HEAT, TEMPERATURE, & THERMAL ENERGY

Energy – A property of matter describing the ability to do _____.

Work - is done when an object is moved through a distance by a force acting on the object.

Kinetic Energy – Associated with the _____ of an object.

Potential Energy – Stored energy due to an object's _____.

Internal Energy – Sum of the kinetic and potential energies of the particles in a substance.

1st Law of Thermodynamics: The law of conservation of energy. Energy can be _____ from one form to another but it cannot be created or destroyed.

Units of Energy: Joule ($kg/m^2/s^2$) or 1 calorie = _____

Heat energy (q) is the actual energy _____ between substances. i.e an object cannot possess heat

Why is heat energy essential in modern society?

i) Over 80% of the world's electricity is generated using heat.
ii) Heat energy is required to refine metals.
iii) Heat is required to both shape and weld pieces of metals.
iv) Heat produced by burning fuels operates many different kinds of engines.

The Kinetic Molecular Theory of Heat

Many theories have been developed in order to explain the concept of heat. The theory which appears to best explain heat is called the _____. This theory relates heat to the motion of particles. It is a combination of the _____ and the _____.

**The four main points of this theory are as follows: **

1. All matter is composed of many tiny particles called _____.
2. The molecules are separated from one another by empty space. The _____ _____ the molecules is large _____ to their _____.
3. All molecules are _____ in some manner, and therefore possess _____ energy (energy of motion).
4. When heat is added to matter, the molecules _____ the energy and move _____ (their kinetic energy increases). When heat is _____, the molecules _____ down (their kinetic energy decreases).

Temperature: A measure of the _____ of the molecules in a substance.

Thermal energy - is the total of the _____ of the molecules (energy of motion) and the _____(energy of the bonds holding the molecules together)

Systems: Substances in which a change (physical or chemical) occurs. i.e. reactants and products, represented by a chemical equation)

Surroundings: The rest of the universe! Usually the surroundings are considered to be anything nearby capable of absorbing or releasing thermal energy.

Endothermic: Process in which heat is _____ by the system from the surroundings (_____).

Exothermic: Process in which heat is _____ from the system into the surroundings (_____).

Open System: Both matter and energy can flow freely

Isolated System: Neither matter nor energy can flow freely (ideal but impossible)

Closed System: Energy can flow freely but not _____

CHEMICAL ENERGY AND ENTHALPY CHANGE

Chemical systems include both kinetic and potential energy.

Kinetic Energies: Involved with the motion of particles.

- Electron movement within atoms
- Translation in gas and liquids, the movement of particles in a linear path
- Rotation about a bond axis
- Vibration, the oscillation of atoms connected by chemical bonds

Potential Energies: Involved with particles' positions within an attractive or repulsive force field.

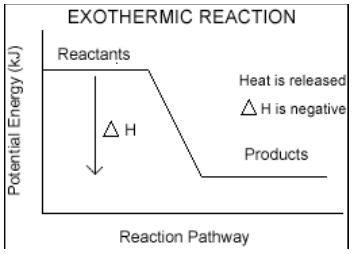
- Van der Walls Forces - Bond energy - Nuclear energy
- It is extremely difficult to measure the sum of all these kinetic and potential energies. Instead we study _____

Enthalpy Change (ΔH): The difference in enthalpies of reactants and products during a change. AKA heat of reaction _____

Hproducts > Δ Hreactants = + Δ H = _____

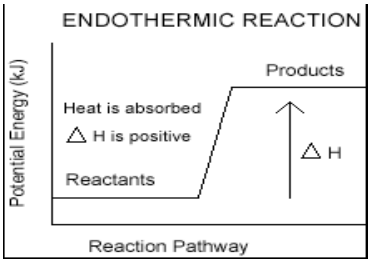
Hreactants > Hproducts = - Δ H = _____

Exothermic Reactions: **Less** energy is required to _____ bonds in the reactants than is _____ by _____ of new bonds in the products.



- The products of _____ reactions have _____ stored potential energy than the reactants had (more energetically stable)

Endothermic Reaction: _____ energy is required to _____ bonds in the reactants than is released by formation of new bonds in the products.



- The products of _____ reactions have _____ stored potential energy than the reactants had (less energetically stable)

REPRESENTING ΔH

1. Thermochemical Equations with ΔH values:

E.g. $2Na(s) + 2\ H_2O(l)$! $2NaOH(aq) + H_2(g)$ $\Delta H = -368.6$ kJ

Remember:

a) ΔH is a "_____" property, it is affected by _____ and _____.
I.e. If a reaction produces water in the form of a gas or a liquid, the enthalpy change will be different since the enthalpy of liquid water is lower than the enthalpy of water vapour.

$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$ $\Delta H° = -571.0$ kJ | $2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$ $\Delta H° = -483.6$ kJ

Scientists will often report results at _____ and use the symbol ΔH° to indicate that the value is the "standard enthalpy of reaction".

b) Exothermic reactions in one direction, become endothermic reactions in the reverse direction. (I.e. change the sign of ΔH)

$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$ $\Delta H° = -483.6$ kJ | $2H2O(g) \rightarrow 2H_2(g) + O_2(g)$ $\Delta H° = +483.6$ kJ

c) The value of ΔH depends on the _____ amounts of reactants and products involved.

