

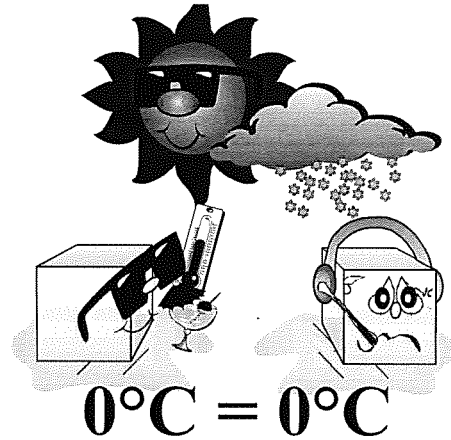
Thermochemistry

Chapter 10

- Heating/cooling curve
- Reaction mechanisms
- Potential Energy diagrams
- Entropy
- Enthalpy
- Heat of Reaction
- Spontaneity
- Gibbs Free Energy
- Hess's Law

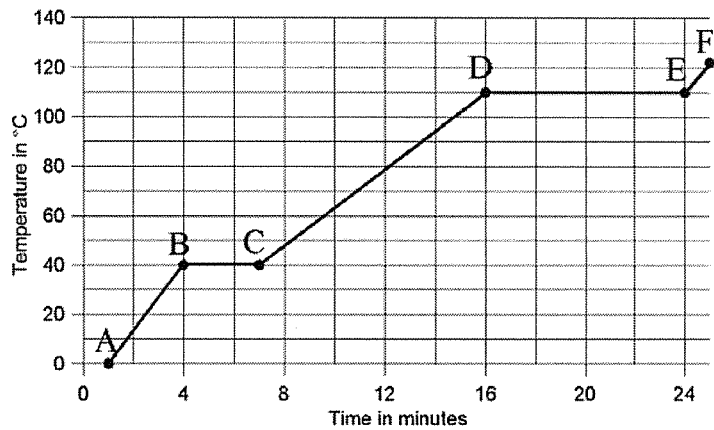
Heating/Cooling Curve

As a substance is heated, its particles begin to move faster and spread apart. The speed of the particles is related to their kinetic energy. The relative position of the particles is related to their potential energy. As solids, liquids, and gases are heated, most of the energy that is absorbed is converted to kinetic energy, and the temperature goes up. But as a substance melts or vaporizes, its particles spread out tremendously. As a result, the energy absorbed produces changes in the potential energy of the particles, so the temperature does not change as the phase changes. For that reason, the freezing point and the melting point of a substance are the same.



Base your answers to the following questions on the graph below which shows 10.0 kg of a substance that is solid at 0°C and is heated at a constant rate of 60 kilojoules per minute.

- _____ 1. What is the temperature at which the substance can be both in the solid and the liquid phase?
- _____ 2. During which lettered intervals is the internal potential energy of the substance increasing?
- _____ 3. During which lettered intervals is the kinetic energy of the particles increasing?
- _____ 4. How much heat is added to the substance from the time it stops melting to the time that it begins to boil?
- _____ 5. What is the total heat needed to melt the substance (starting at time 0)?
- _____ 6. What is the total heat needed to vaporize the substance (starting at time 0)?
- _____ 7. What is the heat of vaporization of the substance?
- _____ 8. During which lettered intervals is the substance solid?
- _____ 9. During which lettered intervals is the substance in the liquid phase?
- _____ 10. During which lettered intervals is the substance in the vapor phase?
- _____ 11. What is the temperature at which the substance can be both in the liquid and the vapor phase?



Variables that Effect Reaction Rates

Aim

- to describe the influences on reaction rates

Notes

Nature of reactants

- ★ chemical reactions occur by breaking and rearranging existing bonds
- ★ the less electrons need to be rearranged, the faster the reaction is
 - ☆ Reactions between ionic substances in aqueous solution are rapid
 - ★ double replacement reactions
 - ☆ Reactions in which covalent bonds are broken occur slowly at room temperature
 - ★ decomposition of hydrogen peroxide

Concentration of reactants - an increase in concentration results in an increase in the frequency of collisions

- ★ usually as the concentration increases, the reaction rate increases
 - ☆ if the concentration of only the reactants that are NOT involved in the rate determining step are increased, the number of collisions are increased without effecting the reaction rate
- ★ gas and liquid - increasing pressure increases the concentration of the gas

Surface area - increasing the surface area of reactants increases the opportunity for collisions

Temperature - as temperature increases so does the reaction rate

- ★ Increasing temperature increases kinetic energy of the particles increasing both the frequency and effectiveness of collisions
- ★ An increase in temperature of 10°C approximately doubles the speed of many reactions

Catalysts - speed up reactions without being permanently altered

- ★ Change the reaction mechanism so less activation energy is required

Answer the questions below by circling the number of the correct response

- The net effect of a catalyst is to change the
 - potential energy of the reactants
 - potential energy of the products
 - heat of reaction
 - rates of both the forward and reverse reactions
- An increase in temperature increases the rate of a chemical reaction because the
 - activation energy increases
 - activation energy decreases
 - number of molecular collisions increases
 - number of molecular collisions decreases
- Which change may occur in a reaction system when a catalyst is added?
 - The equilibrium point is reached more rapidly.
 - The potential energy of the reactants increases.
 - The potential energy of the products decreases.
 - The heat of reaction becomes smaller.
- As the concentration of a reactant in a chemical reaction increases, the rate of the reaction generally
 - decreases
 - increases
 - remains the same
- As the rate of a given reaction increases due to an increase in the concentration of the reactants, the activation energy for that reaction
 - decreases
 - increases
 - remains the same
- An increase in the rate of all chemical reactions results from
 - an increase in pressure
 - a decrease in pressure
 - an increase in temperature
 - a decrease in temperature
- If the pressure on a gaseous system is increased, the rate of reaction increases because
 - the activation energy is increased
 - the temperature is decreased
 - the concentration is increased
 - the volume is increased
- The rate of a reaction may be increased by
 - an increase in concentration
 - a catalyst
 - an increase in temperature
 - all of the above.

Collision Theory and Reaction Mechanisms

Aim

- Explain the mechanisms by which reactions occur

Notes

Chemical kinetics - reaction rates and mechanisms

- ★ Collision theory - in order for a reaction to occur, particles of the reactant must collide
 - ☆ Effective collision - one in which the colliding particles approach each other at the proper angle and with the proper amount of energy
 - ☆ The greater the rate of effective collisions, the greater the reaction rate is
- ★ Reaction mechanisms
 - ☆ Effective collisions between more than two particles at a time are rare
 - ☆ If all the particles shown on the reactant side of a balanced equation had to collide for a reaction to occur, the reaction would not take place
 - ☆ Chemical reactions occur by a series of intermediate steps between the initial reactants and final products
 - ★ Each step probably involves a collision of only two particles
 - ★ The series of steps that lead from reactants to products is called a **reaction mechanism**
 - ★ The slowest step of the reaction mechanism is called the **rate determining step**
 - ★ increasing the concentration of the reactant(s) that enter the rate determining step increases the reaction rate
 - ★ increasing the concentration of only reactants not involved in the rate determining step has little effect on the reaction rate
 - ★ Transition state theory - intermediate products form that exist for only brief periods of time while the atoms rearrange themselves
 - ★ intermediate products have high energy because they are formed by high energy collisions
 - ★ the high energy product is unstable and breaks apart to form the final product(s)
 - ★ the high energy product is called an **activated complex** or a **transition state complex**
 - ★ the energy needed to form the activated complex is the **activation energy**

