, the overall order is the sum $x + y$. In reality, x and y can have any value; whole number, fractional or zero. (We will limit the possibilities to 0, 1, and 2.) When one of the exponents is zero, this simply means that the rate of reaction does not depend on the concentration of that substance.

The proportionality represented by equation (2) can be converted to an equality by introducing a proportionality constant, k , which we can call the rate constant. The resulting equation, termed the **rate law** for the reaction, is

$$\text{Rate} = k[A]^x[B]^y \quad (3)$$

Again, the values of x , y and k can only be determined experimentally.

The most common method for experimentally determining the form of the rate law for a reaction is the method of initial rates. The initial rate of a reaction is the instantaneous rate determined just after the reaction begins. The idea is to determine the instantaneous rate before the initial concentrations of reactants have changed significantly. Several experiments are carried out using different initial concentrations, and the initial rate is determined for each run. The results are then compared to see how the initial rate depends on the initial concentrations of reactants. This allows the form of the rate law to be determined.

Classwork Example on Empirical Determination of Rate Laws

The determination of these quantities is always an **empirical process** – that means they can only be deduced from **experimental data** (not from a simple examination of the balanced equation).

NOTE: For the scope of this course (in order to simplify the possibilities of mathematical analysis) **we will limit the values of the exponents to 0, 1 or 2** (zero, first or second “order” with respect to the concentration of an individual reactant).

This will be best understood if we do the three example problems that follow.

EXAMPLE: For the generic reaction represented by the following equation:



The following data has been taken

Experiment	[A]	[B]	[C]	Rate ([D]/sec)
1	1.0 M	1.0 M	3.0 M	0.15 M/sec
2	1.0	2.0	3.0	0.30
3	1.0	2.0	9.0	2.70
4	2.0	1.0	3.0	0.15

1) Determine the rate law. (I.e. find the **exponents** in the equation: Rate = k [A]^x[B]^y[C]^z.)

General Instructions on use of data to determine exponents:

1. *Decide which reactant concentration you are going to find the exponent of. Look at the **CONCENTRATIONS** of the reactants in each experiment and **select 2 experiments that differ only in the concentration of the reactant you are analyzing.** This is an application of the concept of control in experimental design. If there is a variation in the rate you know it is due to the change in the concentration of the reactant you are analyzing.*
2. *Compare the change in concentration to the corresponding change in rate according to the following general equation:*

$$\left(\frac{[\text{reactant a}]_{\text{expt 1}}}{[\text{reactant a}]_{\text{expt 2}}} \right)^x = \frac{\text{rate}_{\text{expt 1}}}{\text{rate}_{\text{expt 2}}}$$

NOTE: In order to avoid fractional values, it will be easier to solve if you put the higher concentration in the numerator

To determine the exponent of the [A] in the above example – use experiments _____ and _____.

OR reasoning by inspection

x = _____ and therefore the reaction is _____ order with respect to the [A].

Experiment	[A]	[B]	[C]	Rate ([D]/sec)
1	1.0 M	1.0 M	3.0 M	0.15 M/sec
2	1.0	2.0	3.0	0.30
3	1.0	2.0	9.0	2.70
4	2.0	1.0	3.0	0.15

To determine the exponent of the [B] – use experiments _____ and _____.

OR reasoning by inspection

y = _____ and therefore the reaction is _____ order with respect to the [B].

To determine the exponent of the [C] – use experiments _____ and _____.

OR reasoning by inspection

z = _____ and therefore the reaction is _____ order with respect to the [C].

Therefore, the rate law is:

_____ and the reaction is _____ order overall.

2) Determine the value and units of k.

General Instructions: Substitute data from any experiment into the rate law. Treat the units like algebraic variables – combining and canceling similar units.

3) Calculate the rate if the initial concentration of each reactant is 2.0 M.

General Instructions: Substitute the concentrations and the value for the rate constant into the rate law.

Answers:

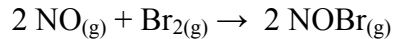
1) rate = $k[A]^0[B]^1[C]^2$

2) $k = 0.017 \text{ 1/M}^2\text{-sec}$

3) rate = 0.14 M/sec

Rate Law Problems (Answers on p.52)

25. Below are some data collected in a series of experiments on the reaction of nitrogen monoxide and bromine at 273°C.



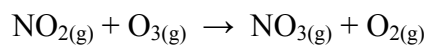
Experiment	Initial Concentration of NO (M)	Initial Concentration of Br ₂ (M)	Initial Rate of Formation of NOBr (M/sec)
1	0.10	0.10	12
2	0.10	0.20	24
3	0.20	0.10	48

a. Determine the rate law for the reaction. The rate law for the reaction will have the form:

$$\text{Rate} = k [\text{NO}]^x [\text{Br}_2]^y$$

- b. Compute the value of the rate constant with proper units.
c. What is the overall order of the reaction?

