

Chemical Reactivities: Fundamental and Nuclear Reactions, Energetics and Kinetics

Objectives for Chemical Reactivities: Fundamental and Nuclear Reactions, Energetics and Kinetics

Properly prepared students, in random order, **will**

- 1) Be able to describe, explain and demonstrate the difference between a chemical change and a physical change;
- 2) Be able to describe, explain, demonstrate, give examples of and identify the 6 different types of chemical reactions;
- 3) Be able to explain how to balance and demonstrate balancing simple chemical reactions;
- 4) Be able to define what a mole of any substance is;
- 5) Be able to use “mole terminology” in calculating/solving chemical problems that require mole, molecular weight and product calculations;
- 6) Be able to use Avogadro’s number in chemical problem solving;
- 7) Be able to determine moles, grams and atoms in chemical problems;
- 8) Be able to determine, in a calculating manner, the empirical and molecular formulas of compounds;
- 9) Be able to use information on a simple mass spectrum to determine the molecular formula of a simple compound;
- 10) Be able to calculate theoretical reaction yields;
- 11) Be able to determine limiting reagents in chemical reactions;
- 12) Be able to calculate the per cent composition of elements in a chemical compound;
- 13) Be able to explain the difference between kinetic and potential energy;
- 14) Be able to explain and illustrate what gravitational potential energy is;
- 15) Be able to explain the Law of Conservation of Energy;
- 16) Be able to explain, using examples and diagrams, the First Law of Thermodynamics;
- 17) Be able to explain, using examples and diagrams, the Second Law of Thermodynamics;

- 18) Be able to explain, using examples and diagrams, the Third Law of Thermodynamics;
- 19) Be able to calculate/determine the solutions for thermodynamic systems of a single system;
- 20) Be able to calculate/determine the solutions for thermodynamic systems of a dual system/nature;
- 21) Be able to explain and calculate how heat leaves humans;
- 22) Be able to explain and differentiate between enthalpy, entropy, free energy, energy of activation;
- 23) Be able to explain and diagram Fick's Law and its application to respiration;
- 24) Be able to explain the difference between, and the significance of, positive and negative Gibbs' free energy differences (ΔG);
- 25) Be able to explain (and state 4 causes of) pulmonary edema and the effect it has on respiration;
- 26) Be able to demonstrate graphically the difference between spontaneous and non-spontaneous reactions using free energy changes;
- 27) Be able to explain what exergonic and endergonic reactions are and diagram what their energy curves look like;
- 28) Be able to define, explain and apply the terms reaction rate, probability factor, collision factor and energy factor;
- 29) Be able to explain and diagram what the energy of activation is;
- 30) Be able to explain and illustrate the effect of temperature on reaction rate;
- 31) Be able to explain and mathematically calculate the dependence of the fraction of particles with energy at or above the energy of activation on the absolute temperature and the gas constant;
- 32) Be able to describe, explain and give an example of a chain initiation reaction;
- 33) Be able to describe, explain and give examples of chain propagation reactions;
- 34) Be able to describe, explain and give examples of chain termination reactions;
- 35) Be able to explain and illustrate examples of transition stages;
- 36) Be able to explain what reaction intermediates are;
- 37) Be able to explain the speed of a reaction based on its energy of activation;
- 38) Be able to explain the bonding of intermediates based on their energy of activation;
- 39) Be able to explain the molecular geometry of a carbon-based reactant as one of its hydrogen atoms is abstracted/extracted;

- 40) Be able to explain what a rate limiting reaction is;
- 41) Be able to identify and explain what the energy of activation and enthalpy of the reaction are on an energy curve;
- 42) Be able to identify and illustrate primary, secondary and tertiary carbon and hydrogen atoms in organic molecules;
- 43) Be able to explain in an elementary manner what the effect of temperature is on hydrogen atom extraction;
- 44) Be able to calculate the percentage of primary, secondary and/or tertiary mono-halogenated organic compounds produced during a halogenation reaction;
- 45) Be able to define and differentiate fusion and fission;
- 46) Be able to define, explain and differentiate between subcritical, critical and super-critical mass;
- 47) Be able to describe the design of a nuclear fission reactor;
- 48) Be able to explain how tritium is generated using a lithium blanket;
- 49) Be able to explain how the control and fuel rods work in a fission nuclear reactor to control the core;
- 50) Be able to explain the value of heavy water in a nuclear reactor;
- 51) Be able to compare and contrast in writing between regular chemical reactions and nuclear chemical reactions;
- 52) Be able to explain and provide examples of isotopes, isobars, isotones and isomers;
- 53) Be able to explain what ionizing radiation is and how its intensity varies by the inverse square law using the proper formulas;
- 54) Be able to explain what a radionuclide is and how to use the band of stability in the process;
- 55) Be able to define what a plasma is and how plasmas are confined;
- 56) Be able to solve nuclear reactions for α , β , K capture, neutron emission, positron emission;
- 57) Be able to explain, illustrate and differentiate between the photoelectric effect, Compton scattering and pair production;
- 58) Be able to explain the difference between the source of X and γ radiation;
- 59) Be able to explain how an x-ray anode works and why heat is given off the anode during x-ray generation;

60) Be able to maneuver between Planck's and Einstein's equations to solve problems about EME;

61) Be able to explain why Lucite shielding is used for protection with β -emitters instead of lead shielding;

62) Be able to explain what RBE means and how it applies to the various nuclear emissions;

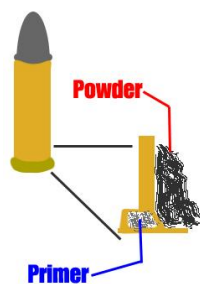
63) Be able to solve the decay equation for radio-dating problems;

64) Be able to solve for the half life using the decay equation;

65) Be able to provide one protective mechanism against α radiation;

and demonstrate that comprehension and applications thereof per assessment tool at no less than a score of 75%.

Chemical Reactions

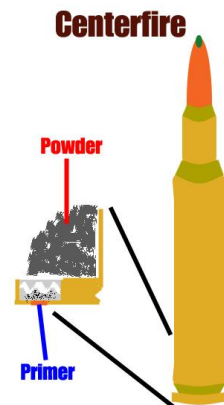


Rimfire

Just mixing chemicals together is a physical change. Adding energy that drives a reaction is a chemical change, e.g., Firing pin, Match, Spark, Heat or Force.

Now that we've gone through some elementary bonding concepts, it's time to get down to some nitty-gritty with reactions. Chemical reactions may be subdivided into two main categories: non-redox and redox.

Each of these two categories may be further sub-divided into three more categories, apiece. The categories of reactions are illustrated, below:



Centerfire

Chemical Reactions					
Non-Redox			Redox		
Combination	Double Replacement (Metathesis)	Decomposition	Combination	Single Replacement (Substitution)	Decomposition

Since both main categories of reactions contain specifically combination and decomposition reactions, we'll examine each of those headings by comparing the redox version against the non-redox version, first.

Decomposition Reactions	
In this kind of reaction, a single substance is broken down to form 2 or more simpler substances	
$X \rightarrow Y + Z$	
Redox Examples	Non-Redox Examples
$2\text{MgO} \rightarrow 2\text{Mg} + \text{O}_2$ $2\text{Ag}_2\text{O} \rightarrow 4\text{Ag} + \text{O}_2$ $\text{ZrI}_4 \rightarrow \text{Zr} + 2\text{I}_2$ $\text{KClO}_3 \rightarrow \text{KCl} + \text{O}_2$	$\text{MgCO}_3 \rightarrow \text{MgO} + \text{CO}_2$ $\text{H}_2\text{CO}_3 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$ $\text{PbCO}_3 \rightarrow \text{PbO} + \text{CO}_2$

The fastest way to identify whether a reaction is a redox or non-redox type is to look at the reaction and see if there is a change in charge or not. If an element is used or formed, it's probably a redox. If there's no charge change, it's probably a non-redox.