Answer the questions below by circling the number of the correct response

- | | |
|--|---|
| <p>1. An increase in temperature increases the rate of chemical reactions. This is primarily because the</p> <ul style="list-style-type: none"> (1) concentration of the reactants increases (2) number of effective collisions increases (3) activation energy increases (4) average kinetic energy decreases | <p>2. An increase in temperature increases the rate of a chemical reaction because the</p> <ul style="list-style-type: none"> (1) activation energy increases (2) activation energy decreases (3) number of molecular collisions increases (4) number of molecular collisions decreases |
|--|---|

Energy and Entropy

Aim

- Explain the mechanisms by which reactions occur

Notes

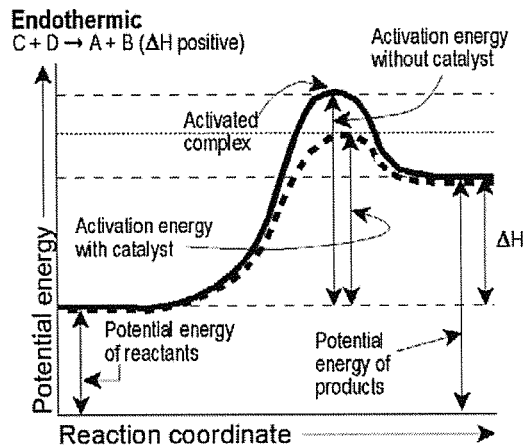
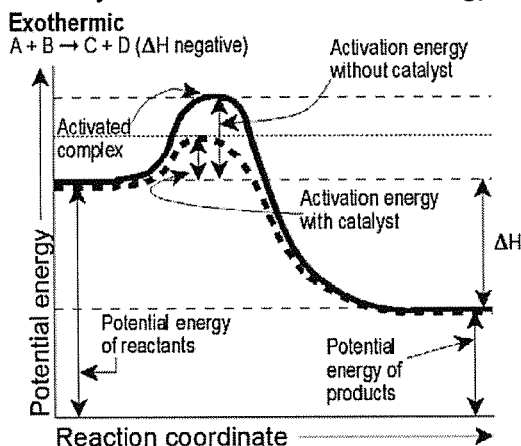
Role of energy in reactions

- ★ In order for a reaction to begin, energy is needed
 - ☆ The energy needed to begin the reaction is the activation energy
 - ☆ The activation energy comes from effective collisions
- ★ During a chemical reaction, heat may be released or absorbed
 - ☆ Heat released or absorbed during a chemical reaction is called heat of reaction or enthalpy (ΔH)
 - ☆ Enthalpy is the difference between the potential energy of the products and the reactants

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

- ☆ Exothermic reactions - reactions in which energy is released
 - ★ the potential energy of the products is lower than the potential energy of the reactants
 - ★ ΔH is negative
 - ★ catalysts reduce the activation energy but have no effect on the change in enthalpy

- ☆ Endothermic reactions - reactions in which energy is absorbed
 - ★ the potential energy of the products is higher than the potential energy of the reactants
 - ★ ΔH is positive
 - ★ catalysts reduce the activation energy but have no effect on the change in enthalpy



Entropy - randomness or disorder

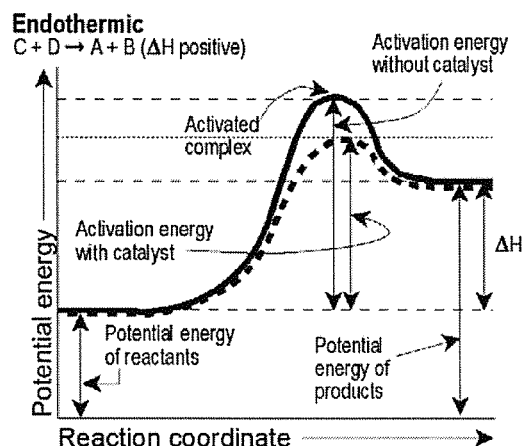
- ★ In nature, processes tend toward low energy and high entropy

Answer the questions below by circling the number of the correct response

- The difference between the heat content of the products and the heat content of the reactants is
 (1) entropy of reaction (3) free energy
 (2) heat of reaction (4) activation energy
- The purpose of the catalyst in a reaction is to
 (1) change the activation energy required of the reaction
 (2) provide the energy necessary to start the reaction
 (3) increase the amount of product formed
 (4) decrease the amount of reactants used
- Given the reaction $A + B \rightleftharpoons AB + 210 \text{ kJ}$. If an activation energy of 21 kJ is required, the activation energy of the reverse reaction is
 (1) 21 kJ (3) 210 kJ
 (2) 189 kJ (4) 231 kJ
- The difference between the potential energy of the reactants and the potential energy of the products is
 (1) ΔG (3) ΔS
 (2) ΔH (4) ΔT
- When a catalyst is added to a system at equilibrium, there is a decrease in the activation energy of
 (1) the forward reaction, only
 (2) the reverse reaction, only
 (3) both the forward and reverse reaction
 (4) neither the forward nor the reverse reactions
- The net effect of a catalyst is to change the (1) potential energy of the reactants, (2) potential energy of the products, (3) heat of reaction, (4) rates of both forward and reverse reactions
- Heat of reaction, ΔH , is equal to
 (1) $H_{\text{products}} + H_{\text{reactants}}$ (3) $H_{\text{products}} \times H_{\text{reactants}}$
 (2) $H_{\text{products}} - H_{\text{reactants}}$ (4) $H_{\text{products}}/H_{\text{reactants}}$
- An increase in temperature increases the rate of chemical reactions. This is primarily because the
 (1) concentration of the reactants increases
 (2) number of effective collisions increases
 (3) activation energy increases
 (4) average kinetic energy decreases
- An increase in temperature increases the rate of a chemical reaction because the
 (1) activation energy increases
 (2) activation energy decreases
 (3) number of molecular collisions increases
 (4) number of molecular collisions decreases
- For a given chemical reaction, the potential energy of the reactants is less than the potential energy of the products. This reaction is (1) endothermic and energy is absorbed, (2) endothermic and energy is given off, (3) exothermic and energy is absorbed, (4) exothermic and energy is given off
- As a catalyst increases the rate of a reaction, the activation energy of the reaction (1) decreases, (2) increases, (3) remains the same
- In a chemical reaction, the products have a lower potential energy than the reactants. This reaction must have a negative
 (1) ΔG (3) ΔH
 (2) ΔS (4) ΔX

Role of Energy in Reactions

In order for a reaction to begin, energy is needed to form an activated complex. The energy needed to form an activated complex is called activation energy. It comes from effective collisions. Activation energy is needed whether heat is absorbed or released during a chemical reaction. Heat absorbed or released during a chemical reaction is called **heat of reaction** or **enthalpy** (ΔH). Enthalpy is the difference between the potential energy of the products and the reactants ($\Delta H = H_{\text{products}} - H_{\text{reactants}}$). In exothermic reactions, ones in which energy is released, the potential energy of the products is lower than the potential energy of the reactants and ΔH is negative. For endothermic reactions, ones in which energy is absorbed, the potential energy of the products is higher than the potential energy of the reactants and ΔH is positive. Catalysts reduce the activation energy for both exothermic and endothermic reactions but have no effect on the change in enthalpy.