26. One of the reactions that can take place in polluted air is the reaction of nitrogen dioxide, NO_2 , with ozone, O_3 .



The following data were collected on this reaction at 25°C .

Experiment	Initial $[\text{NO}_2]$ (M)	Initial $[\text{O}_3]$ (M)	Initial Rate of Formation of O_2 (M/sec)
1	5.0×10^{-5}	1.0×10^{-5}	0.022
2	5.0×10^{-5}	2.0×10^{-5}	0.044
3	2.5×10^{-5}	2.0×10^{-5}	0.044

Using these data,

a. What is the order for each reactant?

What is the overall reaction order?

b. Write the rate law for the reaction.

c. Calculate the value of the rate constant with proper units.

d. Predict the rate of react if the initial $[\text{NO}_2] = 7.5 \times 10^{-5}$ M and the initial $[\text{O}_3] = 4.5 \times 10^{-5}$ M.

27. The reaction between bromate ions and bromide ions in acidic aqueous solution is given by the following reaction



The table below gives the results from four experiments.

Experiment	$[\text{BrO}_3^-]_i$	$[\text{Br}^-]_i$	$[\text{H}^+]_i$	Measured Initial Rate (M / sec)
1	0.10	0.10	0.10	8.0×10^{-4}
2	0.20	0.10	0.10	1.6×10^{-3}
3	0.20	0.20	0.10	3.2×10^{-3}
4	0.10	0.10	0.20	3.2×10^{-3}

Using this data:

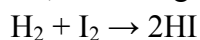
- What is the order for each reactant?
What is the overall reaction order?
- Write the rate law for the reaction.
- Calculate the value of the rate constant with proper units.

UNIT 9 KINETICS GRADED HOMEWORK ASSIGNMENT #8

DO THIS ASSIGNMENT ON A SEPARATE SHEET OF PAPER

- G1.a. White phosphorous reacts rapidly with oxygen when exposed to air. What can you say about the magnitude of the activation energy for this reaction?
- b. The metallic luster of fine copper wool doesn't readily change unless it is put into a crucible and heated to a high temperature. This causes the copper to darken as it reacts with oxygen. How, do you think the activation energy of this reaction compares with that of the phosphorus reaction in described in part (a)?

- G2. Hydrogen and iodine react at 400°C, according to the equation:



Explain, in terms of the Collision Theory, how the following would affect the rate:

- Increasing the temperature
 - Increasing the concentration of hydrogen
 - Increasing the concentration of both the hydrogen and the iodine
 - Adding a catalyst
- G3.a. Which will burn fastest, a solid log, a split log, or wood shavings?
- b. Explain your answer in terms of the Collision Theory.

Lab 9-1: HEAT OF SOLUTION

BACKGROUND

When one drops a sugar cube ($C_{12}H_{22}O_{11}$) into a cup of coffee or adds table salt ($NaCl$) to a pot of water, a spontaneous reaction occurs... the solute dissolves. The probable mechanism by which a solid dissolves in a liquid can be thought of in a series of three steps.

Step 1 Solute particles become attached to and surrounded by solvent molecules.

This action is **exothermic** because the solvent molecules are attracted to the solute particles and form an connection. The solvent molecules and solute particles do NOT form a true chemical bond, but the energy result is analogous.

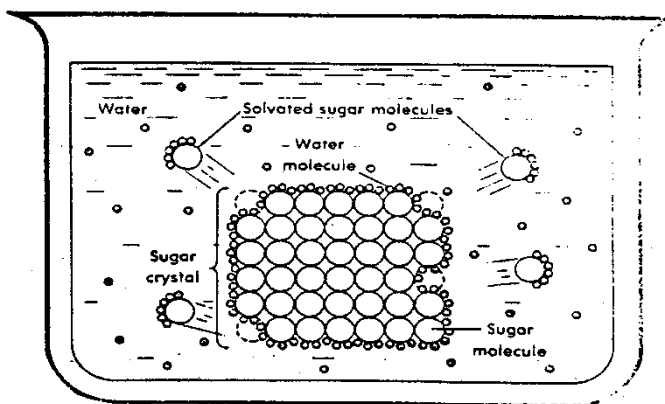
Step 2 Solute particles are separated from the solid mass.

This action absorbs energy. It is **endothermic** because solute particles are attracted to each other, and energy is required to "pull" the solute particles apart.

Step 3 Solvent molecules are moved apart to "make room" for solute particles as they disperse.

This action is also **endothermic** because there are also significant attractive forces between the solvent water molecules. Again, energy is required to separate the molecules.

An illustration of this **solvation** process is pictured below.



If the exothermic action (step 1) is less than the sum of the endothermic actions (steps 2 and 3), then the net change is endothermic. Consequently, the temperature of the solution decreases as the solid dissolves.