$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$ $\Delta H° = -571.0$ kJ

$H_2(g) + 1/2O_2(g) \rightarrow H_2O(l)$ $\Delta H = 1/2(-571\ kJ) = -285.5$ kJ

2. Thermochemical Equations with Energy Terms:

Endothermic (energy is absorbed) $2H_2O(g) + 483.6\ kJ \rightarrow 2H_2(g) + O_2(g)$

Exothermic (energy is released) $2H_2(g) + O_2(g) \rightarrow 2H_2O(g) + 483.6\ kJ$

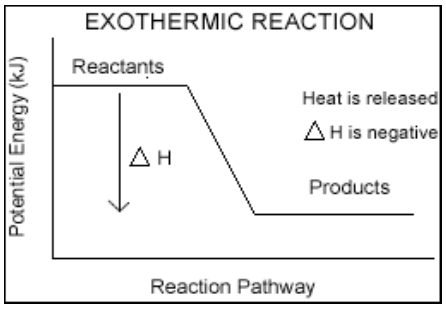
3. Molar Enthalpies of Reaction:

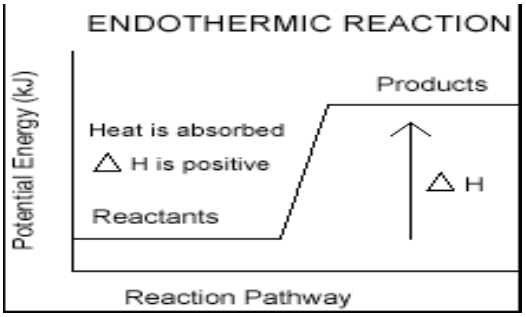
The enthalpy change associated with 1 mole of a substance. The particular reactant or product must be specified.

$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$ $\Delta H° = -571.0$ kJ/mol O2

2H2(g) + O2(g) → 2H2O(l) ΔH°= -285.5/mol H2

4. Potential Energy Diagrams:





Stoichiometry and Thermochemical Equations

The enthalpy of reaction is _____ dependent on the quantity of products.

$$\frac{\Delta H_2}{\Delta H_1} = \frac{n_2}{n_1}$$

EXAMPLE:

1. What is the enthalpy change when 1.0 kg of Al reacts completely with excess Cl_2 according to the following equation?

$$2Al_{(s)} + 3Cl_{2(g)} \rightarrow 2AlCl_{3(s)} \quad \Delta H^{o}_{rxn} = -1408 \text{ kJ}$$

RELATING HEAT CHANGE & TEMPERATURE CHANGE

Heat Capacity: _____ energy required to raise the temperature of a substance (_____) by 1°C or 1K. _____

Specific Heat Capacity: Amount of heat energy required to raise the temperature of _____ of a substance by 1°C or 1K. _____

You are provided a glass of milk and a swimming pool full of milk.
Which will have the higher heat capacity?
Which will have the higher specific heat capacity?

Molar Heat Capacity: Amount of heat energy per _____ required to raise the temperature of 6.02 X 1023 molecules of a substance by 1°C or 1K. _____

Factors which affect heat capacity:

1. **Mass -** the greater the number of molecules which need their average kinetic energy increased, the _____ required.

2. **Temperature Change** - the _____, ie. from 10°C to 30°C, compared to 10°C to 15°C, the greater the amount of heat is required.
3. **Type of Substance** - each substance has a different density and a different ability to absorb heat.

CALCULATING QUANTITIES OF HEAT

It is difficult to measure the quantity of heat transferred during a temperature change. Instead, we can calculate the quantity of heat using a simple formula, _____, where ___ is the quantity of heat transferred, ___ is the mass of the substance, ___ is the specific heat capacity (page 234 of text), and _____ , the change in temperature of the substance.

$$Q_{gained} = - Q_{lost}$$

1. Calculate the amount of energy needed to heat 100 g of H_2O from 20°C to 45°C.

2. A 24.6g sample of nickel is heated to 110°C and then placed in a coffee cup calorimeter containing 125g of water at a temperature of 23°C. After the nickel cools the final temperature of the metal and water is 24.83°C. Assuming that no heat has escaped to the surroundings or has been absorbed by the calorimeter, calculate the specific heat of nickel.

Calorimetry

The science of _____ the change in heat of _____ or _____ _____

A _____ is an insulated reaction vessel in which a reaction can occur and where the change in temperature of the system can be measured

How does a Calorimeter work?

Calorimetry measures changes in temperature of a system being studied in order to "track" heat change

The calorimeter _____ the system from its surroundings

The examples we will look at in class will involve _____:

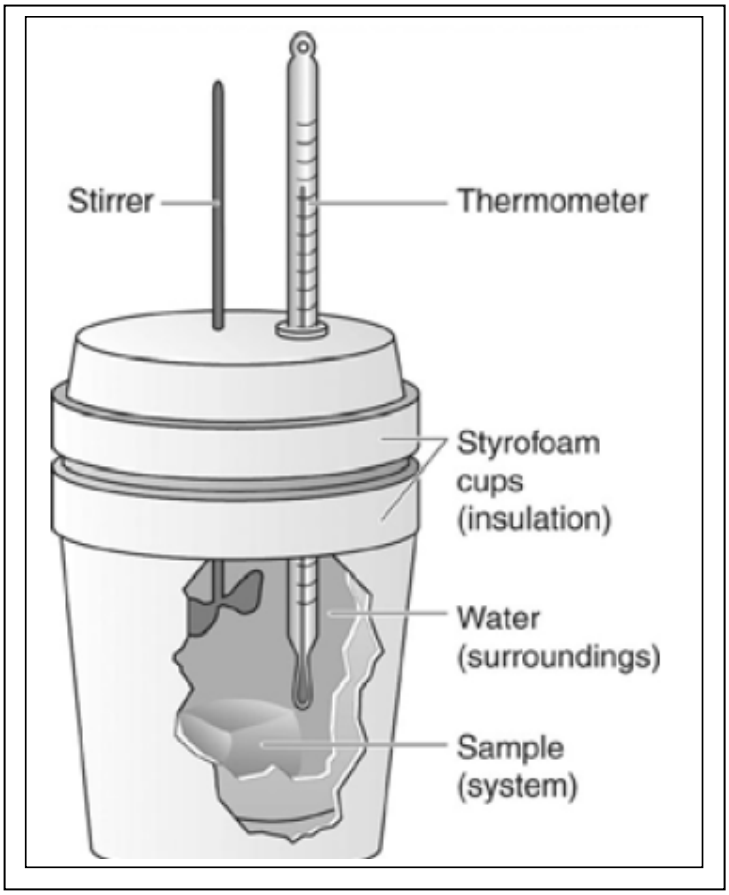
When pressure is kept constant heat measured represents the enthalpy change:

Assumptions:

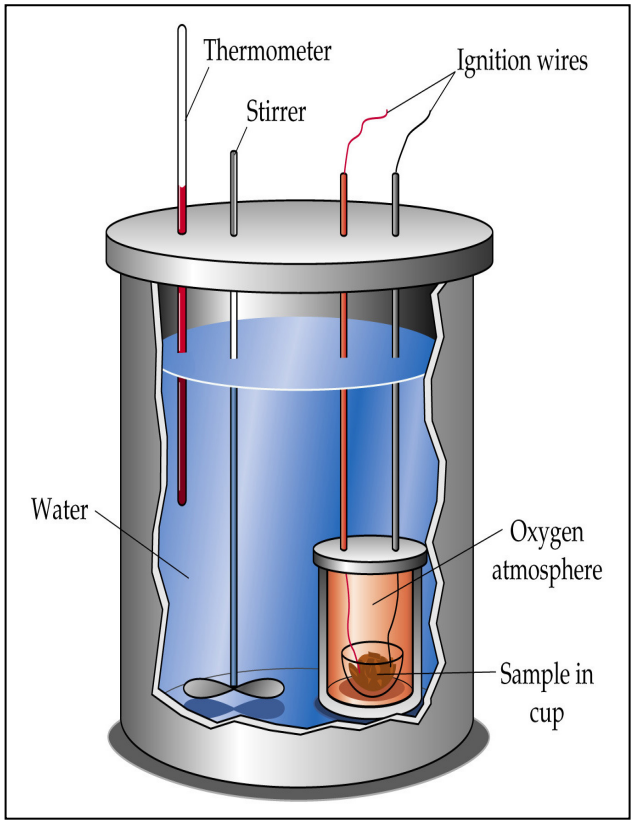
- _____ is transferred between the calorimeter and the outside environment
- Any heat absorbed or released by the calorimeter itself is _____.
- A dilute aqueous solution is assumed to have a density and specific heat capacity equal to that of _____ (i.e. $D_{solution}$ = 1.0 g/ml, $c_{solution}$ = 4.18 J/g°C)

Types of Calorimeters

Coffee-cup Calorimeter



Bomb Calorimeter



Limitations:

- Cannot be used for reactions involving _____
- Cannot be used for ____ temperature reactions

Points:

- Reaction takes places in a sealed metal container
- Temperature difference of the _____ is measured
- Calculations are more complex because they must take into account heat flow through the **metal** container

Determining the Enthalpy of a Chemical Reaction

EXOTHERMIC: $Q_{reaction} = -Q_{solution}$

ENDOTHERMIC: $-Q_{reaction} = Q_{solution}$

1. 50.0 ml of 0.300 M $CuSO_{4(aq)}$ solution is mixed with an equal volume of 0.600 M $NaOH_{(aq)}$ solution. The initial temperature of both solutions is 21.4°C. After mixing the solutions in the coffee-cup calorimeter, the highest temperature that is reached is 24.6°C. Determine the enthalpy change, ΔH, of the reaction and then write the thermochemical equation.

Hess's Law of Heat Summation

Recall: Calorimetry is an accurate technique for determining enthalpy changes of a system.

- How do chemists deal with chemical systems that _____ be analyzed using this technique:

• **Slow reactions**

• **Small changes in enthalpy**

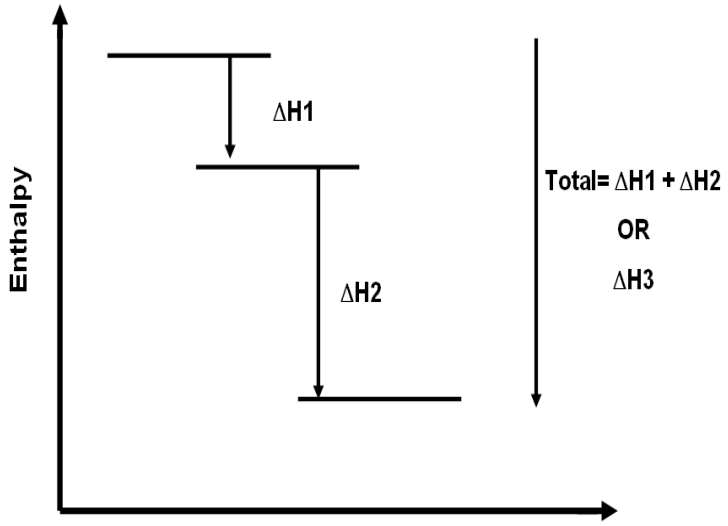
- The net changes in some properties of a system are independent of the way the system changes from the initial state to the final state.