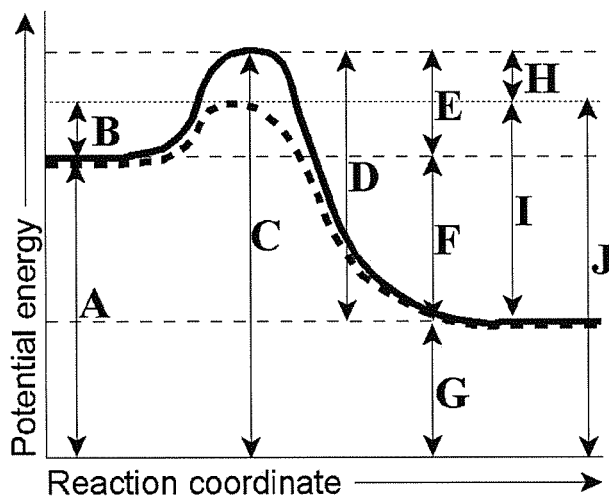
Answer the questions below based on the reading and the graph above, and based on your knowledge of chemistry.

- Based on the graph above:
 - Which has the highest energy—the reactants, the products, or the activated complex? _____
 - Which has the lowest energy—the reactants, the products, or the activated complex? _____
- If the reactants have a potential energy of 10.2 kJ/mol and the products have a potential energy of 15.7 kJ/mol, what is ΔH ? _____
- What effect do catalysts have on ΔH ? _____
- Catalysts are used to speed up chemical reactions. Based on the graph above, how do they do this? _____

- What is an endothermic reaction? What information on the graph above shows that the reaction pictured is endothermic? _____

Interpreting Reaction Coordinates

The diagram below shows the reaction coordinate for a reversible catalyzed and uncatalyzed reaction. Referring to the diagram, answer the questions that follow.



- | | |
|--|--|
| <p>_____ 1. The reaction shown above is (a) endothermic, (b) exothermic.</p> <p>_____ 2. Which lettered arrow represents the energy of the reactants for the forward reaction?</p> <p>_____ 3. Which lettered arrow represents the energy of the reactants for the reverse reaction?</p> <p>_____ 4. Which lettered arrow represents the energy of the products for the forward reaction?</p> <p>_____ 5. Which lettered arrow represents the energy of the products for the reverse reaction?</p> <p>_____ 6. Which lettered arrow represents ΔH for the forward catalyzed reaction?</p> <p>_____ 7. Which lettered arrow represents ΔH for the forward uncatalyzed reaction?</p> <p>_____ 8. Which lettered arrow represents ΔH for the reverse catalyzed reaction?</p> <p>_____ 9. Which lettered arrow represents ΔH for the reverse uncatalyzed reaction?</p> | <p>_____ 10. Which lettered arrow represents activation energy for the forward catalyzed reaction?</p> <p>_____ 11. Which lettered arrow represents activation energy for the forward uncatalyzed reaction?</p> <p>_____ 12. Which lettered arrow represents activation energy for the reverse catalyzed reaction?</p> <p>_____ 13. Which lettered arrow represents activation energy for the reverse uncatalyzed reaction?</p> <p>_____ 14. Which lettered arrow represents energy of the activated complex for the catalyzed reaction?</p> <p>_____ 15. Which lettered arrow represents energy of the activated complex for the uncatalyzed reaction?</p> <p>_____ 16. Which lettered arrow represents the difference between the activation energies of the catalyzed the uncatalyzed reactions?</p> <p>_____ 17. Which lettered arrow represents the difference between the energies of the activated complex for the catalyzed the uncatalyzed reactions?</p> <p>_____ 18. The reverse reaction is (a) endothermic, (b) exothermic.</p> |
|--|--|

NAME: _____ DATE: _____ SECTION _____ LAB _____

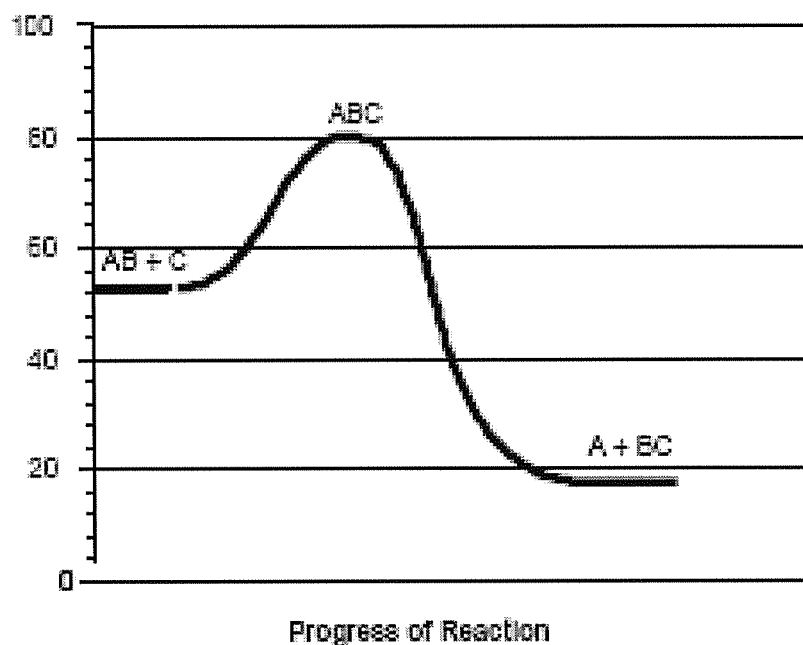
DO YOU HAVE THE POTENTIAL

Background:

Energy diagrams are used throughout chemistry as a way to describe the relationship between the energies of species involved in chemical processes. In general, the energy of a chemical species is represented by a horizontal line on the diagram. The y-axis represents energy and is numerically meaningful. The x-axis has no numerical meaning but instead represents the progress from one chemical species to another as the reaction proceeds. This is called the "Reaction Coordinate". Chemical reaction proceeds from the reactants to a high energy intermediate called the activated complex then to the products. Take note some reactions may have multiple intermediates.



Use the following *Potential Energy Diagram* to answer the questions 1 through 7.



- 1) Determine and explain if the reaction is exothermic or endothermic.
- 2) Which species show the reactants and determine their potential energy?
Species: _____ PE: _____ kJ
- 3) Which species show the products determine their potential energy?
Species: _____ PE: _____ kJ

4) Which species show the activated complex and determine its potential energy?

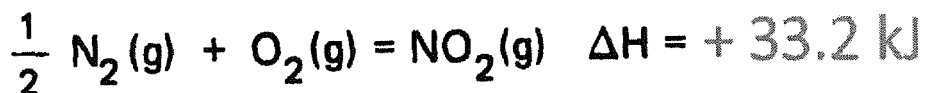
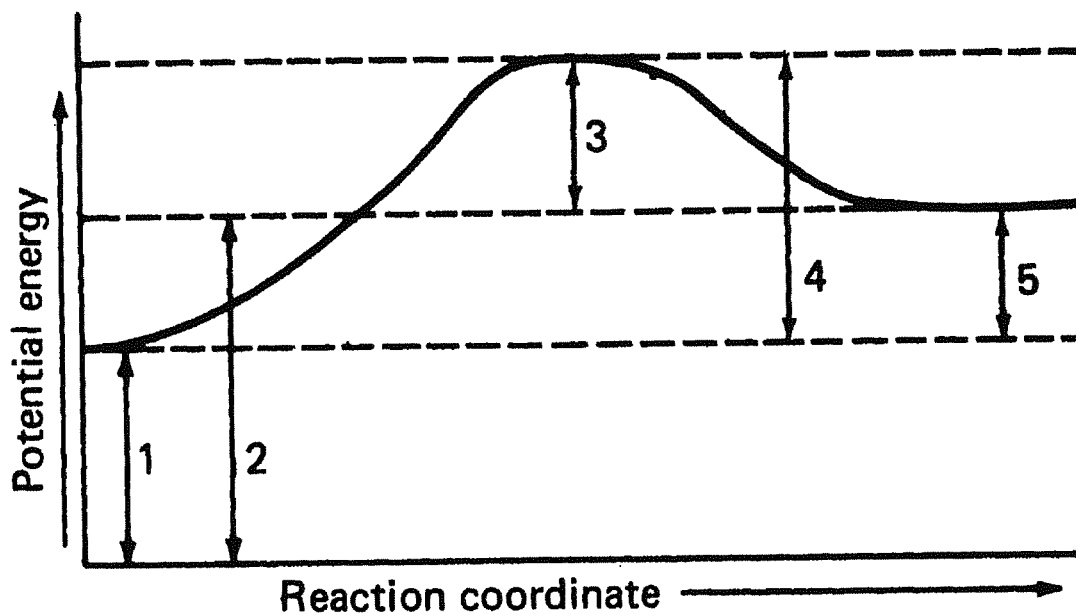
Species: _____ PE: _____ kJ