If the energy involved in step 1 is greater than the sum of the energies involved in steps 2 and 3, the net change is exothermic. As a result, the temperature of the solution increases as the solid dissolves.

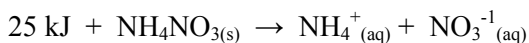
The MOLAR HEAT OF SOLUTION (ΔH_{soln}) is the heat **released or absorbed when one mole of a substance is dissolved** in a solvent (usually water).

When the dissolving process is **exothermic**, ΔH_{soln} is given a **negative** sign.

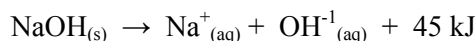
When the dissolving process is **endothermic**, ΔH_{soln} is given a **positive** sign.

Chemical equations for a dissolving usually indicate only the solute undergoing a change of phase and dissociation if it is ionic. Inclusion of the energy term follows the same format as reactions.

For the dissolving of NH_4NO_3 (an endothermic process):



For the dissolving of $NaOH$ (an exothermic process):



You will determine the molar heat of solution of calcium chloride dihydrate and sodium nitrate

EQUIPMENT AND REAGENTS

Styrofoam cup calorimeter	water
Magnetic stirrer and stir bar	Solid $\text{CaCl}_2 \cdot 2 \text{H}_2\text{O}$
LabQuest and temperature sensor	Solid NaNO_3
100 mL graduated cylinder	

The styrofoam cup calorimeter is a simple calorimeter often used in the general chemistry laboratory. It consists of two nested polystyrene foam cups partially filled with water. The calorimeter has a cover through which a thermometer is inserted. Very little heat flows through the walls of the cup. The water in the cup can be thought of as the immediate surroundings that have been thermally insulated from the larger surroundings. The water acts as a “heat reservoir”. If a reaction is endothermic, heat will be absorbed from the water during the reaction, and the water temperature will decrease. On the other hand, if the reaction is exothermic, heat will be released to the water during the reaction, and the water temperature will increase.

The magnetic stirrer will be used to insure that the temperature of the solution is uniform throughout.

DO NOT TURN ON THE HEAT AS YOU OPERATE THE STIRRER.

The temperature sensors and the Labquest. You and your partner will have a LabQuest unit. Temperature sensors will be attached to Channel 1 and Channel 2.

PROCEDURE

1. Make sure you know which channel your temperature sensor is connected to.
2. Turn on the LabQuest. After a few seconds the temperature in °C should appear on the display. Determine which display corresponds to your sensor.
3. Mass about 5 grams of solute directly into the calorimeter cup and record the exact mass.
4. Measure about 50 mL of water into the graduated cylinder and record the exact volume.
5. Put the temperature sensor into the water and record the (initial) temperature.
6. Pour the water into the calorimeter. Quickly put the lid on the calorimeter, put the temperature sensor through the hole in the lid and turn the stirrer up to a moderate speed. Hold the calorimeter so it does not tip over.
7. Monitor the temperature and record the maximum or minimum temperature as the final temperature.
8. The solution can be discarded in the sink.
- 9. Repeat Steps 1-6 for the other solute**
- 10. When you are finished, touch File on the LabQuest screen, touch Quit and hold down the power button until the LabQuest shuts down.**
11. RINSE THE CUPS THOROUGHLY and place them in your rack to dry.
12. Sponge down your countertop.

ANALYSIS AND CONCLUSIONSCALCULATIONS

The heat transferred to or from the calorimeter water (Q_{expt}) can be calculated by making use of the following relationship:

$$Q_{\text{expt}} = (\text{mass of water}) (\text{specific heat of water}^*) (\text{final temperature} - \text{initial temperature})$$

* specific heat of water = 4.18 Joule/gram·°C

The molar heat of solution (ΔH_{soln}) can then be calculated by the following relationship:

$$\Delta H_{\text{soln}} = \frac{-Q_{\text{expt}}}{\text{moles solute}}$$

For each solute:

1. Calculate the amount of heat energy that was transferred to or from the calorimeter water during the dissolving process. (use only the mass of the water ignore the mass of the solute)
(density of water is 1.00 g/mL)
2. Calculate the number of moles of solute that dissolved.
3. Calculate the molar heat of solution (in kJ/mole). Be sure your answer has the proper sign on it. Put your answers in your Results Table.
4. The accepted values for the molar heats of solution of the two solutes used in this experiment are given in the table below. To compare your experimental results to these accepted values calculate the percent differences between your experimental values and the accepted values.

$$\% \text{ difference} = \frac{(\text{experimental value} - \text{accepted value})}{\text{accepted value}} (100)$$

solute	ΔH_{soln}
$\text{CaCl}_2 \cdot 2 \text{H}_2\text{O}$	-48 kJ/mol
NaNO_3	+20 kJ/mol

6. What are the most likely sources of discrepancy for each experiment? Suggest a specific error in each of your experiments that could account for any discrepancy.