What does this have to do with _____ changes**???**

• If a set of reactions occurs in different steps but the initial reactants and final products are the same, the overall enthalpy change is the same.

Hess's Law of Summation

For any reaction that can be written in a _____, the standard heat of reaction is the same as the sum of the _____ of reaction for the steps



Combining and Manipulating Chemical Equations: A 7-Step process

1. Ensure ALL chemical equations are correctly balanced
2. Examine the given equations to see how they compare with the _____
3. "_____" equations to obtain reactants and products on the correct sides

-ANY time you Flip (or reverse) an equation you _____ multiple the associated enthalpy change by [-1]

4. _____ coefficients in an equation by an integer or fraction if required

- _____ the enthalpy value for this equation by the same factor

5. Write the manipulated equations so that their _____ line up
6. Add reactants and products on each side, _____ that appear on _____ _____
7. _____ the enthalpy changes for the combined reactions

** ALL equations need to add together to arrive at the TARGET equation**

Example 1

What is the enthalpy change for the formation of two moles of nitrogen monoxide from its elements? $N_2(g) + O_2(g) \rightarrow 2NO_{(g)}$!H° _ ?

(1) $1/2\ N_{2(g)} + O_{2(g)} \rightarrow NO_{2(g)}$ $\Delta H°$ +34 kJ
(2) $NO_{(g)} + 1/2\ O_{2(g)} \rightarrow NO_{2(g)}$ $\Delta H°$-56 kJ

Example 2

What is the enthalpy change for the formation of one mole of butane (C_4H_{10}) gas from its elements? The reaction is: $4\ C_{(s)} + 5\ H_{2(g)} \rightarrow C_4H_{10(g)}$ $\Delta H°$ = _ ?

The following known equations, determined by calorimetry, are provided:
(1) $C_4H_{10(g)} + 13/2\ O_{2(g)} \rightarrow 4\ CO_{2(g)} + 5\ H_2O_{(g)}$ $\Delta H°$- 2657.4 kJ
(2) $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$ $\Delta H°$ - 393.5 kJ
(3) $2\ H_{2\ (g)} + O_{2(g)} \rightarrow 2\ H_2O_{(g)}$ $\Delta H°$- 483.6 kJ

STANDARD ENTHALPIES OF FORMATION

- Reactions in which compounds are formed from their elements (in their standard states) are called _____.

  E.g. $C_{(s)} + O2(g) \rightarrow CO2(g)$ $\Delta H°f = -393.5kj/mol$
- $\Delta H°f$ = standard enthalpy of formation ** Table of values on p. 250, p. 597 **
- Always written for one mole of product.
- The product may be in any state but the reactant elements must be in their standard states.
- The standard enthalpy of formation of an element in its standard state is _____.

  $H_{2(g)} \rightarrow H_{2(g)}$ $\Delta H°_f = 0$

$$\Delta H = \Sigma\, n\Delta H°f(\text{products}) - \Sigma\, n\Delta H°f(\text{reactants})$$

EXAMPLE:

1. Iron(III)oxide reacts with carbon monoxide to produce elemental iron and carbon dioxide. Determine the enthalpy change of this reaction,

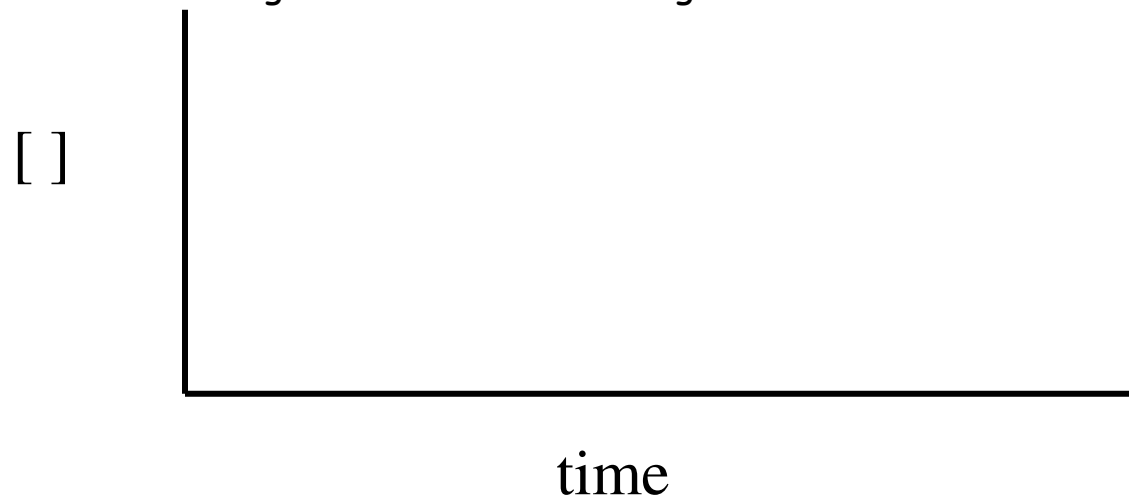
   ___$Fe_2O_{3(s)}$ + ___$CO_{(g)}$ → ___$CO_{2(g)}$ + ___$Fe_{(s)}$