5) Determine the activation energy for the forward reaction. _____ kJ

6) Determine the heat of reaction. _____ kJ

7) Determine the activation energy for the reverse reaction. _____ kJ

Use the following *Potential Energy Diagram* to answer the questions 8 through 21.



8) Determine if the reaction is exothermic or endothermic. Give one reason in terms of the diagram. Give one reason based on the balanced equation.

Diagram:

Equation:

9) Place the chemical formulas representing the reactants in their proper position on the diagram.

10) Place the chemical formulas representing the products in their proper position on the diagram.

11) On the diagram above circle the activated complex.

12) Draw a line 6 on the above diagram to represent the potential energy of the activated complex.

13) Which lines could be added together to show the potential energy of the activated complex?

Line: _____ + Line: _____

14) Describe what line 1 represents.

15) Describe what line 2 represents.

16) Describe what line 5 represents.

17) Which line shows the activation energy for the forward reaction? Line: _____

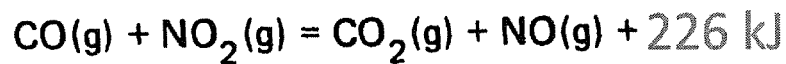
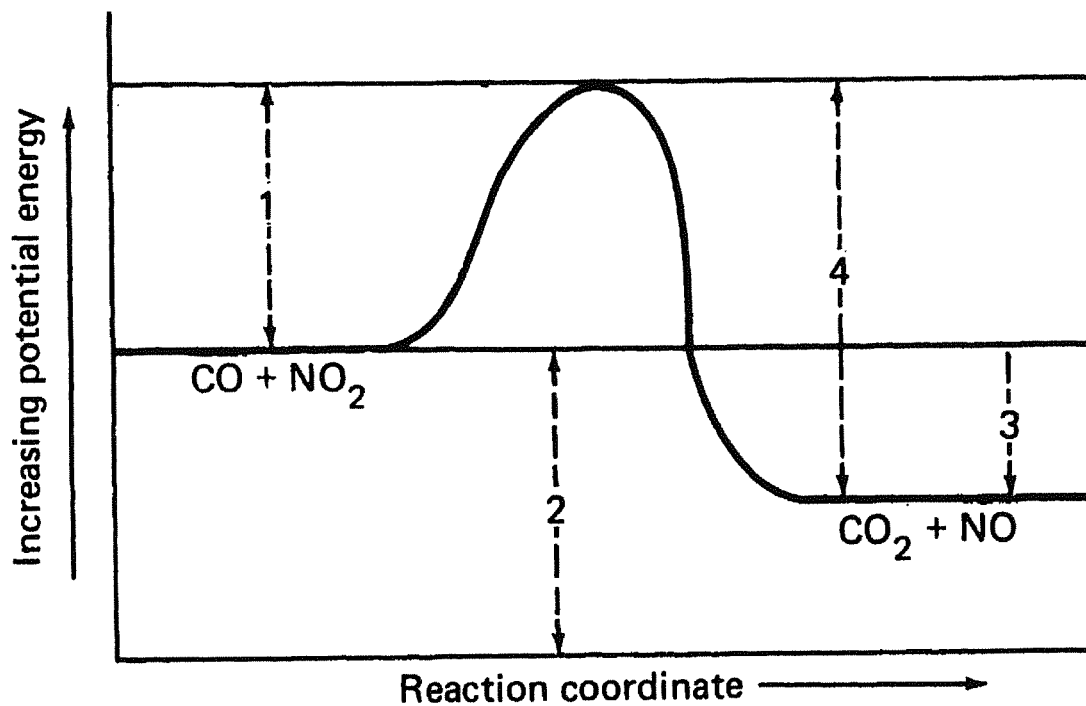
18) On the above diagram draw the potential energy diagram with the addition of a catalyst. In your own words describe how the diagram has changed.

19) Which 2 lines can be subtracted to obtain ΔH , the heat of reaction. Line: _____ - Line: _____

20) How much energy is required for this reaction if 4 mols of NO_2 (g) are produced?

21) Describe the reaction's change in entropy. Explain.

For the following diagram interpret the meaning of the numbered lines and write at least 8 questions below based on the diagram.



22) Determine the enthalpy of the reactants.

_____ kJ

23) Determine the enthalpy of the products.

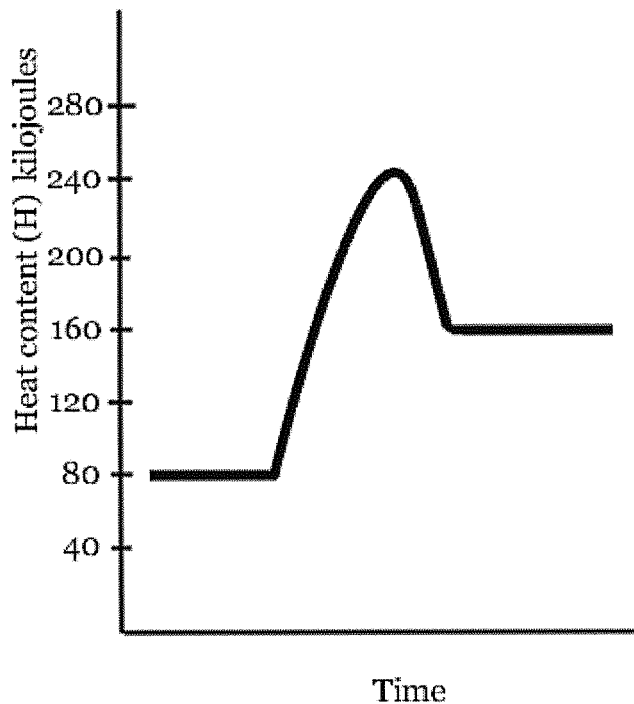
_____ kJ

24) Determine the enthalpy of the activated complex.

_____ kJ

25) Determine the activation energy of the forward reaction.

_____ kJ



26) Describe if the reaction is endothermic or exothermic.