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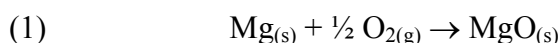
Lab 9-2:
THE HEAT OF FORMATION OF MAGNESIUM OXIDE

BACKGROUND

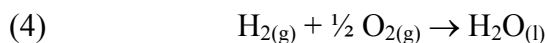
During any chemical reaction, a certain amount of chemical energy is changed into thermal energy, or vice versa. This energy change can be measured as heat released or absorbed during the reaction. The quantity of heat released or absorbed during a chemical reaction is called the HEAT OF REACTION. It is customary to measure this heat in Kilojoules/mole.

When a reaction can be expressed as the algebraic sum of a sequence of two or more simpler reactions, the heat of reaction is the algebraic sum of the heats of these simpler reactions. This generalization (**Hess' Law**) has been found to be true for every reaction that has been tested.

In this experiment, you will use Hess' Law to determine ΔH for a reaction that is difficult to measure directly, the synthesis of magnesium oxide from its elements. Magnesium metal combines with oxygen very rapidly and the reaction is quite exothermic. Before electronic flashes cameras used disposable flash bulbs. These flashbulbs contained a thin ribbon of magnesium. In the presence of oxygen (with a little spark to get the reaction started), the magnesium burns in oxygen and produces a significant amount of light. This overall reaction is labeled as reaction (1)



Notice that this equation can be obtained by combining equations 2, 3 and 4.



In this experiment you will determine ΔH for reactions 2 and 3 by carrying out these reactions in a calorimeter. The standard heat of formation of liquid water (4) can be determined by consulting the appropriate reference table (p.23). Then by combining equations 2, 3 and 4 and summing the corresponding heats of reaction, you can determine ΔH for reaction 1.

METHOD

After the Purpose and before the Data Table, write an experimental METHOD. It can be a general overview of the experiment, but it should be complete and descriptive. It does not have to be a step-by-step procedure, but it can be if you want detailed instructions as you perform the experiment. There are some specifics at the top of the next page.

HINT: The experimental procedure for this lab is very similar to the procedure you used in Lab 9-1: Heat of Solution.

HELPFUL INFORMATION FOR YOUR METHOD:

- Perform reactions (2) and (3) and record the data you need to calculate the heat evolved or absorbed as these reactions proceed. You are already familiar with the use of the coffee cup calorimeter and the LabQuest temperature sensor.
- The pieces of magnesium ribbon are pre-cut. Be sure to measure the length of the Mg ribbon and record the mass per cm. Use one piece of magnesium for about 50 mL of 1M HCl.
- You will obtain reasonable changes in temperature if you use about 0.5 grams of MgO for about 50mL of 1M HCl.

<u>MATERIALS</u>	<u>REAGENTS</u>
Styrofoam calorimeter	Magnesium ribbon
100 ml graduated cylinder	Magnesium oxide
LabQuest unit	1M HCl
LabQuest temperature sensor	
Magnetic stirrer and stir bar	

PRELAB ASSIGNMENT

After you construct your Data Table, answer the following questions at the beginning of the Analysis section of your lab. Your answers will be checked before you can begin lab work.

1. Combine equations (2), (3) and (4) to obtain equation (1).
2. Look up the standard heat of formation of liquid water.

ANALYSIS AND CONCLUSIONS

1. Calculate the heat absorbed by the solution in the calorimeter for reaction (2) (MgO & HCl). (Assume the density of the HCl is 1.00 g/mL and the specific heat of the solution is 4.18 J/g·°C)
2. Calculate the number of moles of MgO reacted.
3. Calculate ΔH for reaction (2) (expressed in kJ/mol of MgO).
4. Calculate the heat absorbed by the solution in the calorimeter for reaction (3) (Mg & HCl). (Assume the density of the HCl is 1.00 g/mL and the specific heat of the solution is 4.18 J/g·°C)
5. Calculate the mass of Mg reacted.
6. Calculate the number of moles of Mg reacted.
7. Calculate ΔH for reaction (3) (expressed in kJ/mol of Mg).
8. Look at your prelab assignment and calculate the heat of formation of magnesium oxide (ΔH for reaction 1) by applying Hess' Law.
9. The standard heat of formation of MgO is -602 kJ/mol. What is the percent difference between your results and the accepted value?