RATES OF REACTIONS

The change in _____ of a reactant or product per unit _____. For example:

$A + B \rightarrow AB$

Rate = $\frac{\text{decrease in [A]}}{\text{change in time}}$ or $\frac{\text{increase in [AB]}}{\text{change in time}}$



Rates are usually determined at the _____ of the reaction due to the _____amount of reactant present (max. collisions). The average or instantaneous reaction rate can be determined from a graph using the slope formula. e.g.

i) Average rate = use first and last points
ii) Instantaneous rate = slope of tangent

Determining Average and Instantaneous Rates of Reactions Graphically

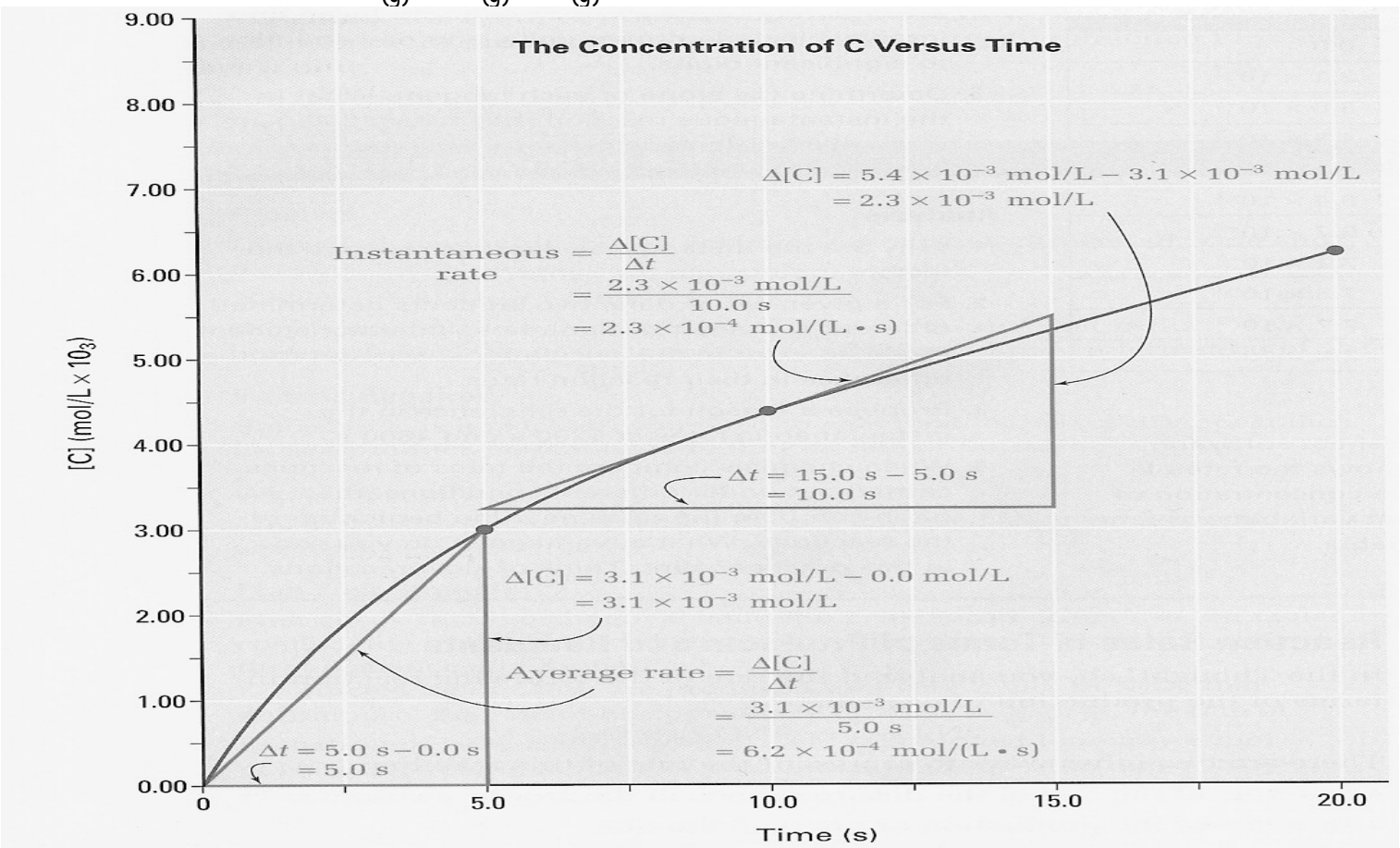
Instantaneous Rate of Reaction

- the rate of reaction at a particular time
- found using slope of _____ (the best straight-line approximation to the curve at a particular point. Only touches curve at one point)

Average Rate of Reaction

- the mean change in concentration of reactants or products per unit of time
- found by determining slope of _____ (a line that intersects two or more points on the curve)

For the reaction: $A_{(g)} \rightarrow C_{(g)} + D_{(g)}$



- For each line, a _____ slope means a _____ rate of reaction
- As the reaction proceeds the reactants are used up and the slope of the tangent decreases, therefore rate of reaction decreases.