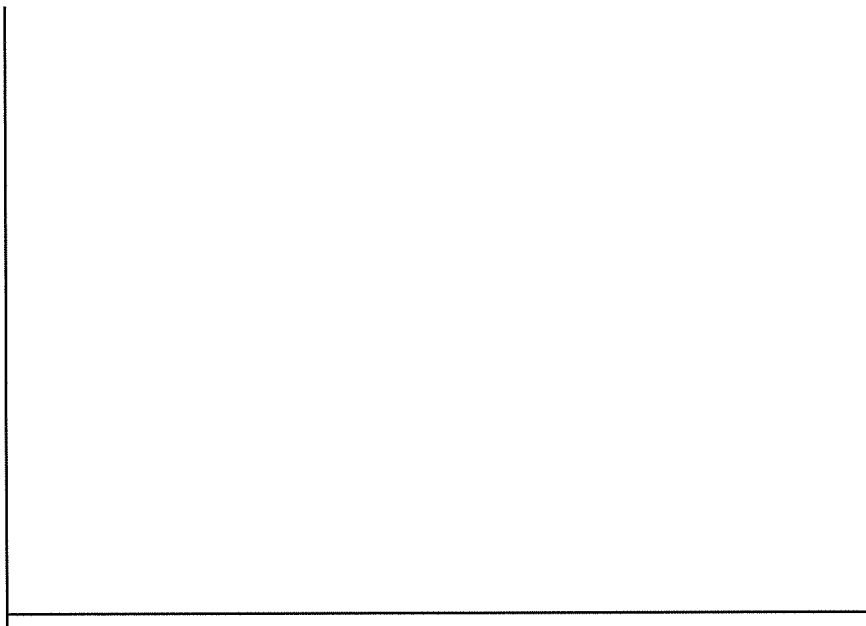
27) Determine the heat of reaction (ΔH). _____ kJ

28) Determine the activation energy of the reverse reaction. _____ kJ

29) On the above diagram draw a curve showing the activation energy of a catalyzed reaction.

30) On the blank PE Diagram below draw the following:

- a) Label each axis and create a scale.
- b) PE of Reactants = 350 kJ
- c) PE of Products = 175 kJ
- d) Activation Energy = 100 kJ
- e) Catalyzed Activation Energy = 45 kJ (in a different color or dashed line)



Reflection:

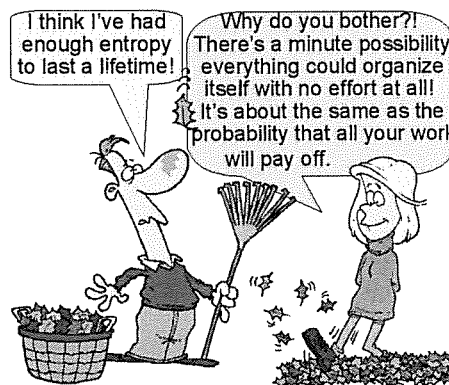
Describe a potential energy diagram. Include the terms activation energy, heat of reaction, exothermic and endothermic.



WHAT IS ENTROPY?

A Fine Mess

No matter how careful you are, your room always becomes messy. It's not surprising. There are very few arrangements of all your things that are organized. There are thousands of arrangements that are disorganized. Probability favors disorganization or randomness, also known as **entropy**. In nature, high entropy is favored, yet many things that occur naturally are quite organized. This is because nature also favors low potential energy or **enthalpy**. Entropy and enthalpy sometimes conflict with each other. Consider steam and snowflakes, both arrangements of water. Steam has very high entropy. The particles are spread out randomly. Snowflakes have low entropy. The particles are arranged in repeating geometric patterns. In order to spread the particles out, as in steam, it is necessary to overcome the hydrogen bonds that hold water molecules together. This requires a lot of energy. As a result, water has a high boiling point. Snowflakes, therefore, have low enthalpy, while steam has high enthalpy.



Answer the questions below based on your reading above, and on your knowledge of chemistry.

- Dry ice is solid carbon dioxide [CO₂(s)]. Carbon dioxide occurs naturally as a gas in the atmosphere [CO₂(g)].
 - Which form of carbon dioxide has higher entropy? _____
 - Which form of carbon dioxide has higher enthalpy? _____
- Gasoline burns according to the following equation: 2C₈H₁₈(ℓ) + 25O₂(g) → 16CO₂(g) + 18H₂O(g).
 - What happens to the enthalpy during this reaction. Explain. _____

 - What happens to the entropy during this reaction. Explain. _____

- For each of the following, the products have higher entropy than the reactants. Explain why.
 - H₂O(s) → H₂O(ℓ) _____
 - 2C₂H₆(g) + 7O₂(g) → 4CO₂(g) + 6H₂O(g) _____
 - I₂(s) → I₂(g) _____

Your Reaction Is Making Me HOT!

Introduction:

Change in Enthalpy

Much of our discussion of the energetic of chemical reactions will focus on the heat transferred under constant pressure conditions created by the Earth's atmosphere. Because this energy is so central in chemistry, we define a quantity called **enthalpy** in dealing with heat absorbed or released under constant pressure. Enthalpy is denoted with the symbol H . The enthalpy of individual reactants or products is difficult to measure but can easily measure the change in enthalpy ΔH . ΔH is equal to the difference in enthalpy of the reactants and products, also called **the heat of reaction**. The change in enthalpy is equal to the heat lost or gained by the system under constant pressure:

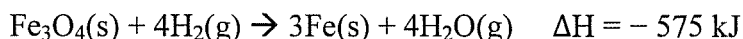
$$\Delta H = H_{\text{products}} - H_{\text{reactants}} = q$$

The sign of ΔH gives us information about the reaction. Since ΔH is a measure of energy, it is measured in Joules or kilojoules. $\Delta H = -$ indicates a reaction which released energy, energy is produced; the reactants are higher in energy than the products. $\Delta H = +$ indicates a reaction which absorbed energy, energy is taken in as a reactant; the reactants are lower in energy than the products. Table I in the CRT give information about ΔH .

Reversible Reactions

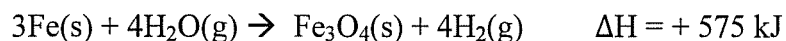
A reversible reaction is a reaction that do not goes to completion and occur in both the forward and reverse direction. Where reactants can combine to form products but the product can also combine to form reactants. A double headed arrow is commonly used to show reaction which can go both ways. Here is an example:

When hydrogen gas is passed over iron oxide, iron and steam are produced:



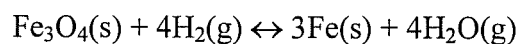
This is the forward reaction.

Passing steam over red-hot iron gives the opposite reaction: iron oxide is produced, and hydrogen gas is liberated.



This is the reverse reaction.

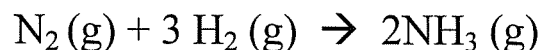
The fact that this reaction under certain conditions can be reversed is shown by using a double headed arrow.



For any reaction the reverse reaction has an opposite sign for ΔH .

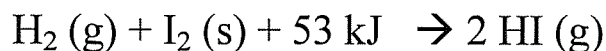
Problems:

Use the following reactions to answer questions 1 to 3



- 1) Based on Table I of the CRT is this an exothermic or endothermic reaction? Explain.
- 2) Rewrite the equation with its ΔH value in the proper position in the equation.
- 3) Give the reaction's reverse reaction with its correct value for ΔH .

Use the following reaction to answer questions 4 through 7.

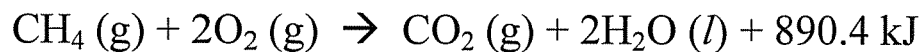


- 4) Based on the above reaction will heat be absorbed or released? Explain.
- 5) What will occur to the surroundings temperature?
- 6) What is the correct value for ΔH ? Give correct value and sign.

$$\Delta H = \underline{\hspace{2cm}} \text{ kJ}$$

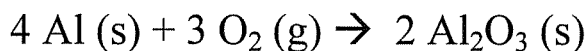
- 7) Give the reaction's correct reverse reaction with energy in its proper position.