As always, you should compile your results in some sort of table

10. What are the most likely sources of discrepancy?

Lab 9-3: FACTORS THAT AFFECT THE RATE OF REACTION

BACKGROUND: COLLISION THEORY

For a chemical reaction to occur, the reacting molecules must collide with each other. It is only when reactant molecules come in contact with each other that there is a chance for them to react. This common sense idea forms the basis of the **collision theory** of chemical kinetics. Basically, this theory states that *the rate of a reaction depends on the number of effective collisions occurring between reactant molecules per second.*

If the rate of a chemical reaction were only dependent on the number of collisions between reactant molecules per second (frequency), then most chemical reactions would take place in a fraction of a second. You know, for example, that hydrogen and oxygen molecules can react to form water. In a 10L balloon filled with hydrogen and oxygen at room temperature, hydrogen and oxygen molecules collide with each other about 10^{30} times per second. If all of the collisions were **effective collisions**, this reaction would occur in a fraction of a second. In fact, this is a very slow reaction under these conditions.

Similar observations are found for many other reactions, which suggest that there are common factors that determine whether or not a collision will yield a chemical change. One of these is the kinetic energy that the molecules possess at the moment they begin to collide. As two molecules approach each other, the electron clouds begin to repel each other and the molecules slow down. As this happens, the **kinetic energy** of the molecules is gradually converted to **potential energy**. If the pair of colliding molecules has little kinetic energy to begin with -- that is, if they were not moving very fast -- they come to a stop before their electron clouds have penetrated each other very much, and then they fly apart again, chemically unchanged.

When two fast moving molecules collide, they have a lot of kinetic energy that can be converted to potential energy. This means that they are able to overcome substantial forces of repulsion between their electron clouds, and they approach each other quite closely. Reactant bonds are broken as product bonds form and a chemical change takes place. *From the preceding discussion, we see that an effective collision, one that changes reactant molecules into product molecules, occurs only if the molecules collide with sufficient force.* The minimum kinetic energy that molecules must bring to their collisions for a chemical reaction to occur is called **activation energy**.

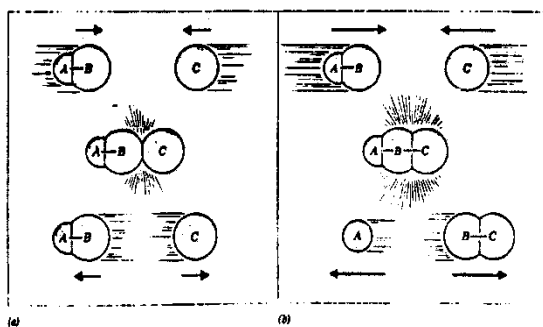
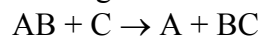
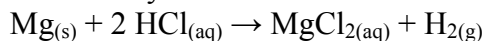


Figure: (a) when two slow moving molecules collide, their electron clouds cannot interpenetrate much and they just bounce off each other, chemically unchanged. (b) When fast moving molecules collide, atoms approach each other much more closely as their electron clouds interpenetrate. This can lead to bond making and bond breaking. The net change here is:



In this experiment you will determine the effect that various factors have on the rate of the reaction between magnesium metal and hydrochloric acid.



You will then explain your findings in terms of the Collision Theory.

PRE-LAB ASSIGNMENT

Your teacher will do a demonstration that will help you determine the effect of **reactant surface area**

You are responsible for determining the effect of the following factors on the rate of reaction

reactant concentration

reactant temperature increase

reactant temperature decrease

investigation of a proposed catalyst for the reaction

You must write a “Method” that includes enough detail so that it is clear to your instructor exactly how you plan to carry out this experiment. You are to plan the procedure for this experiment by yourself. How will you determine the effect of each factor, etc.? **Remember that in a well designed experiment, only one factor is varied at a time.**

Design a set of experiments that will allow you to investigate the following questions:

PROCEDURE

The **rate** of this reaction can be determined by measuring the amount of time that elapses while the reaction is occurring.

$$\text{(average) Rate} = \frac{\Delta m_{\text{Mg}}}{\Delta t}$$

You will be given the equipment and the reactants below:

<u>Equipment</u>		<u>Reagents</u>
2 test tubes	ice water bath	5-6 cm strip of Mg
scissors	stopwatch (or LabQuest)	1 M HCl (use 2-5mL)
metric ruler	thermometer	1 M CuSO ₄ (use 10-20 drops)
hot water bath		

ANALYSIS AND CONCLUSIONS

- 1.a. How does the amount of surface area the reactants have in contact affect the rate of reaction?
 - b. How can your results concerning surface area be explained in terms of collision theory?
- 2.a. How does the concentration of HCl affect the rate of this reaction?
 - b. How can your results concerning concentration of HCl be explained in terms of collision theory?
- 3.a. How does increasing the temperature of the reactants affect the rate of reaction?
 - b. How can your results be explained in terms of collision theory?
- 4.a. How does decreasing the temperature of the reactants affect the rate of reaction?
 - b. How can your results be explained in terms of collision theory?
- 5.a. What is a catalyst? How does a catalyst change the rate of a chemical reaction?
 - b. Is CuSO₄(aq) a catalyst in this reaction or does CuSO₄ also react with one of the reactants?
 - c. What evidence do you have for either (or both) positions?