Reaction Rates in Terms of Reactants and Products

There are two ways to represent the rate of a reaction:

1. Rate of disappearance of reactant
2. Rate of appearance of product

For example;

___ $N_2O_{5\,(g)}$ → ___ $NO_{2\,(g)}$ + ___$O_{2\,(g)}$ (balance first)

For every ____mol of O_2 produced ____mol of NO_2 is produced.

For every ____mol of O_2 produced ____mol of N_2O_5 are consumed.

EXAMPLE 2.
Consider the reaction:

$1\ IO_3^-{}_{(aq)} + 5\ I^-{}_{(aq)} + 6\ H^+{}_{(aq)} \rightarrow 3I_{2(aq)} + 3H_2O_{(l)}$

What are the rates of reaction with respect to the various reactants and products?
The rate of reaction with respect to iodate ions (rate of consumption of IO_3^-) is determined experimentally to be 3.0×10^{-5} mol/(L•s).

Influencing the Rate of Reaction

_____ states that in order for reactions to occur molecules must collide.

- These collisions must be "effective" collisions, that is:

1. _____ of molecules must be correct
2. There must be sufficient _____

Factors that Effect the Rate of Reaction

a. Temperature

- When two chemicals react, their molecules have to collide with each other with sufficient energy for the reaction to take place. By heating the mixture, you will raise the _____ energy of the molecules involved in the reaction.

b. Concentration of Reactants

- Increasing the concentration of the reactants will increase the _____ of collisions between the two reactants.

c. Catalysts

- A catalyst is a substance that lowers the amount of _____, (EA), necessary to initiate a chemical reaction, but is not consumed in the reaction.

d. Surface Area of a solid reactant

- If a solid particle is broken up, the surface area of the molecule is increased. Increased surface area means an increased number of possible _____ for reaction to occur.

e. Pressure of gaseous reactants & products

- By increasing the pressure, molecules are forced **closer** together which will increase the frequency of collisions between them.

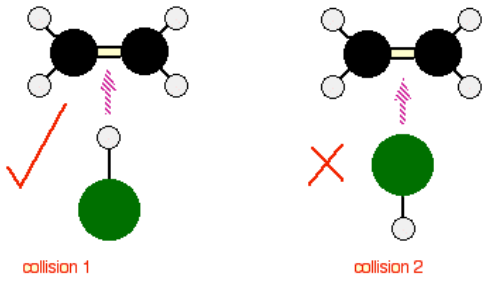
Activation Energy

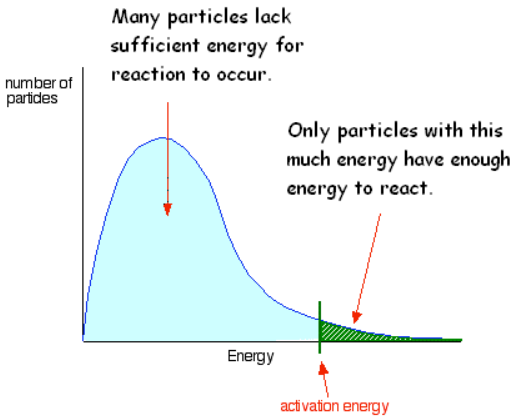
Recall - For a reaction to occur:

a. particles must collide in a specific orientation

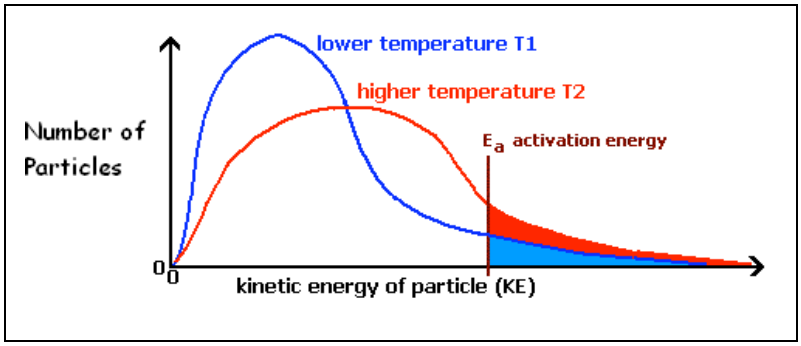
b. particles must collide with sufficient kinetic energy

- _____ is the minimum collision energy required for a successful reaction to occur.
- Diagrams called _____ _____ are plots of kinetic energy vs. number of particles.





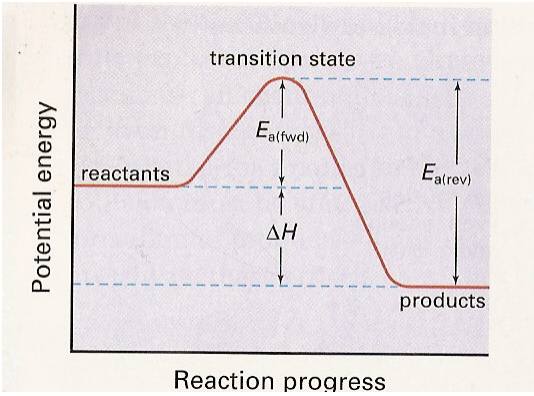
- As temperature increases the kinetic energy of molecules increases. Therefore more particles will have sufficient energy required to react.