Use the following equation to answer questions 8 through 12



- 8) Based on the above reaction will heat be absorbed or released? Explain.
- 9) What will occur to the surroundings temperature?
- 10) When 1.0 mole of $\text{CH}_4 (\text{g})$ (methane) combusts it produces 890.4 kJ of heat energy. How much heat will be released when 4.0 moles of methane are combusted?
- 11) How much heat will be released when 8.0 grams of methane are combusted?

Use the following reaction to answer questions 12 through 15.



- 12) Based on Table I, determine if the reaction is exothermic or endothermic. _____
- 13) Rewrite the equation with ΔH in its proper position in the reaction.
- 14) Determine the change in enthalpy if 24 moles of Al are reacted with excess oxygen.
- 15) Based on Table I discuss why Al_2O_3 is a very stable product.

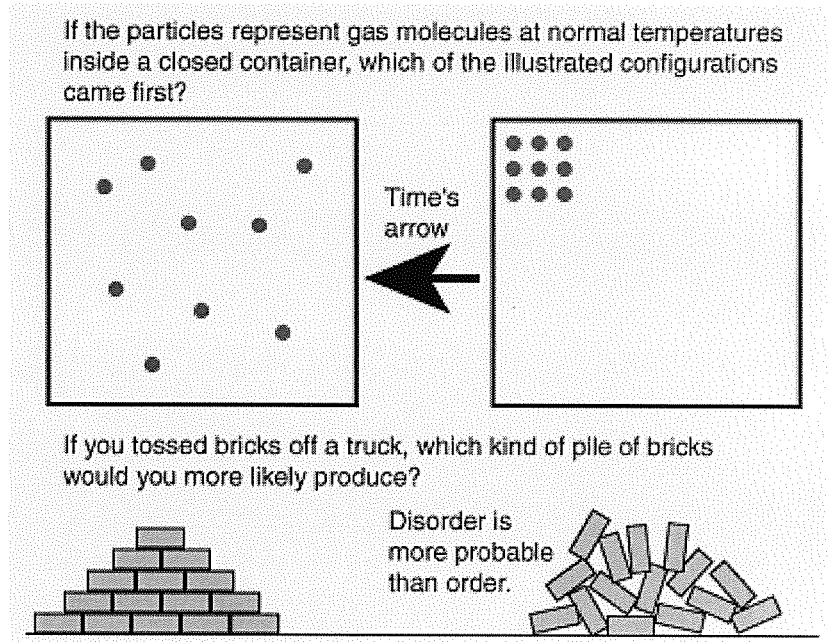
Reflection: Define ΔH in terms of the reactants and products.

Everything Falls Apart

Background:

Entropy is a physical quantity that can be interpreted as a measure of the disorder of a physical system. One of the ideas involved in the concept of entropy is that nature tends from order to disorder in isolated systems. This tells us that the right hand box of molecules happened before the left.

Entropy may be termed as the property of a system which measures the degree of disorder or randomness in the system. It is generally expressed by the symbol, S . Entropy like enthalpy, is a state function and change in entropy therefore, depends only on the initial and final states of the system. The change in entropy during the process when a system undergoes a change from one state to another is represented by ΔS .



The physical meaning of entropy is that entropy is a measure of degree of disorder (or randomness) of a system. The relation between entropy and disorder provides a suitable explanation for entropy change in various processes. The greater the disorder in a system, the higher is the entropy. A process is more likely to occur if it is accompanied by an increase in entropy; that is, ΔS is positive.

Procedure:

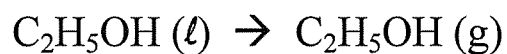
Each of the following scenarios show an increase in entropy. As a group analysis the scenario and determine why entropy is increasing.

1) A sample of Iron has its temperature change from 20°C to 150°C.

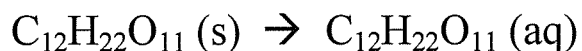
2) A sample of ice changes phase to liquid water.



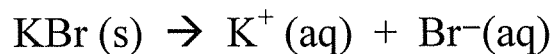
3) A sample of ethanol evaporates to form ethanol vapor.



4) A sample of sugar dissolves in water.



5) A sample of potassium bromide dissolves in water.



6) A sample of dinitrogen tetraoxide reacts to form two molecules of nitrogen dioxide.



7) A sample of calcium carbonate decomposes into calcium oxide and carbon dioxide.



Use the following information to answer questions 8 through 11.

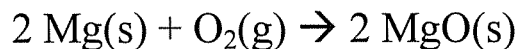
Naphthalene is a crystalline, aromatic, white, solid hydrocarbon with formula $C_{10}H_8$ and the structure of two fused benzene rings. It is best known as the traditional, primary ingredient of mothballs. It is volatile, forming a flammable vapor, and readily changes from a solid at room temperature directly to a gas, producing a characteristic odor that is detectable at concentrations as low as 0.08 ppm by mass.



- 8) Name the phase change which naphthalene undergoes at room temperature. _____
- 9) Describe naphthalene's change in entropy as it undergoes the above phase change.
- 10) Calculate naphthalene's gram formula mass. _____ g/mol
- 11) Determine the minimum mass in grams which naphthalene can be detected in 10. kg of air.

Reflection:

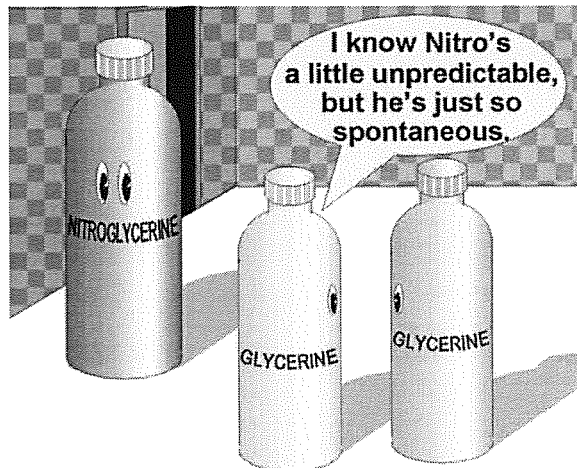
- A) Describe and explain the change in entropy shown in the following reaction.



- B) Describe the 3 phases of matter in terms of entropy.

Being Spontaneous

Whether a reaction proceeds spontaneously or not depends on the balance between two natural tendencies: [1] The drive toward greater stability (reduced potential energy); and [2] The drive toward less organization (increased entropy). In nature, systems tend toward the lowest possible energy or enthalpy (H). Exothermic reactions are favored (ΔH is negative). In nature, systems also tend toward greater randomness (disorder) or entropy (S). When entropy increases, ΔS , the change in entropy is positive. High entropy is favored by increased temperature. The Gibbs free energy change (ΔG) predicts whether or not a reaction is spontaneous. It takes into account the change in enthalpy and the change in entropy. The Gibbs free energy change is the difference between the energy change (ΔH) and the product of the absolute or Kelvin temperature (T) and the entropy change (ΔS)




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

Chemical dating preferences

For a system at equilibrium, $\Delta G = 0$. In order for a system to change spontaneously, the resulting ΔG must be negative. If the drive toward lower energy and higher entropy cannot be satisfied at the same time, the type of change that will be favored will depend on the temperature. At low temperatures, the term $T\Delta S$ will be small, and ΔH will have the greatest effect on the free energy. At high temperatures, the term $T\Delta S$ will be large, and ΔS will have the greatest effect on the free energy.