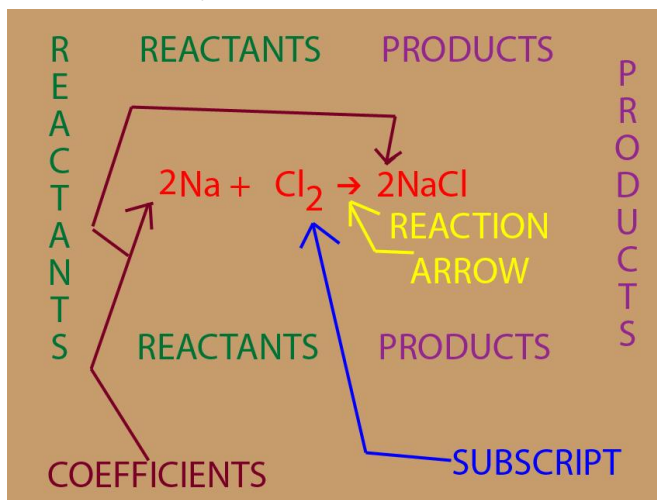
Combination Reactions	
These reactions are also known as (aka) addition or synthesis reactions. In this type of reaction, 2 or more substances react to form a single substance	
$D + E \rightarrow F$	
Redox Examples	Non-redox Examples
$2\text{Ca} + \text{O}_2 \rightarrow 2\text{CaO}$ $\text{H}_2 + \text{Cl}_2 \rightarrow 2\text{HCl}$ $4\text{Al} + 3\text{O}_2 \rightarrow 2\text{Al}_2\text{O}_3$ $\text{Zr} + 2\text{I}_2 \rightarrow \text{ZrI}_4$ $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$	$\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$ $\text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_3$

The fastest way to identify whether a reaction is a redox or non-redox type is to look at the reaction and see if there is a change in charge or not. If an element is used or formed, it's probably a redox. If there's no charge change, it's probably a non-redox.

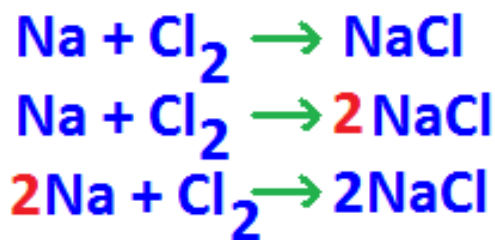
Replacement Reactions	
Single Replacement	Double Replacement
Always redox; 1 element reacts with a compound and displaces another element from the compound.	aka Metathesis or neutralization reaction; not redox; "partner swapping"; tends to occur in aqueous solution.
$A + \text{CX} \rightarrow \text{C} + \text{AX}$	$\text{CX} + \text{DY} \rightarrow \text{CY} + \text{DX}$
Iron stripped from ore with C: $3\text{C} + 2\text{Fe}_2\text{O}_3 \rightarrow 4\text{Fe} + 3\text{CO}_2$	$\text{KOH} + \text{HNO}_3 \rightarrow \text{KNO}_3 + \text{H}_2\text{O}$

Now that we've got the 6 fundamental types of reactions down, let's take a look at chemical reaction nomenclature, Figure, Below.

Those chemicals that are on the left of the arrow are the reactants and those on the right are the products. Reactants under go change during the reaction and products are substances that are formed as a result of the reaction. A coefficient goes in front of the whole chemical formula and applies to the whole chemical formula just like an algebraic equation. A subscript goes beneath and behind the only element to which it applies. In the example, overall, there are 2 chlorine atoms on the reactant side and two on the product side of the reaction.



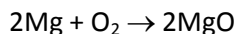
The whole reaction in the graphic is balanced, i.e., there are the same numbers of sodium atoms on both sides of the reaction and there are the same numbers of chlorine atoms on both sides of the reaction. The balanced reaction is consistent with the Law of Conservation of Matter: atoms are neither created nor destroyed in chemical reactions, only rearranged.



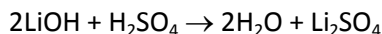
So with this succinct introduction, let's begin balancing some simple chemical reactions. Probably the very best thing to remember about these is that if you make like atoms in compounds are ions and know their charges -- or can derive them quickly -- you can balance most in a short time with a little practice.

Our first example is $\text{Mg} + \text{O}_2 \rightarrow \text{MgO}$.

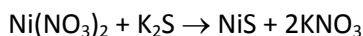
On the left side of the reaction, both elements have an individual charge of zero. On the right side, the Mg has an effective charge of +2 (it's in group II) and oxygen an effective charge of -2 (it's in group VI). The charges balance out. The drawback is that there are 2 oxygens on the left and one on the right. We'll put a 2 in front of the MgO which also gives us 2 magnesiums on the right. Put a 2 in front of the Mg on the left and the equation is balanced:



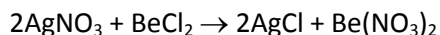
The second example is $\text{LiOH} + \text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{O} + \text{LiSO}_4$. In this example, the Li has an effective charge of +1. The hydroxide ion (OH-) has a charge of -1. Sulfuric acid is balanced as sulfate is -2 and there are 2 hydrogens to balance that. Water is balanced, charge-wise. Since we already knew that Li has a charge of +1 and sulfate of -2, we know that there has to be 2 lithiums to make lithium sulfate -- we'll add that 2 as a subscript behind the Li to make Li_2SO_4 . Since there are 2 lithiums on the right, we'll put a 2 in front of the LiOH to make 2LiOH . There are 6 oxygens on the left. To make 6 on the right, we'll put a 2 in front of the water. The final balanced equation is:



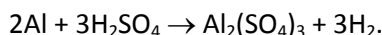
The third example is $\text{Ni}(\text{NO}_3)_2 + \text{K}_2\text{S} \rightarrow \text{NiS} + \text{KNO}_3$. Nitrate has a charge of -1. There are 2 of them to balance out for the +2 charge on the nickel. Two potassiums neutralize the charge from the sulfide (-2). This equation is actually much easier than the previous one. We know there are 2 potassiums and 2 nitrates on the left of the reaction, hence, we'll put a 2 in front of the KNO_3 on the right. The balanced reaction is:



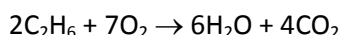
Our fourth example is: $\text{AgNO}_3 + \text{BeCl}_2 \rightarrow \text{AgCl} + \text{BeNO}_3$. Ag has a charge of +1; nitrate, -1. Be is in group II and has a charge of +2; chloride of -1. There are 2 chlorides to balance out the charge with the Be. Let's start by putting a 2 in front of the AgCl to balance out the chlorides on each side of the reaction. When we do that, we have to put a 2 in front of the AgNO_3 . Since we've done that, we've got to put parentheses around the NO_3 in BeNO_3 to make $\text{Be}(\text{NO}_3)_2$. The balanced equation is:



The fifth example is $\text{Al} + \text{H}_2\text{SO}_4 \rightarrow \text{AlSO}_4 + \text{H}_2$. Al on the left has zero charge -- it's an element. Sulfate is -2 and hydrogen is +1 on the left side; on the right, hydrogen has zero charge -- another element. On the right, Al has a +3 charge. Let's focus on the AlSO_4 . Al has a charge of +3; SO_4 has a charge of -2. In order for these two to balance, there has to be some lowest number common to them. In this case, it's 6 ($2 \times 3 = 6$). The balanced form, then is $\text{Al}_2(\text{SO}_4)_3$. This means that a 2 goes in front of the Al on the left and a 3 goes in front of the sulfuric acid; a 3 goes in front of the elemental hydrogen on the right. The balanced reaction is:



The last reaction is $\text{C}_2\text{H}_6 + \text{O}_2 \rightarrow \text{H}_2\text{O} + \text{CO}_2$. In this instance, it's actually easier to forget charges and focus on absolute numbers. There are 2 carbons on the left. We need to put a 2 in front of the carbon dioxide on the right. There are 6 hydrogens on the left. We need to put a 3 in front of the water on the right. There are 7 oxygens on the right, now. To make 7 on the left, we put a $3\frac{1}{2}$ in front of the O_2 . It's actually balanced this way. The issue, though, is that most chemists hate using fractions in balanced reactions. Hence, we'll just double every coefficient and obtain the following as the balanced reaction:



And this is exactly how easy it is as long as you remember to keep track of the charges or the absolute numbers.

The Mole

When you go to the bakery to buy 12 rolls, you are also buying a dozen rolls. When you go to the feed store and buy a ton of corn, you are also buying 2000 pounds of corn. When you buy a lot that measures about 44,000 square feet, you are also buying an acre. All of these are just another way of saying the same thing.

Chemists do the same thing: when speaking about the number of particles contained in a sample of element or compound with its atomic or molecular mass expressed in grams, they are also speaking about a mole of that substance.

For example, if you look at sulfur on the periodic table, you see that it has a mass of 32.1. That means that one mole of sulfur has a mass of 32.1 grams. Since we've discussed the mole, we can now put units on the atomic mass that are better than atomic mass units: grams per mol (g/mol). If we were to look at chlorine on the periodic table, we now know that it has a mass of 35.5 grams per mole. That means that if we have 35.5 grams of chlorine, we have one mole of chlorine -- just another way of saying something in another way.

Let's look at some numerical examples.

Example 1: Determine the mass in grams of 1.35 mol S.

$$(1.35 \text{ mol S}) \frac{(32.1 \text{ g S})}{(1 \text{ mol S})} = 43.34 \text{ g S}$$

Example 2: Determine the mass in grams of 1.5 mol Cu.

$$(1.5 \text{ mol Cu}) \frac{(63.55 \text{ g Cu})}{(1 \text{ mol Cu})} = 95.33 \text{ g Cu}$$

Example 3:

Determine the mass in grams of 0.5 mol Ca.

$$(0.5 \text{ mol Ca}) \frac{(40.1 \text{ g Ca})}{(1 \text{ mol Ca})} = 20.05 \text{ g Ca}$$

Example 4:

Determine the mass in grams of 0.10 mol HCl.