Unit 9 Practice Test

Part 1: Multiple Choice

Base your answers to the next five questions (1-5) on the potential energy diagram below.

1. The heat of reaction (ΔH_{rxn}) for this reaction is represented by arrow:

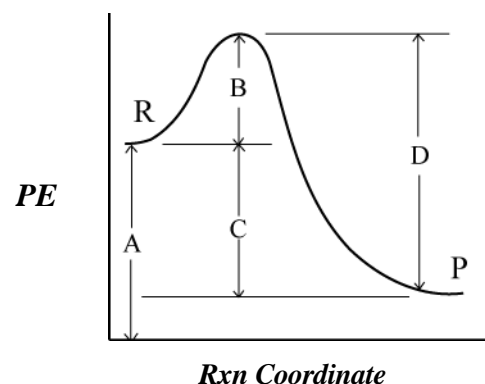
A B C D

2. The activation energy for the forward reaction is represented by arrow:

A B C D

3. The forward reaction results in:

A. a decrease in enthalpy and is therefore exothermic.
 B. an increase in enthalpy and is therefore exothermic
 C. an increase in enthalpy and is therefore endothermic
 D. a decrease in enthalpy and is therefore endothermic.



4. If a catalyst were introduced to the reaction, it would change the height of arrow

A B C D

5. You will learn in the next unit that some reactions are reversible. The activation energy for the reverse reaction is indicated by arrow(s)

A. (A + B) B. B C. (C + B) D. (B + C + D)

6. When solid ammonium nitrate (NH_4NO_3) is added to water, the solution feels cold. Which one of the following statements best describes this observation?

A. $\text{NH}_4\text{NO}_3(\text{s}) \rightarrow \text{NH}_4\text{NO}_3(\text{aq}) + 28.4 \text{ kJ}$
 B. $\text{NH}_4\text{NO}_3(\text{s}) \rightarrow \text{NH}_4\text{NO}_3(\text{aq}) \quad \Delta H = +28.4 \text{ kJ}$
 C. $\text{NH}_4\text{NO}_3(\text{s}) \rightarrow \text{NH}_4\text{NO}_3(\text{aq}) \quad \Delta H = -28.4 \text{ kJ}$
 D. the reaction is exothermic.

7. If a reaction is exothermic:

A. the “energy” term is written on the left side of the equation, and the sign of ΔH_{rxn} is negative.
 B. the “energy” term is written on the left side of the equation, and the sign of ΔH_{rxn} is positive.
 C. the “energy” term is written on the right side of the equation, and the sign of ΔH_{rxn} is negative.
 D. the “energy” term is written on the right side of the equation, and the sign of ΔH_{rxn} is positive.

8. Consider the following:

The standard heat of formation of a compound is -78.9 kJ . This means

I. if one mole of the compound is formed from its elements, 78.9 kJ of heat will be released.
 II. decomposing two moles of the compound (into its elements) requires 157.8 kJ of energy.

A. only statement I is true C. neither statement A nor statement B is true
 B. only statement I is true D. statements I and II are both true

9. Which change is accompanied by an increase in entropy?

A. $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{s})$ C. $\text{NaCl}(\text{s}) \rightarrow \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq})$
 B. $\text{H}_2\text{O}(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$ D. $\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$

10. Spontaneous change is favored when
- enthalpy is increasing and entropy is decreasing
 - enthalpy is decreasing and entropy is increasing
 - both enthalpy and entropy are decreasing
 - both enthalpy and entropy are increasing
11. Which (if any) of the following increases as a result of raising the pressure on a system of reactant gases?
- activation energy
 - average kinetic energy of the reacting molecules
 - fraction of collisions that result in a reaction
 - Increasing the pressure does not increase A, B or C
12. If a substance is added to a reaction and the reaction begins to take longer, the substance is called a(n)
- inhibitor
 - enzyme
 - catalyst
 - activated complex
13. Zinc reacts with hydrochloric acid according to the following reaction.
- $$\text{Zn}_{(s)} + 2 \text{HCl}_{(aq)} \rightarrow \text{H}_{2(g)} + \text{ZnCl}_{2(aq)}$$
- Which of the following is true?
- The average rate of this reaction can only be expressed by as the amount of zinc consumed in a given period of time.
 - The average rate of this reaction can only be expressed as the amount of hydrogen produced in a given period of time.
 - The average rate of this reaction can be expressed as *either* the amount of zinc consumed *or* the amount of hydrogen produced in a given period of time
 - The average rate of this reaction can *not* be expressed in terms of the amount of zinc consumed *or* the amount of hydrogen produced in a given period of time
14. Hydrogen peroxide decomposes more rapidly at a higher temperature because of an:
- increase in the frequency of collisions between reactant molecules
 - increase in the fraction of effective collisions between reactant molecules
- I only
 - II only
 - both I and II
 - neither I nor II