Based on your reading above, fill in the table below and answer the questions that follow.

Reaction Conditions			Is the reaction spontaneous? (Yes, No, Likely, or Unlikely)
Temperature	ΔH	ΔS	
High	+	-	
High	+	+	
High	-	-	
High	-	+	
Low	+	-	
Low	+	+	
Low	-	-	
Low	-	+	

Continue 

Activity 6-4

Spontaneous Reactions

1. Define *entropy*. _____

2. What is the symbol for entropy change? _____

3. Entropy change can be represented by the equation

$$\Delta S = S_{\text{PRODUCTS}} - S_{\text{REACTANTS}}$$

What is the meaning of this equation? _____

4. Describe how the two factors, entropy change and enthalpy change, determine whether a reaction will proceed spontaneously. _____

5. The algebraic combination of these two factors is given as the equation for free energy change, ΔG . Complete this equation.

$$\Delta G = \text{_____} - \text{_____}$$

6. Reactions are spontaneous when the value for ΔG is _____ (*positive/negative*).

7. When $\begin{pmatrix} \Delta H \\ \text{is} \\ \text{negative} \end{pmatrix}$ and $\begin{pmatrix} \Delta S \\ \text{is} \\ \text{positive} \end{pmatrix}$, the sign of ΔG must be _____.

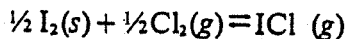
A negative value for ΔH and a positive value for ΔS apply to a reaction that _____ (*is/is not*) spontaneous at any temperature. Both factors that determine spontaneity are _____ (*favorable/unfavorable*). When $\Delta H < 0$, the chemical change moves the system to a _____ (*higher/lower*) enthalpy; energy is _____ (*taken on/given off*). When $\Delta S > 0$, the chemical change moves the system to a _____ (*greater/lesser*) entropy; the system becomes _____ (*more/less*) disordered.

8. When $\begin{pmatrix} \Delta H \\ \text{is} \\ \text{positive} \end{pmatrix}$ and $\begin{pmatrix} \Delta S \\ \text{is} \\ \text{negative} \end{pmatrix}$, the sign of ΔG must be _____.

A positive value for ΔH and a negative value for ΔS apply to a reaction that _____ (*is/is not*) spontaneous at any temperature. Both factors that determine spontaneity are _____ (*favorable/unfavorable*). When $\Delta H > 0$, the chemical change moves the system to a _____ (*higher/lower*) enthalpy; energy is _____ (*taken on/given off*). When $\Delta S < 0$, the chemical change moves the system to _____ (*greater/lesser*) entropy; the system becomes _____ (*more/less*) disordered.

9. When $\left(\begin{array}{c} \Delta H \\ \text{is} \\ \text{positive} \end{array}\right)$ and $\left(\begin{array}{c} \Delta S \\ \text{is} \\ \text{positive} \end{array}\right)$, or when $\left(\begin{array}{c} \Delta H \\ \text{is} \\ \text{negative} \end{array}\right)$ and $\left(\begin{array}{c} \Delta S \\ \text{is} \\ \text{negative} \end{array}\right)$, the sign of ΔG depends upon the magnitude of the contribution to ΔG by the _____ (enthalpy/entropy) change which, in turn, is determined by the _____ (pressure/temperature) of the system.

10. For the reaction



$$\Delta H = 4.2 \times 10^3 \text{ cal/mole} \quad \Delta S = 18.5 \text{ cal/mole K}$$

Using the formula $\Delta G = \Delta H - T\Delta S$, calculate ΔG at 298 K.

$$\Delta G \text{ at } 298 \text{ K} = \underline{\hspace{2cm}}$$

At 298 K, is this reaction spontaneous or not spontaneous? _____

11. For this same reaction, calculate the temperature at which $\Delta G = 0$, using the values for ΔH and ΔS above.

$$T = \underline{\hspace{2cm}}$$

12. At temperatures above the value determined in question 11, the reaction _____ (is/is not) spontaneous because the value of ΔG is _____ (positive/negative).

13. At temperatures below the value determined in question 11, the reaction _____ (is/is not) spontaneous because the value of ΔG is _____ (positive/negative).

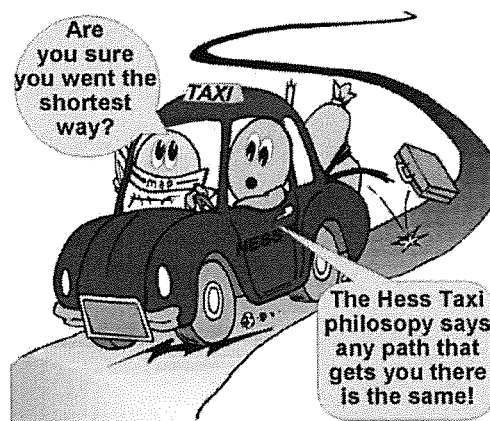
Gibb's Free Energy Worksheet

1. A certain chemical reaction is exothermic with a standard enthalpy of -300 kJ mol^{-1} . The entropy change for this reaction is $53 \text{ J mol}^{-1} \text{ K}^{-1}$. Calculate the free energy change for this reaction at $25 \text{ }^\circ\text{C}$. Is the reaction spontaneous?
2. A certain chemical reaction is endothermic with a standard enthalpy of $+300 \text{ kJ mol}^{-1}$. The entropy change for this reaction is $454 \text{ J mol}^{-1} \text{ K}^{-1}$. Calculate the free energy change for this reaction at $25 \text{ }^\circ\text{C}$. Is the reaction spontaneous?
3. A certain chemical reaction is exothermic with a standard enthalpy of -100 kJ mol^{-1} . The entropy change for this reaction is $-135 \text{ J mol}^{-1} \text{ K}^{-1}$. Calculate the free energy change for this reaction at $25 \text{ }^\circ\text{C}$. Is the reaction spontaneous?
4. A certain chemical reaction is exothermic with a standard enthalpy of -200 kJ mol^{-1} . The Free energy change for this reaction is -160 kJ mol^{-1} . Calculate the entropy change for this reaction at $25 \text{ }^\circ\text{C}$.
5. A certain chemical reaction is exothermic with a standard enthalpy of -250 kJ mol^{-1} . The entropy change for this reaction is $-80 \text{ J mol}^{-1} \text{ K}^{-1}$. Calculate the temperature above which or below which the reaction becomes spontaneous.