Solution: This one is slightly different: it involves a compound instead of just an element. Go to the periodic table and look up the atomic masses of H and Cl. Add them up (1 + 35.5 = 36.5 g/mol). NOW it's just like the other problems.

$$(0.1 \text{ mol HCl}) \frac{(36.5 \text{ g HCl})}{(1 \text{ mol HCl})} = 3.65 \text{ g HCl}$$

Example 5: Determine the mass in grams of 0.4 mol acetic acid (HC₂H₃O₂).

Solution: Do just like the previous example. Go to the periodic table and look up the atomic masses for H, C and O (1, 12 and 16 g/mol). Multiply the mass of H by 4, C by 2 and O by 2 – there are 4-H, 2-C and 2-O. Add the totals up (4 + 24 + 32 = 60 g/mol). Do it just like the previous problem:

$$(0.4 \text{ mol HC}_2\text{H}_3\text{O}_2) \left(\frac{60 \text{ g Acetic Acid}}{1 \text{ mol Acetic Acid}} \right) = 24 \text{ g Acetic Acid (HC}_2\text{H}_3\text{O}_2 \text{ or HOAc)}$$

Example 6: 15 g HCl is how many mol HCl?

Solution: This is just a variation on a theme we've already done:

$$(15 \text{ g HCl}) \left(\frac{1 \text{ mol HCl}}{36.5 \text{ g HCl}} \right) = 0.411 \text{ mol HCl}$$

Example 7: 30 g H₂SO₄ is how many mol H₂SO₄?

Solution: Go to the periodic table and find the atomic masses for H (1), S (32.1) and O (16). The molecular weight of sulfuric acid is 98 g/mol.

$$(30 \text{ g H}_2\text{SO}_4) \left(\frac{1 \text{ mol H}_2\text{SO}_4}{98 \text{ g H}_2\text{SO}_4} \right) = 0.306 \text{ mol H}_2\text{SO}_4$$

Example 8: You have been given 49 g H_2SO_4 . You were told that this was 0.5 mol. What is the molecular weight of sulfuric acid?

Solution: This is easier than it looks. As long as you remember that the units on molecular weight are g/mol, you'll always be able to do this sort of problem:

$$\text{Molecular Weight} = \frac{\text{grams}}{\text{mol}} = \frac{49 \text{ g } H_2SO_4}{0.5 \text{ mol } H_2SO_4} = 98 \frac{\text{g}}{\text{mol}}$$

Avagadro's Number

One mole is not only equal to the gram-formula weight of a compound, but it is also equal to Avagadro's number (N_{Av}). This number is a constant and has many different units. For now, this number is 6.023×10^{23} atoms/mol.

Examples and Applications

Example 1: 1×10^{23} atoms of NaOH is how many g NaOH?

Solution: Look up the atomic mass of Na (23), O (16) and H (1). Add 'em up (40 g/mol) for the molecular weight of NaOH:

$$(1 \times 10^{23} \text{ atoms NaOH}) \left(\frac{1 \text{ mol NaOH}}{6.023 \times 10^{23} \text{ atoms}} \right) \left(\frac{40 \text{ g NaOH}}{1 \text{ mol NaOH}} \right) = 6.64 \text{ g NaOH}$$

Example 2: 4×10^{23} atoms of $NaC_2H_3O_2$ is how many g $NaC_2H_3O_2$?

Solution: Look up the atomic mass of Na (23), C (12), H (1) and O (16) on the periodic table. Add 'em up (82 g/mol) for the molecular weight of sodium acetate.

$$4 \times 10^{23} \text{ atoms } NaC_2H_3O_2 \left(\frac{1 \text{ mol } NaC_2H_3O_2}{6.023 \times 10^{23} \text{ atoms } NaOAc} \right) \left(\frac{82 \text{ g NaOAc}}{1 \text{ mol NaOAc}} \right) = 54.46 \text{ g NaOAc}$$

Example 3: 18.25 g of HCl is how many atoms of HCl?

Solution: Just run it backwards:

$$(18.25 \text{ g HCl}) \left(\frac{1 \text{ mol HCl}}{36.5 \text{ g HCl}} \right) \left(\frac{6.023 \times 10^{23} \text{ atoms HCl}}{1 \text{ mol HCl}} \right) = 3.012 \times 10^{23} \text{ atoms HCl}$$

Example 4: 49 g H₂SO₄ is how many atoms of H₂SO₄?

$$(49 \text{ g H}_2\text{SO}_4) \left(\frac{1 \text{ mol H}_2\text{SO}_4}{98 \text{ g H}_2\text{SO}_4} \right) \left(\frac{6.023 \times 10^{23} \text{ atoms H}_2\text{SO}_4}{1 \text{ mol H}_2\text{SO}_4} \right) = 3.012 \times 10^{23} \text{ atoms H}_2\text{SO}_4$$

That subject has been pretty well beaten to death.

Let's move onto another type of calculation: percent composition. For any compound, XY, the per cent composition of X or Y in XY is as follows:

$$\%X = \frac{X}{X+Y} \times 100 = \frac{\text{molecular weight of } X}{\text{molecular weight of } X + \text{molecular weight of } Y} \times 100$$

The per cent composition of Y in XY is as follows:

$$\%Y = \frac{Y}{X+Y} \times 100 = \frac{\text{molecular weight of } Y}{\text{molecular weight of } X + \text{molecular weight of } Y} \times 100$$

Example 1:

Calculate the per cent composition of N in (NH₄)₂CO₃.

Solution: Go to the periodic table and look up the masses of N (14), H (1), C (12) and O (16). Add 'em up (96 g/mol):

$$\% N = \frac{28 \text{ grams of nitrogen}}{96 \text{ grams } (\text{NH}_4)_2\text{CO}_3} \times 100 = 29.17\% \text{ nitrogen}$$

Example 2:

Calculate the per cent composition of carbon in CaC₂O₄.

Solution: as before. Ca's atomic mass is 40.1 g/mol.

$$\% C = \frac{24 \text{ grams C}}{128.1 \text{ g CaC}_2\text{O}_4} \times 100 = 18.74\% C$$

Example 3:

Calculate the % S in Fe_2S_3 .

Solution: Same as before.

$$\% S = \frac{96 \text{ g } S}{207.7 \text{ g } Fe_2S_3} \times 100 = 46.22\% S$$

Review example:

How many atoms of S are in the previous example? Solution:

$$(96 \text{ g } S) \frac{1 \text{ mol } S}{32 \text{ g } S} \frac{6.023 \times 10^{23} \text{ atoms } S}{1 \text{ mol } S} = 1.807 \times 10^{24} \text{ Atoms}$$

Empirical Formulas

The empirical formula of a compound is defined as the "simplest whole number ratio of the atoms" in a compound. The best way to learn how to determine the empirical formula of a compound is to see the mechanics involved with the arithmetic manipulation of data:

E.g. 1: A compound contains 92.3% carbon and 7.7% hydrogen. Calculate the empirical formula of the compound.

To solve this problem, there are four steps:

1) "Convert" % to grams.

$$92.3 \text{ g} + 7.7 \text{ g} = 100 \text{ g sample}$$

2) Determine the number of moles of each atom in the sample.

$$92.3 \text{ g } C * \frac{1 \text{ mol}}{12 \text{ g } C} = 7.69 \text{ mol} \approx 7.7 \text{ mol}$$

$$7.7 \text{ g } H * \frac{1 \text{ mol}}{1 \text{ g } H} = 7.7 \text{ mol}$$

3) Divide both numbers of moles by the smallest number of moles (this step reduces the numbers to usable amounts).