Potential Energy Diagrams

- When molecules collide, kinetic energy of the particles is converted to _____ energy. Potential energy diagrams are used to illustrate the change in potential energy during a reaction.

Exothermic reaction



Endothermic Reaction

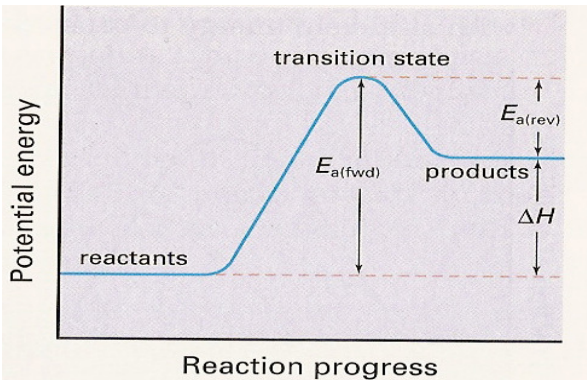
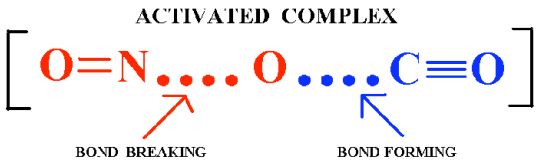


Diagram Terminology

- **Ea** – activation energy
- For an exothermic reaction: $Ea_{(rev)} = Ea_{(fwd)} + \Delta H$
- For an endothermic reaction: $Ea_{(rev)} = Ea_{(fwd)} - \Delta H$
- _____ – point when reactants are converted to product.
- _____ – chemical species that exist at the transition state. For example:

$$NO_2 + CO \longrightarrow NO + CO_2$$



Questions:

1. It is a general rule that with a 10°C temperature increase most reaction rates will double. This is not the result of doubling the number of collisions. Explain.

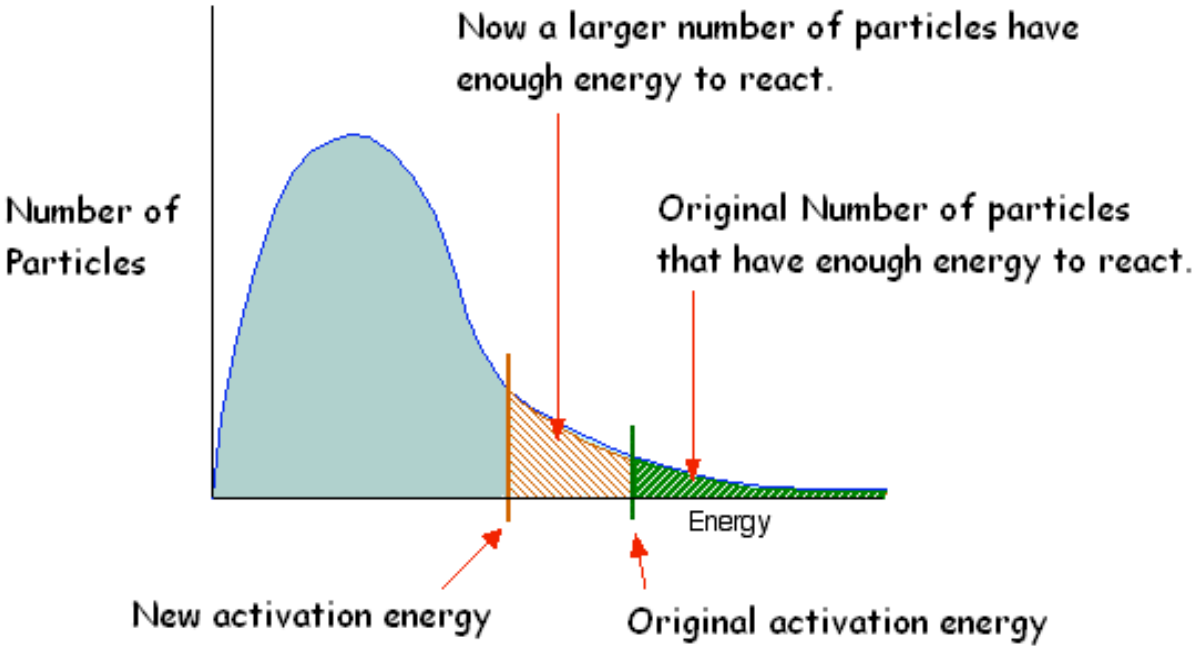
2. Sketch a PE diagram for the following reactions. Include labels for Ea, ΔH, & transition state.