Applying Hess's Law

Suppose you climb from the first rung of a ladder to the fifth rung of the ladder. Your potential energy has increased by the height of four rungs. Should you climb down from the first rung to the floor, climb up to the sixth rung, and down one to the fifth rung, the potential energy change is the same. The path is different, but the change in energy from the initial position to the final position is the same. This is the concept behind Hess's law. If a reaction occurs through a series of steps, the enthalpy change going from reactant to product is equal to the sum of the enthalpy changes for each of the steps.

$$\Delta H = \Delta H_A + \Delta H_B + \Delta H_C + \dots$$

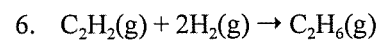
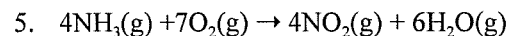
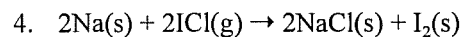
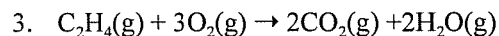
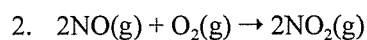
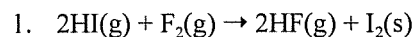


For example, under standard conditions (1 atm and 298K) the heat of formation for carbon dioxide is -393.3 kJ/mol [$\text{C(s)} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) \quad \Delta H_f = -393.3 \text{ kJ/mol}$] and the heat of formation of carbon monoxide is -110.4 kJ/mol [$\text{C(s)} + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CO(g)} \quad \Delta H_f = -110.4 \text{ kJ/mol}$]. Notice the coefficient in front of the oxygen is $\frac{1}{2}$. This makes it possible to write a balanced equation in which 1 mol of product forms. This is necessary because the enthalpy is in kJ/mol. From two equations above, it is possible to determine the heat of reaction for the oxidation of carbon monoxide to carbon dioxide by following some simple rules: [1] Manipulate the equations so they add together to give the desired results; [2] The enthalpy of formation of an element under standard conditions is zero; [3] When a reaction is reversed the sign of the enthalpy is changed, but the magnitude is the same; [4] If a balanced equation is multiplied by a coefficient, the enthalpy associated with the equation is multiplied by the same number; and [5] If the same substances are on both the product and reactant side when the equations are added together, subtract them from both sides. See below.

<u>Sample Problem</u>		
What is the heat of reaction (ΔH) for the reaction $2\text{CO(g)} + \text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g})$		
<u>Equations</u> (from above)		<u>Explanation</u>
$2\text{CO(g)} \rightarrow 2\text{C(s)} + \text{O}_2(\text{g}) \quad \Delta H_f = 110.4 \text{ kJ/mol} \times 2 =$	220.8 kJ/mol	<ul style="list-style-type: none"> Reverse the reaction so CO is on the reactant side. Reverse the sign of ΔH_f. Multiply by the coefficient 2. Multiply by the coefficient 2.
$2\text{C(s)} + 2\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) \quad \Delta H_f = -393.3 \text{ kJ/mol} \times 2 =$	-786.6 kJ/mol	
$2\text{CO(g)} + 2\text{C(s)} + 2\text{O}_2(\text{g}) \rightarrow 2\text{C(s)} + \text{O}_2(\text{g}) + 2\text{CO}_2(\text{g})$	-565.8 kJ/mol	<ul style="list-style-type: none"> Add the equations and the enthalpies
$2\text{CO(g)} + \text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) \quad \Delta H = -565.8 \text{ kJ/mol}$		<ul style="list-style-type: none"> Subtract $\text{O}_2(\text{g})$ and 2C(s) from both sides

CONTINUE

Determine the heat of reaction at 1 atm. and 298 K for each of the reactions below by referring to the table at the right showing standard enthalpies of formation.



STANDARD ENERGIES OF FORMATION OF COMPOUNDS AT 1 atm AND 298 K		
Compound	Heat (Enthalpy) of Formation * kJ/mol (ΔH_f°)	Free Energy of Formation kJ/mol (ΔG_f°)
Aluminum oxide $\text{Al}_2\text{O}_3(\text{s})$	-1674.1	-1580.9
Ammonia $\text{NH}_3(\text{g})$	-46.0	-16.3
Barium sulfate $\text{BaSO}_4(\text{s})$	-1471.8	-1361.0
Calcium hydroxide $\text{Ca}(\text{OH})_2(\text{s})$	-985.2	-897.9
Carbon dioxide $\text{CO}_2(\text{g})$	-393.3	-394.2
Carbon monoxide $\text{CO}(\text{g})$	-110.4	-137.1
Copper (II) sulfate $\text{CuSO}_4(\text{s})$	-770.8	-661.3
Ethane $\text{C}_2\text{H}_6(\text{g})$	-84.4	-33.0
Ethene (ethylene) $\text{C}_2\text{H}_4(\text{g})$	52.3	68.1
Ethyne (acetylene) $\text{C}_2\text{H}_2(\text{g})$	226.6	209.0
Hydrogen fluoride $\text{HF}(\text{g})$	-270.9	-273.0
Hydrogen iodide $\text{HI}(\text{g})$	26.3	1.7
Iodine chloride $\text{ICl}(\text{g})$	18.0	-5.4
Lead (II) oxide $\text{PbO}(\text{s})$	-215.3	-188.1
Magnesium oxide $\text{MgO}(\text{s})$	-601.1	-568.9
Nitrogen monoxide $\text{NO}(\text{g})$	90.3	86.5
Nitrogen dioxide $\text{NO}_2(\text{g})$	33.0	51.4
Potassium chloride $\text{KCl}(\text{s})$	-436.4	-408.8
Sodium chloride $\text{NaCl}(\text{s})$	-410.9	-383.7
Sulfur dioxide $\text{SO}_2(\text{g})$	-296.4	-299.7
Water $\text{H}_2\text{O}(\text{g})$	-241.6	-228.2
Water $\text{H}_2\text{O}(\text{l})$	-285.5	-237.0

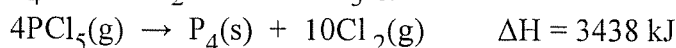
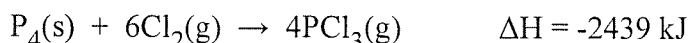
* Minus sign indicates an exothermic reaction.
Sample equations:
 $2\text{Al}(\text{s}) + \frac{3}{2}\text{O}_2(\text{g}) \rightarrow \text{Al}_2\text{O}_3(\text{s}) + 1674.1 \text{ kJ}$
 $2\text{Al}(\text{s}) + \frac{3}{2}\text{O}_2(\text{g}) \rightarrow \text{Al}_2\text{O}_3(\text{s}) \quad \Delta H = -1674.1 \text{ kJ/mol}$



Mr. Hess

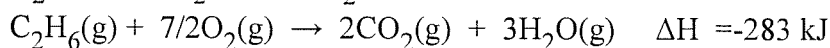
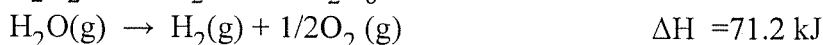
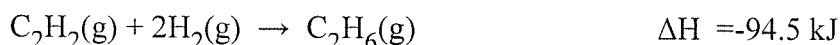
The following is a list of some extra Hess's Law problems. They will not be collected, nor will these particular questions be asked on an exam. Doing these problems, however, will certainly help you understand Hess's Law better. Good luck!

(1) Find the ΔH for the reaction below, given the following reactions and subsequent ΔH values:
 $\text{PCl}_5(\text{g}) \rightarrow \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$



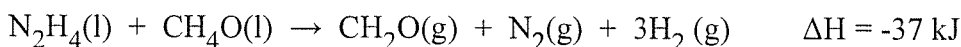
answer = 249.8 kJ

(2) Find the ΔH for the reaction below, given the following reactions and subsequent ΔH values:
 $2\text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{C}_2\text{H}_2(\text{g}) + 5/2\text{O}_2(\text{g})$



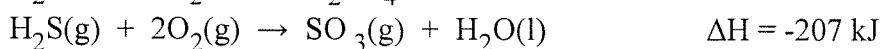
answer = 235 kJ

(3) Find the ΔH for the reaction below, given the following reactions and subsequent ΔH values:
 $\text{N}_2\text{H}_4(\text{l}) + \text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$



answer = -18 kJ

(4) Find the ΔH for the reaction below, given the following reactions and subsequent ΔH values:
 $\text{H}_2\text{SO}_4(\text{l}) \rightarrow \text{SO}_3(\text{g}) + \text{H}_2\text{O}(\text{g})$



answer = 72 kJ