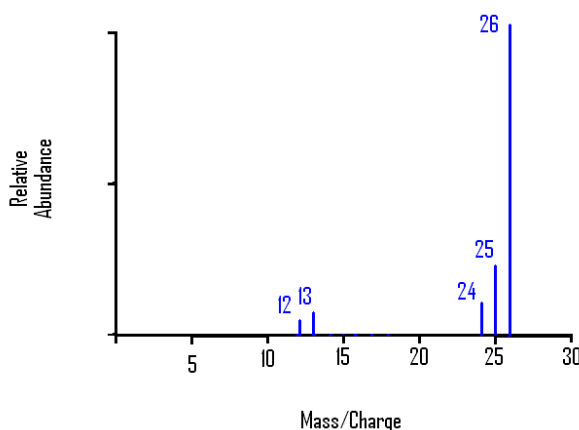
$$\text{For C: } \frac{7.7}{7.7} = 1$$

4) Write the empirical formula. C_1H_1 or CH. What, though, would you do if you were told that the compound had a molecular weight of 26 and you needed to calculate the molecular formula? The simplest is to divide the molecular weight (26) by the empirical weight (13) and see that it is 2 (or twice as heavy as the empirical formula). Double the formula and you get: C_2H_2 or acetylene (ethyne). We take advantage of this knowledge when we perform mass spectroscopy.

$$\text{For H: } \frac{7.7}{7.7} = 1$$

Acetylene (Ethyne) Mass Spectrum

Sample contains C and H. There is another way to determine the compound. That's to look at the smaller fragments and work forward. The smallest peak is 12 m/z; The next smallest peak is 13 m/z; 12 is pretty clear to be C; 13 is equally as clear because there is only one element with a mass of 1: H, therefore, 13 must be for CH; the 25 peak is C_2H and the 24 peak is C_2 . The peak with the highest MW is 26. $26/13 = 2$, hence, the compound must be C_2H_2 , or ethyne.

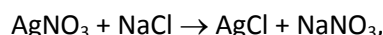


Chemical Reactions and the Mole

An earlier lecture dealt with the mole at the end of that section. This discussion combines what you have already learned about the mole with what you've just learned about chemical reactions.

Example 1:

For the balanced chemical reaction



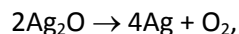
determine the following: if 1 mole of $AgNO_3$ reacts with 1 mole of $NaCl$, how many moles of $AgCl$ will be formed?

Solution: ALWAYS start by looking at the equation and making sure that it's balanced. It's the chemical version of a recipe and is very important in these types of questions. Secondly, always start with what you KNOW.

$$(1 \text{ mol } AgNO_3) \left(\frac{1 \text{ mol } AgCl}{1 \text{ mol } AgNO_3} \right) = 1 \text{ mol } AgCl \text{ formed}$$

Note that we started with the 1 mol of AgNO_3 that we knew about and then using factor labeling, built in the stoichiometry (atomic book keeping) from the balanced equation and solved the problem.

Example 2: For the following balanced chemical reaction



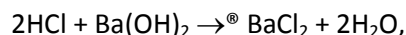
determine the following: if 1.5 mol Ag_2O are heated to decomposition, how many mol Ag are formed?

Solution: Just as we did, above:

$$(1.5 \text{ mol } \text{Ag}_2\text{O}) \left(\frac{4 \text{ mol Ag}}{2 \text{ mol } \text{Ag}_2\text{O}} \right) = 3 \text{ mol Ag formed}$$

Example 3:

For the following balanced chemical reaction



determine the following: if you have 36.5 g HCl, how many mol BaCl_2 will be produced?

Solution: This is just a variation on an earlier theme:

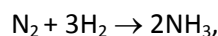
$$(36.5 \text{ g HCl}) \left(\frac{1 \text{ mol HCl}}{36.5 \text{ g HCl}} \right) \left(\frac{1 \text{ mol BaCl}_2}{2 \text{ mol HCl}} \right) = 0.5 \text{ mol BaCl}_2$$

Follow-up: How many grams is this?

$$(0.5 \text{ mol BaCl}_2) \left(\frac{208.3 \text{ g BaCl}_2}{1 \text{ mol BaCl}_2} \right) = 104.2 \text{ g BaCl}_2$$

Example 4:

For the following balanced chemical reaction



determine the following: If you have 14 g nitrogen, how many grams of NH_3 will be formed?

Solution: As before:

$$(14 \text{ g } N) \left(\frac{1 \text{ mol } N}{14 \text{ g } N} \right) \left(\frac{1 \text{ mol } N_2}{2 \text{ mol } N} \right) \left(\frac{2 \text{ mol } NH_3}{1 \text{ mol } N_2} \right) \left(\frac{17 \text{ g } NH_3}{1 \text{ mol } NH_3} \right) = 17 \text{ g } NH_3$$

Note that it was necessary to convert from atomic nitrogen to molecular nitrogen.

Chemical Reactions and Molarity

By definition, molarity (M) is the number of moles of solute (the substance[s] in lesser amounts) per liter of solution.

Example 1:

36.5 g HCl are dissolved in enough water to make 1 liter of solution. What is the molarity of the solution? Solution:

$$M = \frac{\text{mol HCl}}{L} = \frac{(36.5 \text{ g HCl}) \frac{1 \text{ mol HCl}}{36.5 \text{ g HCl}}}{1 L} = 1 M$$

Example 2:

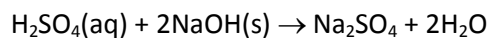
18.25 g HCl are dissolved in enough water to make 250 mL of solution. What is the molarity of the solution?

Solution:

$$M = \frac{\text{mol HCl}}{L} = \frac{(18.25 \text{ g HCl}) \frac{1 \text{ mol HCl}}{36.5 \text{ g HCl}}}{(250 \text{ mL}) \frac{1 L}{1000 \text{ mL}}} = \frac{0.5 \text{ mol}}{0.25 L} = 2 M$$

Example 3:

How many mL of 0.5M H_2SO_4 are required to react with 4 g NaOH from the following reaction?



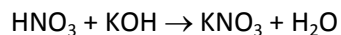
Solution: Don't get hung up the small stuff. Use what you know and factor labeling.

$$(4 \text{ g NaOH}) \left(\frac{1 \text{ mol NaOH}}{40 \text{ g NaOH}} \right) \left(\frac{1 \text{ mol } H_2SO_4}{2 \text{ mol NaOH}} \right) \left(\frac{L}{0.5 \text{ mol } H_2SO_4} \right) \left(\frac{1000 \text{ mL}}{1 L} \right) = 100 \text{ mL}$$

Note how grams were converted to moles and how the reaction stoichiometry played its role, here, too. Also note that the molar concentration of the sulfuric acid was inverted to get the units (and, hence, the answer) correct, as well.

Example 4:

How many mL of 2M HNO_3 are required to react with 5.61 g KOH as follows:



Solution:

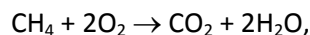
$$(5.61 \text{ g KOH}) \left(\frac{1 \text{ mol KOH}}{56.1 \text{ g KOH}} \right) \left(\frac{1 \text{ mol } HNO_3}{1 \text{ mol KOH}} \right) \left(\frac{L}{2 \text{ mol } HNO_3} \right) \left(\frac{1000 \text{ mL}}{1 L} \right) = 50 \text{ mL}$$

Limiting Reagents

Now that we've explored moles, chemical reactions and moles and molar concentration and reactions, it is time to explore the concept of limiting reagents (reactants). A limiting reagent (reactant) is the reactant (reagent) present in the smallest amount based on stoichiometry and molecular weight.

Example – 1

For the following chemical reaction,



determine which reactant is the limiting reagent if you have 20 g CH_4 and 100 g oxygen.

Solution: ALWAYS pick the same product for the multiple parts to this question. It doesn't matter if it's the carbon dioxide or the water -- just make sure you pick and use the same one for each problem as you solve it.

Solution:

Step 1: Determine the amount of carbon dioxide produced from the 20 g CH₄:

$$(20 \text{ g } CH_4) \left(\frac{1 \text{ mol } CH_4}{16 \text{ g } CH_4} \right) \left(\frac{1 \text{ mol } CO_2}{1 \text{ mol } CH_4} \right) \left(\frac{44 \text{ g } CO_2}{1 \text{ mol } CO_2} \right) = 55 \text{ g } CO_2$$

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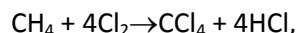
Step 2: Determine the amount of carbon dioxide produced from the 100 g of oxygen:

$$(100 \text{ g } O_2) \left(\frac{1 \text{ mol } O_2}{32 \text{ g } O_2} \right) \left(\frac{1 \text{ mol } CO_2}{2 \text{ mol } O_2} \right) \left(\frac{44 \text{ g } CO_2}{1 \text{ mol } CO_2} \right) = 68.6 \text{ g } CO_2$$

As the methane caused the production of the least amount of CO₂, it is the limiting reagent, i.e., no matter how much oxygen is available, this reaction will produce no more than 55 g CO₂.

Example 2:

For the following balanced reaction,



if you have 4 g CH₄ and 15 g chlorine, which is the limiting reagent?