Part 2: Questions and Problems

14. How much energy would be required to convert an ice cube weighing 13.5 g and having a temperature of $-30.0\text{ }^{\circ}\text{C}$ to water having a temperature of $55\text{ }^{\circ}\text{C}$? (express your answer in kJ)

specific heat of ice = $2.03\text{ J/g}\cdot^{\circ}\text{C}$
specific heat of water = $4.18\text{ J/g}\cdot^{\circ}\text{C}$
specific heat of steam = $1.96\text{ J/g}\cdot^{\circ}\text{C}$
molar heat of fusion of H_2O = 6.01 kJ/mole
molar heat of vaporization of H_2O = 40.7 kJ/mole

15. Given: $\text{NO}_{2(\text{g})}$ has a $\Delta H^{\circ}_{\text{f}} = +33.9\text{ kJ/mol}$ and $\text{NO}_{(\text{g})}$ has a $\Delta H^{\circ}_{\text{f}} = +90.3\text{ kJ/mol}$

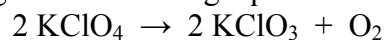
What is the heat of reaction for the reaction $2\text{NO}_{(\text{g})} + \text{O}_{2(\text{g})} \rightarrow 2\text{NO}_{2(\text{g})}$?

16. Use the reaction, $2\text{B}_{(\text{s})} + 3\text{H}_{2(\text{g})} + 31.4\text{ kJ} \rightarrow \text{B}_2\text{H}_{6(\text{g})}$ to answer the next two questions.

a. How much energy is released when 2 moles of B_2H_6 is decomposed into its elements?

b. How much heat is required to react 50.0g of boron (in an excess of hydrogen)?

17. KClO_4 decomposes according to the following equation:



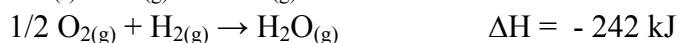
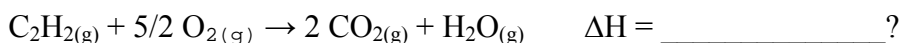
A student allowed 5.44 grams of KClO_4 to decompose in a calorimeter containing 100.0g of water. The temperature of the water in the calorimeter dropped from 24.00°C to 19.85°C .

a. How much heat was lost by the water in the calorimeter? Express your answer in kJ. (specific heat of water = $4.18 \text{ J/g } ^\circ\text{C}$)

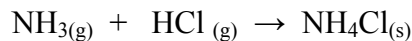
b. How many moles of KClO_4 were decomposed?

c. What is the heat of reaction (ΔH_{rxn}) for the equation above? Include the proper sign.

18. Acetylene (C_2H_2) burns in the presence of oxygen to form carbon dioxide and water according to the first of the following equations. Use the information in the other three equations to determine ΔH for the burning of acetylene in kJoules/mole.



19. Use your standard enthalpy of formation and entropy tables to determine ΔH° and ΔS° for the following reaction:



a. $\Delta H^\circ = ?$

b. $\Delta S^\circ = ?$

- c. Calculate the ΔG° for this reaction at room temperature (20° C).

d. Is the reaction spontaneous at room temperature (as written)? _____

e. At what temperatures would it be spontaneous?

20. For each of the following reactions, determine the sign (+ or -) of ΔH and ΔS . Then determine whether the reaction is always spontaneous, never spontaneous, spontaneous above a minimum temperature (T_{eq}) or spontaneous below a maximum temperature (T_{eq}).

	ΔH	ΔS	Spontaneity
a. $\text{H}_2\text{O}(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l}) + 40.7 \text{ kJ}$	_____	_____	_____
b. $\text{SO}_3(\text{g}) + 99 \text{ kJ} \rightarrow \text{SO}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g})$	_____	_____	_____
c. $\text{N}_2\text{H}_4(\text{l}) \rightarrow \text{N}_2(\text{g}) + 2 \text{H}_2(\text{g}) + 50.4 \text{ kJ}$	_____	_____	_____

21. The data below were collected for the reaction $A + B \rightarrow D + E$

Initial [A] (moles/L)	Initial [B] (moles/L)	Initial Rate of Formation of D (M/minute)
0.10	0.20	200.0
0.10	0.10	50.0
0.30	0.10	150.0

a. Write the rate law for the reaction and give the order with respect to each reactant.

b. Calculate the rate constant, k . (Include the proper units.)

c. When $[A] = 0.020M$ and $[B] = 0.060M$, what will be the rate of formation of D?

Essays

There may be one or more essay questions on the test. The question(s) will be taken from the following topics unless you are notified otherwise.