a. $S_{(s)} + O_{2(g)} \rightarrow SO_{2(g)}$ $\Delta H = -296.06$ kJ

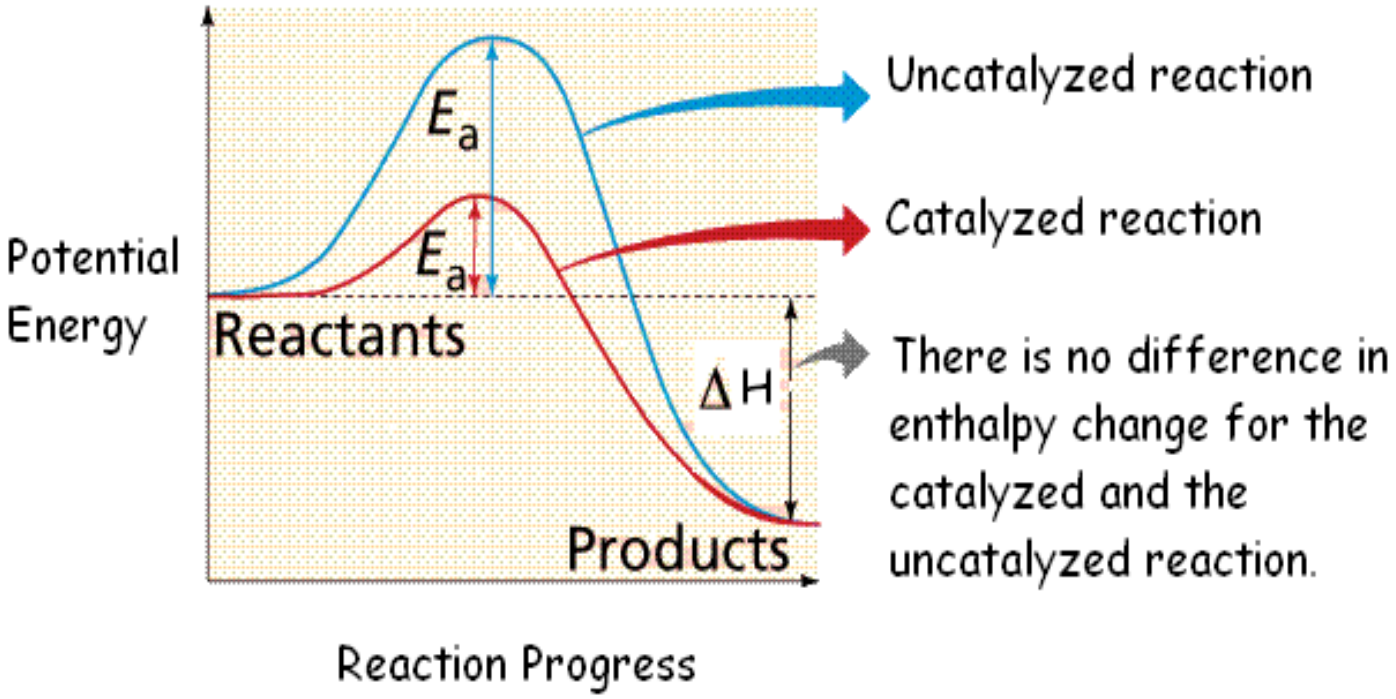
Catalysts

Recall: A catalyst is a substance that _____ the rate of a chemical reaction without being _____ in the reaction.

- A catalyst works by _____ the activation energy of a reaction so that a _____ number of reactants have _____ energy to react.



Potential Energy Diagram



Homogeneous catalysts

- exist in the same phase as the reactants.
- most often catalyze gaseous & aqueous rxns

$$CH_3CO_2CH_{3\,(aq)} + H_2O_{(l)} \xrightarrow{H^+_{(aq)}} CH_3CO_2H_{(aq)} + CH_3OH_{(aq)}$$

Heterogeneous catalysts

- exists in a different phase than reactants.
- without a catalyst this type is very slow

$$3H_{2\,(g)} + N_{2\,(g)} \xrightarrow{Fe_{(S)}} 2NH_{3\,(g)}$$

Enzymes

- Enzymes are organic catalyst used in biological reactions. In an enzymatic reaction the reactant molecule(s) are called the _____ and the _____ is the portion of the enzyme where the substrate binds to the enzyme.

Reaction Mechanisms

- Most reactions occur in a _____ of steps.
- These series of steps are together are called a _____.
- Each individual step is called an _____.
- Molecules that form in one step and are consumed in the next are called _____ _____.

For example this reaction occurs in two steps:

Overall rxn: $2\ NO_{2(g)} + Cl_{2(g)} \rightarrow 2\ NO_2Cl_{(g)}$

Step 1: $NO_{2(g)} + Cl_{2(g)} \rightarrow NO_2Cl_{(g)} + Cl_{(g)}$ (slow)

Step 2: $NO_{2(g)} + Cl_{(g)} \rightarrow NO_2Cl_{(g)}$ (fast)

Each elementary step is classified according to number of reactants.

- **Unimolecular** – elementary reaction with one particle
- **Bimolecular** – elementary reaction with two particles
- **Termolecular** – elementary reaction with three particles (rare)

In an _____ _____, the exponents in the rate law equation are the same as the stoichiometric coefficients.

Elementary Reaction	Rate Law
A → products	Rate = k[A]
A + B → products	Rate = k [A][B]
2A → products	Rate = $k[A]^2$
2A + B → products	Rate = $k\ [A]^2[B]$

Elementary Reaction Rate Law

A reaction mechanism must:

1. contain equations that _____ to give _____ equation
2. contain _____ elementary steps
3. support the experimentally determined _____

- Each elementary reaction has its _____ rate.
- The _____ elementary reaction is called the _____.
- It is assumed that this "slow" step by itself _____ the rate of reaction.
- As a result the rate law for the rate-determining step is the rate law for the overall reaction.
- From the above example the first step is the _____. Therefore the rate law for the first step is the rate law for the overall reaction.

$$\text{Rate} = k[NO_2]^1\ [Cl_2]^1$$