Solution:

Step 1: Determine the amount of CCl₄ (carbon tetrachloride or "carbon tet" as it's known) produced by the 4 g CH₄:

$$(4 \text{ g } CH_4) \left(\frac{1 \text{ mol } CH_4}{16 \text{ g } CH_4} \right) \left(\frac{1 \text{ mol } CCl_4}{1 \text{ mol } CH_4} \right) \left(\frac{153 \text{ g } CCl_4}{1 \text{ mol } CCl_4} \right) = 38.25 \text{ g } CCl_4$$

Step 2: Determine the amount of carbon tet produced by the 15 g of molecular chlorine:

$$(15 \text{ g } Cl_2) \left(\frac{1 \text{ mol } Cl_2}{71 \text{ g } Cl_2} \right) \left(\frac{1 \text{ mol } CCl_4}{4 \text{ mol } Cl_2} \right) \left(\frac{153 \text{ g } CCl_4}{1 \text{ mol } CCl_4} \right) = 7.45 \text{ g } CCl_4$$

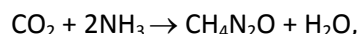
The smallest amount of carbon tet produced is with the 15 grams of molecular chlorine. The molecular chlorine is the limiting reagent.

Reaction Yield

The last topic for this lecture is reaction yield, i.e., relative to how much pen and paper say you're "supposed" to get how much did you really get? To do this we have to calculate per cent yield, which is defined as the per cent of the theoretical amount of product actually produced by a reaction:

$$\% \text{ yield} = \frac{\text{Actual yield}}{\text{Theoretical yield}} * 100$$

Example: For the following reaction,



if you started with 6 g of ammonia and obtained 5 g urea ($\text{CH}_4\text{N}_2\text{O}$), calculate the percent yield.

Solution:

Step 1: Calculate the theoretical yield:

$$(6 \text{ g } \text{NH}_3) \left(\frac{1 \text{ mol } \text{NH}_3}{17 \text{ g } \text{NH}_3} \right) \left(\frac{1 \text{ mol urea}}{2 \text{ mol } \text{NH}_3} \right) \left(\frac{60 \text{ g urea}}{1 \text{ mol urea}} \right) = 10.6 \text{ g urea, theoretically}$$

Step 2: Calculate the percent yield:

$$\% \text{ yield} = \frac{\text{actual yield}}{\text{theoretical yield}} * 100 = \frac{5 \text{ g}}{10.6 \text{ g}} * 100 \approx 50\% \text{ yield}$$

Elements of Thermochemistry



Thermodynamics is the study of the change of energy from one form to another. Energy is the ability to do work. Work is the change in kinetic energy of the object. Kinetic energy is the energy of motion.

$$KE = \frac{1}{2} m v^2$$

Practical Kinetic Energy: The Yellowstone River in the Grand Canyon of the Yellowstone, 23 June 2008.

Potential Energy

Stored energy; Energy of position. If object is above the ground = gravitational potential energy.

Since $Wt = m g$, then,

$$PE_{\text{grav}} = m g h,$$

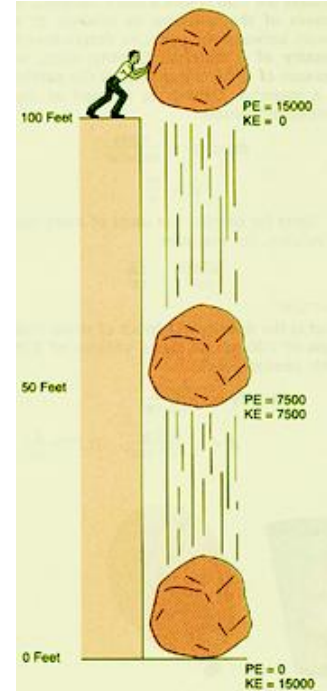
where m = mass, g = gravity, h = height above ground

Kinetic Energy

Energy of motion:

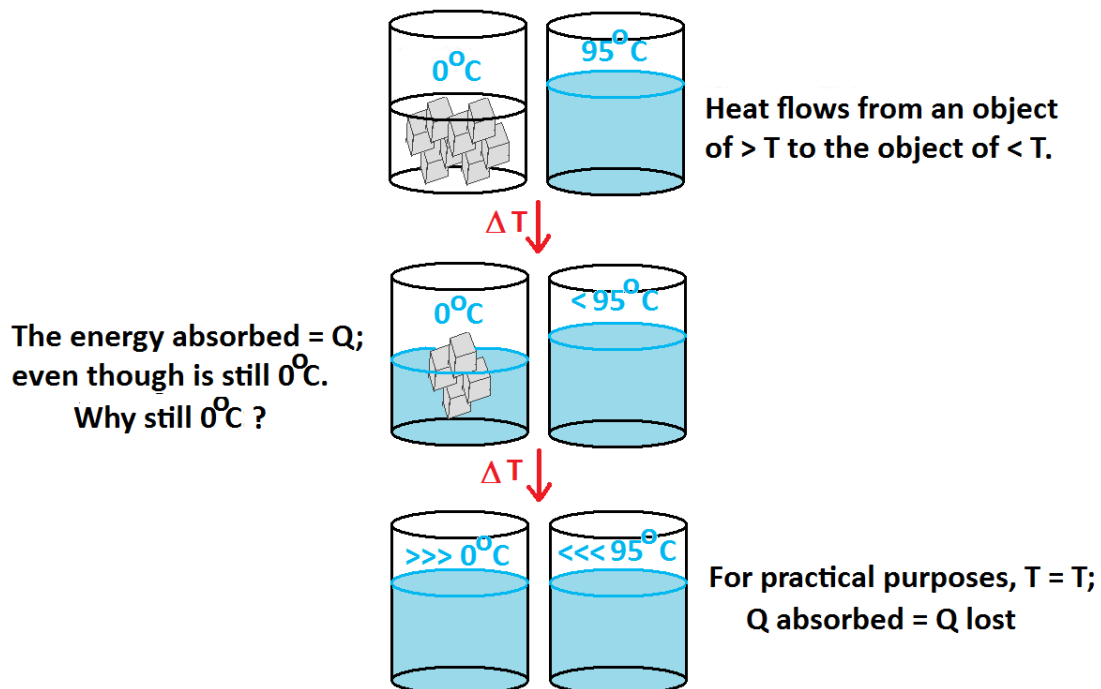
Law of Conservation of Energy

Is the relationship between PE and KE: The total energy is always conserved or energy is neither created nor destroyed – merely transformed



Heat

Heat flows from an object of hotter temperature to an object of cooler temperature. The absorbed energy we represent by "Q".



When talking about heat, it would be helpful to have some terms defined that will allow us to quantitatively determine just how much heat has been transferred between objects or between systems. The first term for discussion is heat capacity (C). Heat capacity is defined as the amount of energy transferred per change in absolute temperature equation at right. C is in units of Joules per mole per Kelvin.

$$C = \frac{Q}{\Delta T}$$

This term (heat capacity) is all fine and dandy -- it doesn't, though, give us a measure in terms of mass and/or amount. To that end we use the term specific heat capacity (c). Specific heat capacity is equal to the heat capacity divided by the molecular weight and is in units of joules per Kelvin per gram. Joules aren't as widely known as are calories. One calorie is equal to 4.184 Joules. One calorie (cal) is defined as the amount of heat necessary to raise the temperature of 1 gram of water by 1° C -- a little less than a perfect definition, yet close enough for our purposes. One Calorie (Cal or kcal) is 1000 calories or 1 kilocalorie (kcal). The kcal is the unit we use for "food calories".

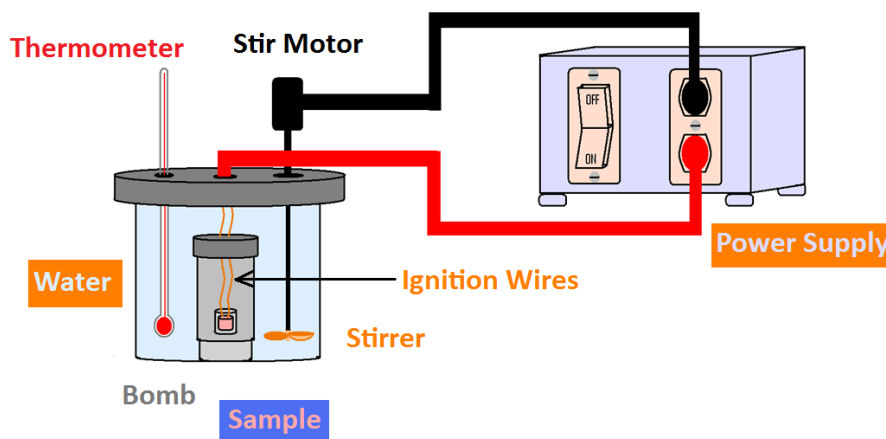
How could we use this information to determine the amount of heat, Q, that has been transferred between two objects? We use a simple equation:

$$Q = m c \Delta T$$

Where Q = the amount of heat in calories or Joules, m = the mass in grams, c = the specific heat in joules per Kelvin per gram OR calories per Kelvin per gram, and ΔT = the change in temperature in Kelvins (also in °C, since the difference is numerically equivalent -- remember, though, to keep your units straight).