- E1. Define enthalpy and/or entropy and explain their significance in the spontaneity of physical or chemical processes.
- E2. Discuss the spontaneity of given physical or chemical process in terms of ΔH , ΔS , ΔG and the equilibrium temperature
- E3. Describe why some collisions are effective, but others are not
- E4. Collision Theory explanation of the effect on the rate of a reaction by changes in the temperature, concentration, or surface area of the reactants.
- E5. Define catalyst and explain the behavior of a catalyst.

Answers to the Unit 7 Practice Test:

- | | | |
|--------------|-------|-------|
| 1. C | 6. B | 11. D |
| 2. B | 7. C | 12. A |
| 3. A | 8. D | 13. C |
| 4. B | 9. C | 14. C |
| 5. C (C + B) | 10. B | |

14. 8.34 kJ

15. -113 kJ

16.a. 62.8 kJ b. 72.6 kJ

17.a. 1.73 kJ (or $Q_{\text{expt}} = -1.73$ kJ)

b. 0.0392 mol

c. +88.3 kJ

18. -1255 kJ

19. a. $\Delta H^\circ = -176.3$ kJ

b. $\Delta S^\circ = -284.9$ J/K

c. $\Delta G^\circ = -92.8$ kJ

d. Spontaneous at room temperature.

e. Would be spontaneous at temperatures < 619 K

20. a. spontaneous at low temperatures

b. spontaneous at high temperatures

c. always spontaneous

21. a. $\text{rate} = k [A]^1 [B]^2$

first order with respect to [A], second order with respect to [B]

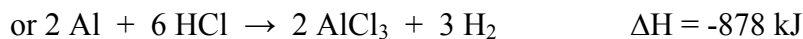
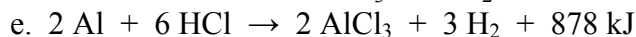
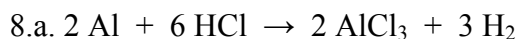
b. $k = 5.00 \times 10^4$ $1/M^2 \cdot \text{min}$

c. 3.60 M/min

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Answers to Unit 7 Homework ProblemsAssignment 3

p.9-10 Problems 8-9

Assignment 6

p. 16-17 problem 17

17.a. (+) (increase in disorder) b. (-) (decrease) c. (-) (decrease)

p.19-21 Problems 20-24

20.

Case	ΔH	ΔS	Under what temperature conditions is the reaction spontaneous? i.e. Under what temperature conditions is ΔG negative? (Remember: $\Delta G = \Delta H - T\Delta S$ and $\Delta G = 0$ at T_{eq})
1	-	+	spontaneous at all temperatures
2	+	-	never spontaneous regardless of temperature
3	+	+	spontaneous at <u>high</u> temperatures (i.e. at temperatures <u>above</u> equilibrium temperature)
4	-	-	spontaneous at <u>low</u> temperatures (i.e. at temperatures <u>below</u> equilibrium temperature)

21.a. $\Delta H = (+)$ (endo) $\Delta S (+)$ (increase in disorder b/c liquid more disordered than solid)b. $\Delta H = (-)$ (exo b/c bond forming) $\Delta S (-)$ (decrease in disorder b/c fewer particles)c. $\Delta H = (-)$ (exo b/c synthesis or combustion) $\Delta S = (-)$ (decrease in disorder b/c fewer particles & liquid less disordered than gases)23.a. Negative b/c heat flows from the H_2O to the surroundings (exo).

b. Negative b/c a solid is less disordered than a liquid.

c.

- In order to be spontaneous, ΔG must be negative when calculated from $\Delta G = \Delta H - T\Delta S$.
- If ΔS is negative then the product $T\Delta S$ will also be negative because Kelvin T is positive.
- When this **negative** product is **subtracted** from ΔH it has the same arithmetic effect as adding the positive value of the product of $T\Delta S$ to ΔH .
- Since ΔH is negative, T must remain **low** in order for the product $T\Delta S$ to remain low and the overall calculation to result in a negative ΔG .

24. Reaction 1 ΔG is (-) (spontaneous) ΔH is (+) (endo) ΔS is (+) (increase in disorder)Reaction 2 ΔG is (-) (spontaneous) ΔH is (-) (exo) ΔS is (+) (increase in disorder)

Assignment 9

Study Guide p.31-33 Problems 25-27

25. Rate = $k[\text{NO}]^2[\text{Br}_2]$

$$k = 1.2 \times 10^4 \text{ 1/M}^2 \cdot \text{sec}$$

3rd order overall

26. Rate = $k[\text{O}_3]$ (zero order with respect to NO_2 and 1st order with respect to O_3)

1st order overall

$$k = 2200 \text{ 1/sec}$$

27. Rate = $k[\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2$

(1st order with respect to BrO_3^- , 1st order with respect to Br^- and 2nd order with respect to H^+)

4th order overall

$$k = 8.0 \text{ 1/M}^3 \cdot \text{sec}$$