The table, below, summarizes the specific heat capacity of some representative substances:

Substance	Specific Heat Capacity (J/K/g)
Water	4.169
Al	0.898
Diamond	0.518
Fe	0.443
b	0.130



Specific heat capacities are measured in a "bomb calorimeter", above: The way this works is that sample is placed in the sample holder in the "bomb" and two wires are set in the substance through the water-tight lid. The lid is sealed, the wires are attached to a power supply, water is poured around the bomb and the stirrer rotates to mix the water. When the temperature of the water is equilibrated, the power is turned on, the sample is ignited and the temperature increase from the sample combustion is

measured by an increased water temperature. The challenge is that you have to remember that the calorimeter also absorbs some heat, so we have to take that into account:

$$\Delta Q_c = m_c c_c \Delta T$$

Where the "c" subscript represents the calorimeter – heat absorbed by it, mass of it, specific heat capacity of it and the change in absolute temperature of the calorimeter. So, when figuring the whole heat transfer, we must write the equation as follows:

$$\Delta Q_{Total} = Q_{Substance} + Q_{Calorimeter}$$

We can then re-write the equation thusly:

$$\Delta Q_{Total} = mc \Delta T + m_c c_c \Delta T$$

The key to this equation and its application is to remember that:

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

Example 1:

50 g of coal are placed in a calorimeter at 20° C. The calorimeter has a mass of 100 g and is made of Fe. 950 J of heat increases the temperature of the calorimeter to 35° C. What is the specific heat capacity of the coal? We know the specific heat capacity of the Fe from the table above: 0.443 J/g/K. The change in temperature = 35° C - 20° C = 15° C which is equivalent to 15 K.

Set up the equation:

$$\Delta Q_{Total} = mc \Delta T + m_c c_c \Delta T$$

Manipulate it:

$$\Delta Q_{Total} - m_c c_c \Delta T = mc \Delta T$$

Rearrange and isolate "c":

$$\frac{\Delta Q_{total} - m_c c_c \Delta T}{m \Delta T} = c = \frac{950 - (100)(0.443)(15)}{(50)(15)} = 0.407 \text{ J/g/K}$$

0.407 J/g/K is equivalent to 0.097 cal/g/K.

Example 2:

100 g tar are placed in a calorimeter at 10° C. The calorimeter has a mass of 200 g and is made of diamond. 10,000 Joules (J) of heat increases the temperature of the calorimeter to 95° C. What is the specific heat capacity of the tar? We already know the specific heat capacity of the diamond from the table, above: 0.518 J/g/K. The temperature difference is equal to 95° C - 10° C, which equals 85° C -- this is equivalent to 85 K. Set up the equation as before and solve for "c":

$$\frac{\Delta Q_{total} - m_c c_c \Delta T}{m \Delta T} = c = \frac{10000 - (200)(0.518)(85)}{(100)(85)} = 0.140 J / g / K$$

This is equivalent to 0.0336 cal/g/K.

Example 3:

75 g aspirin are placed in a calorimeter at 20° C. The calorimeter has a mass of 125 g and is made of lead (Pb). 850 J of heat increases the temperature of the calorimeter to 22° C. What is the specific heat capacity of aspirin? We know the specific heat capacity of Pb from the table: 0.130 J/g/K.

The change in temperature is 2K. Set up the equation, isolate and solve for "c", as before:

$$\frac{\Delta Q_{total} - m_c c_c \Delta T}{m \Delta T} = c = \frac{850 - (125)(0.130)(2)}{(75)(2)} = 5.45 J / g / K$$

This is equivalent to 1.303 cal/g/K.

We saw that the combination of both the substance and the calorimeter contributed to the ΔQ . What about the ΔQ BETWEEN 2 different containers or systems? In that case, $\Delta Q_1 = \Delta Q_2$. Since one system is absorbing heat, the other system must be losing heat. We can use this set up to determine the final temperature of 2 systems mixing.

Example 1:

A Pb pipe of 300 g is at 25° C. If the ends of the pipe are plugged after 300 g water at 90° C are poured into it, what is the final temperature of the new system? Key to this is that the lead pipe is going heat up and the water is going to cool down. The 2 equations, then for the temperature differential are as follow:

$$\Delta T_{Pb} = T_f - 298 \text{ and } \Delta T_{H_2O} = 363 - T_f$$

The heat capacities of Pb and water are as follow, respectively: 0.130 J/K/g and 4.169 J/K/g. Set up the formula and solve for T_f :

$$\begin{aligned} Q_{Pb} &= Q_{H_2O} \\ (300)(0.130)(T_f - 298) &= (300)(4.163)(363 - T_f) \\ 39T_f - 11622 &= 453350.7 - 1251T_f \\ 1290T_f &= 464972.7 \\ T_f &= \frac{464972.7}{1290} = 360 K \text{ or } 87^\circ C \end{aligned}$$

In other words, as we discussed before, lead heats up and water cools down.

Example #2:

A gold container at 30° C has 400 g water at 100° C poured into it. The gold container has a mass of 500 g. What is the T_f ? (the specific heat capacity (c) of Au is 0.130 J/g/K). Key to this is that the gold container is going heat up and the water is going to cool down. The 2 equations, then, for the temperature differential are as follow:

$$\Delta T_{Au} = T_f - 303 \text{ and } \Delta T_{H_2O} = 373 - T_f$$

The heat capacities of Au and water are as follow, respectively: 0.130 J/K/g and 4.169 J/K/g. Set up the formula and solve for T_f :

$$\begin{aligned} Q_{Pb} &= Q_{H_2O} \\ (500)(0.130)(T_f - 303) &= (400)(4.163)(373 - T_f) \\ 65T_f - 19695 &= 621119.6 - 1665.2T_f \\ 1730.2T_f &= 640814.6 \\ T_f &= \frac{640814.6}{1730.2} = 370 \text{ K or } 97^\circ \text{ C} \end{aligned}$$

While we are discussing heat, it's always nice to have a handle on how heat leaves "bodies". It does this by at least three mechanisms -- or at least the mechanisms that are of the greatest significance to those heading into [allied] health care as a profession. The three mechanisms and their definitions are summarized in the table, below:

Mechanism	Definition
Conduction	Heat removal by touching the objects that leads to temperature equilibration between the objects.
Convection	Heat is carried by the medium, e.g., air movement, water moving as it's heating.
Radiation	Heat leaving as "waves of energy" being emitted from the warm object.

An Arithmetic Approach to Temperature Regulation in Humans

When discussing heat regulation, the unit "watt" is fairly common. We are familiar with the term "kilowatt" from our electrical bills at home. What though does it mean in terms of something we have either studied or can easily relate to? A watt is 1 J/sec or 0.24 calories/second. One watt is also equal to 1.44×10^{-2} kcal/minute.

Let's put some perspective on this in terms of exercise activities by men and women:

Perspective			
	Light Exercise	Heavy Exercise	Very Heavy Exercise
Examples	Walking, fishing, golfing	Ice skating, jogging	Running fast, racquet ball
Male	2-5 Cal/min	7.5-10 Cal/min	12.5 Cal/min
Female	1.5-3.4 Cal/min	5.5-7.4 Cal/min	9.5 Cal/min

Examples:

$$\frac{10 \text{ Cal}}{\text{min ute}} * \frac{\text{min ute} - \text{Watt}}{1.4 \times 10^{-2} \text{ Cal}} = 694 \text{ watts}$$

$$\frac{12.5 \text{ Cal}}{\text{min ute}} * \frac{\text{min ute} - \text{Watt}}{1.44 \times 10^{-2} \text{ Cal}} = 868 \text{ Watts}$$

Or about 0.694 kW (Heavy Exercise).

Or about 0.868 kW (Very Heavy Exercise).

Since 1 kW is about 1.34 horsepower, heavy exercise is about 0.92 horsepower and very heavy exercise is about 1.2 horsepower.

Humans and Heat

In humans, as in other mammals, heat is both generated and lost. The table, below, summarizes the sources of heat generated and heat lost:

Heat	
Generated	Lost
Q _m = heat generated from metabolism; 80-1600 W depending on the circumstances	*****
	Q _c = convective heat loss
	Q _r = radiative heat loss
	Q _s = heat loss from the evaporation of sweat
	Q _l = heat loss via lung water loss; a constant: 10.5 W

Of all the terms above, the heat lost by convective, radiative and sweat evaporation mechanisms are calculable, at right:

$$Q_c = \frac{7.1W}{m^2 K} * (SA) * (\Delta T)$$

At a constant temperature,

$$Q_R = \frac{6.5W}{m^2 K} * (SA) * (\Delta T)$$

$$Q_m = Q_c + Q_r + Q_s + Q_l$$

And "SA" is the surface area of the person in square meters. ΔT is equal to the temperature of the skin minus the temperature of the air -- ALWAYS.

$$Q_s = \frac{674Wh}{kg} * \frac{kg \text{ sweat produced}}{\text{hour}}$$

Application

Example 1:

The "average" person" at rest emits 100 W of heat. If the surface area of the person is 1.975 m² and the skin temperature is 37° C and the air temperature is 14.4° C, how much sweat will be produced by this person?

1) the temperature difference is 22.6 K

2) the SA is 1.975 m²

3) $Q_m = 100 \text{ W}$

4) $Q_c = (7.1)(1.975)(22.6) = 316.9 \text{ W}$

5) $Q_R = (6.5)(1.975)(22.6) = 290.1 \text{ Watts}$

6) $Q_s = (674)X$

7) $Q_l = 10.5 \text{ W}$

8) $Q_m = Q_c + Q_R + Q_s + Q_l$

rearrange step 8 and solve for Q_s :

$$Q_m - Q_c - Q_R - Q_l = Q_s$$

$$100 - 316.9 - 290.1 - 10.5 = -517.5 \text{ W} = Q_s$$

$$674X = -517.5$$

$$X = -0.768 \text{ kg sweat produced per hour}$$

Note that the answer is a negative number! This means that the person does not produce sweat and is cold and requires heat.

Example 2:

The "average" person at rest emits 100 W of heat. If the surface area of the person is 1.975 m² and the skin temperature is 37° C and the air temperature is 38° C, how much sweat will be produced by this person?

1) the temperature difference is -1 K

2) the SA is 1.975 m²

3) $Q_m = 100 \text{ W}$

4) $Q_c = -14 \text{ W}$

5) $Q_R = -13 \text{ Watts}$

6) $Q_s = ?$

7) $Q_l = 10.5 \text{ W}$

8) $Q_m = Q_c + Q_R + Q_s + Q_l$

rearrange step 8 and solve for Q_s :

$$Q_m - Q_c - Q_R - Q_l = Q_s$$

$$100 - (-14) - (-13) - 10.5 = 116.5 \text{ W} = Q_s$$

$$674X = 116.5$$

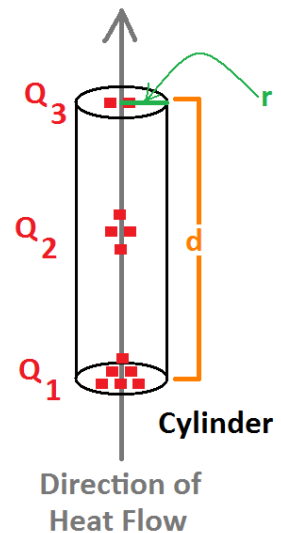
$X = 0.173 \text{ kg}$ sweat produced per hour. This is about 173 mL/hour. At about 30 oz per mL, this is about 5.8 oz/hour.

REMEMBER:

These are approximations and do NOT take into account other biological processes.

Flow of Heat

When discussing heat, it's important to actually comprehend how heat flows. Among other reasons to comprehend heat flows, we can eventually fold a discussion on the flow of heat into a discussion of how gases traverse membranes in the body to provide oxygen to the cells and CO₂ transport out of the body. To begin the discussion, let's examine Fick's Law. Fick's Law says



that the rate of diffusion of heat per unit area through a cylinder in a direction perpendicular to the area is proportional to the heat gradient through the cylinder in that direction.

The heat gradient is defined as:

$$\frac{\Delta Q}{\text{volume} \times d} \Leftrightarrow \frac{H}{d}$$

And the area of the face of the cylinder is πr^2 .

If we combine these two equations with one more:

We get the following:

$$\frac{Q}{t} = \text{Flow of Heat}$$

Where Q is the amount of heat,

t is time,

D is a constant,

$$\frac{Q}{t} = D A \frac{H}{d}$$

A = πr^2 ,

H is the heat per unit volume

$$\frac{m}{t} = D A \frac{\Delta[C]}{d}$$

d is distance or thickness of the cylinder.

This cylinder for heat diffusion may be likened to a semipermeable membrane, therefore, the heat flow is analogous to diffusion of a solute. The rate of diffusion of a solute per unit area in a direction perpendicular to the area is proportional to the concentration gradient in that direction. By substituting mass (m) for amount of heat (Q) and concentration gradient ($\Delta [C]$) for H, then, the mass of solute diffusing per unit time may be expressed as above.

Again, "m" is mass diffusing, "t" is the time in which diffusion is occurring, and $\Delta [C]$ is the concentration gradient. The remainder of the terms are as defined before.

$$\frac{\Delta d}{\Delta t} \propto \frac{A \Delta P}{d}$$

Diffusion is analogous to the flow of gas through semipermeable membranes:

or

Where Δd is the difference in thickness of the membrane, Δt is the time it takes to cross the membrane (time difference) and ΔP is the pressure gradient or pressure difference across the membrane.

$$\frac{\Delta d}{\Delta t} = D \frac{A \Delta P}{d}$$

This last equation tells us that the speed of a gas through a semi-permeable membrane is directly proportional to the cross sectional area of that membrane and the pressure gradient ($P_1 - P_2 = \Delta P$) between the two sides of the membrane. It also tells us that flow is inversely proportional to the thickness (d) of the membrane. This is illustrated at right, top of next page, where a semi-permeable membrane is placed in a tube with gas flowing in one direction through the membrane.

From our previous equation, note that the distance difference per time difference is simply velocity. We can rewrite the equation, now, as follows:

$$\frac{\Delta d}{\Delta t} = v = D \frac{A \Delta P}{d}$$

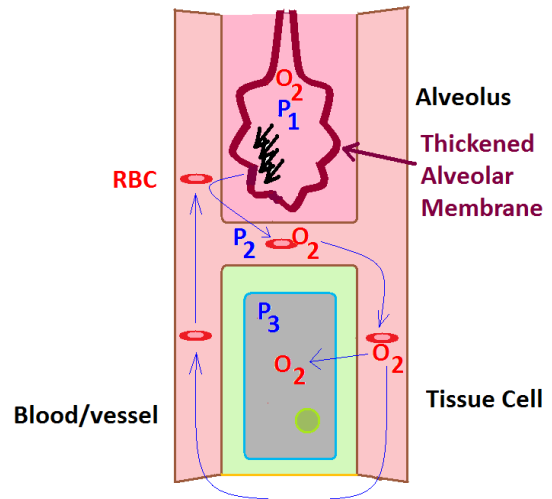
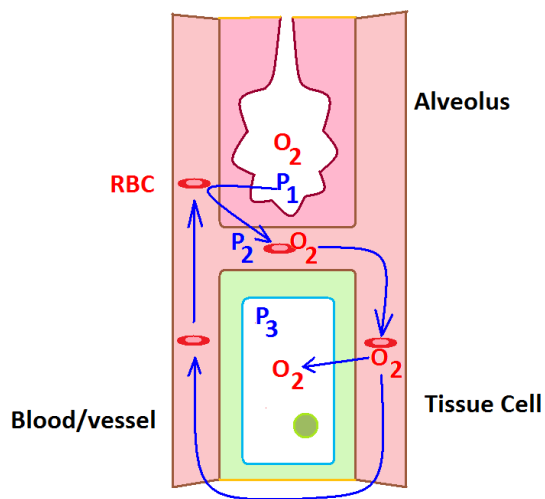
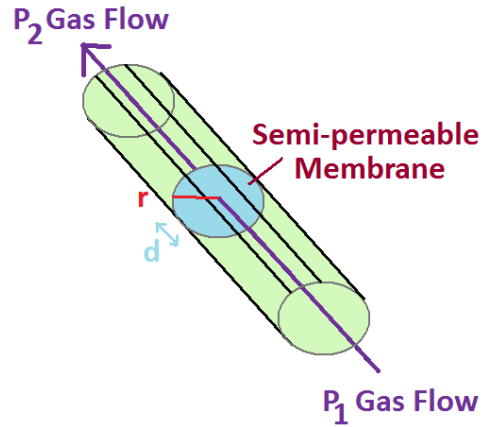
or

$$v = D \frac{A \Delta P}{d}$$

Where the only new variable is "v": velocity (or speed). We may, thus, write the equation as follows:

If d reduces by half, v increases by two-fold. If d increases its thickness by 3 fold, then v reduces to one third its original value. Hence, the thicker the membrane, the slower the diffusion of the gas. Can we apply this

in a clinical perspective? Yes, we can.



Normal Gas Exchange Across Alveolar Membranes. Normal Gas Flow, left; Reduced Gas Flow, right.

If, though, one develops pulmonary edema through heart failure, chemical inhalation, mountain sickness or pulmonary frostbite, then the alveolar membranes thicken as in the figure, right, that makes it very difficult to get gases across the membranes and cause the cells to begin to consider the possibility of their death without treatment as long as the body can function (have you seen "Vertical Limit"?) .

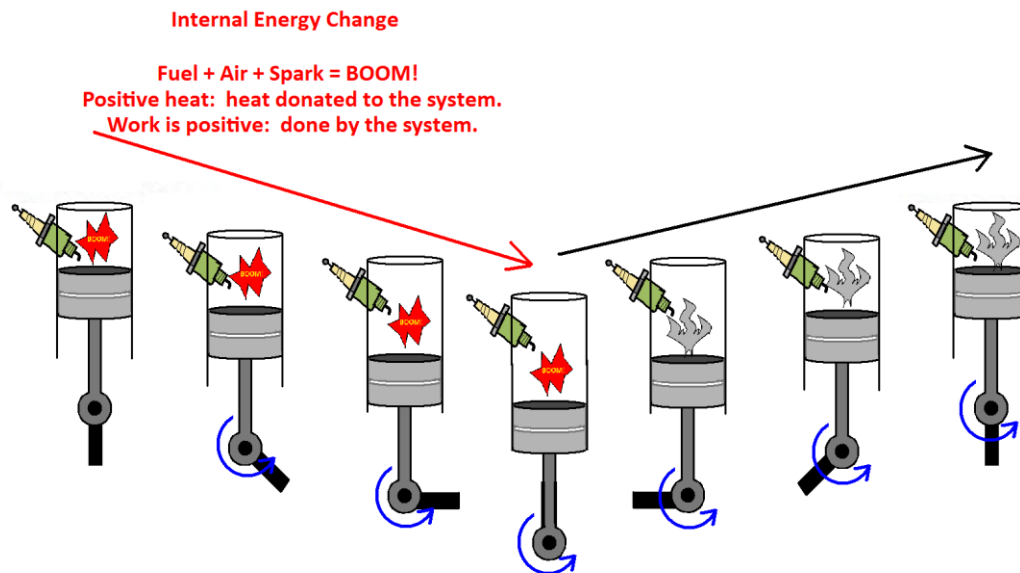
REFERENCE: MacDonald, S. and Burns, D. : Physics for Life and Health Sciences. (Addison-Wesley: London) © 1975.

Introduction to The Laws of Thermodynamics

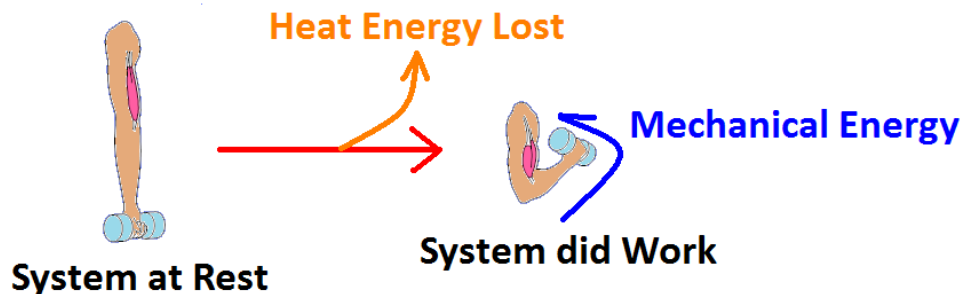
First Law

Represented as ΔH ; Heat of Reaction; Enthalpy

The First Law of thermodynamics says that when heat is added to a system at rest, the system will perform work due to the change in internal energy of the system. A car engine is a good example of this. When gas fills the cylinder and the spark jumps across the plug, the gasoline ignites and explodes, forcing the piston down. This is positive heat, i.e., it is donated to the system. There are internal energy changes and work is positive, i.e., work is done by the system -- the car moves when in gear.

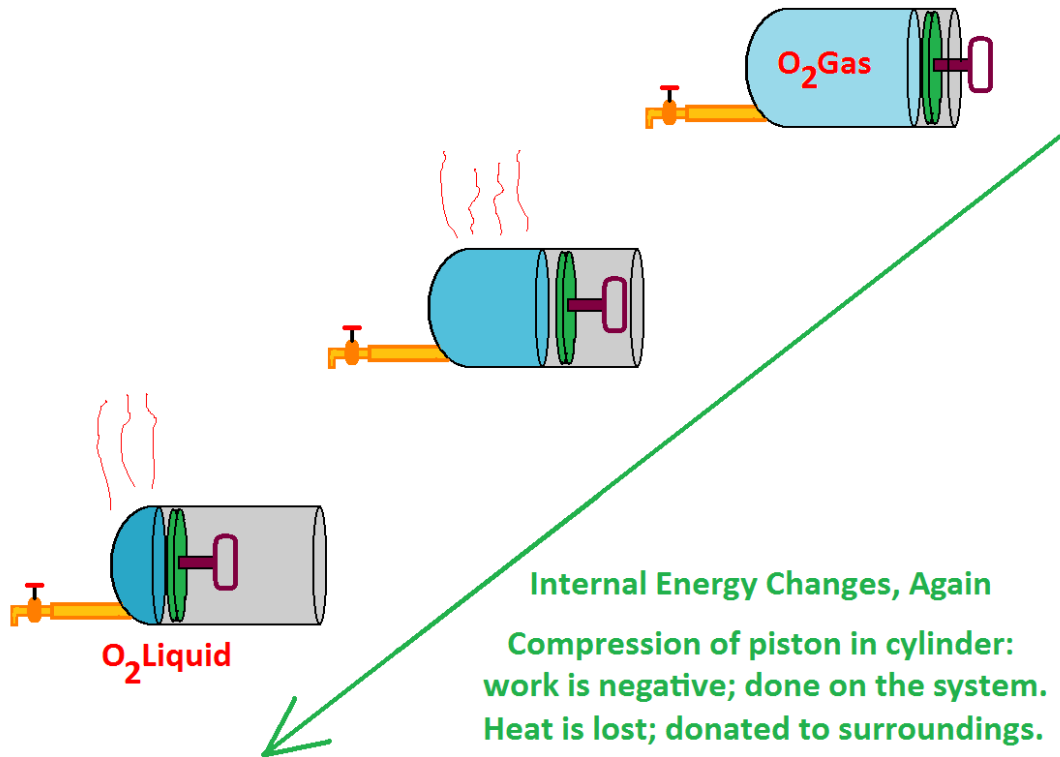


Alternatively, the First Law may be stated as follows: work done BY a system is equal to the change in mechanical energy PLUS the energy that LEAVES the system. Weight lifting is a good example of that. When a system is at rest (e.g., the biceps brachii), nothing happens. When the biceps contracts, the system did work, heat energy is lost and there is a change in mechanical energy.



Another perspective on the First Law is that energy is neither created nor destroyed, but changed from one form to another.

The converse First Law says that work done on a system is equal to the change in mechanical energy PLUS the energy that is absorbed BY the system. A good example of this is compressing a gas to a liquid. When a gas that is compressible is placed inside a cylinder with a piston and the piston is compressed, the work is negative. In other words, work is done ON the system. Heat is lost and donated to the surroundings.



The Second Law of Thermodynamics says that spontaneous changes in the universe are accompanied by increasing entropy in the universe, i.e., chaos is always increasing.

	$DS > 0$ \rightarrow $DS < 0$ \leftarrow		$DS > 0$ \rightarrow $DS < 0$ \leftarrow	
Solid ice: highest order and least entropy		Liquid Water		Water vapor (gas): most disorder and highest entropy

ΔS = ENTROPY = the amount of disorder, chaos, randomness of a system

The Second Law of thermodynamics says that systems prefer a sense of chaos (entropy), i.e., chaos is more probable than an ordered system. For example, in poker, there are only a few hands, e.g., royal flush, with high points. This says, then, that there are MORE hands with NO value. This is entropy. Another example of entropy comes to us from family structure and dynamics: in dysfunctional families there is a high degree of entropy and a low degree of order. In functional families, there is some entropy and more order.

Entropy is ALWAYS increasing -- or at least equals zero. In processes that are reversible, the change in entropy equals zero and chaos equals a constant. In processes that are IRreversible, which includes most natural processes, the change in entropy is greater than or equal to zero always and chaos increases.

Thermodynamics predicts whether a reaction will go as written or not. Thermodynamics does NOT predict how fast the reaction will go -- that's the function of kinetics. How is it possible to predict whether or not a reaction will go? By studying Gibbs Free Energy (G).

In general, When the change in Gibbs Free energy (ΔG) is NEGATIVE, the reaction GOES as written. In general, When the ΔG is POSITIVE, the reaction does NOT go as written. **GIBB'S FREE ENERGY = $\Delta G \Leftrightarrow dG$ is another state function.**

This free energy change is equivalent to expressing arithmetically the difference between a state of minimum energy ($-\Delta H$) and maximum chaos ($+\Delta S$) that occurs when possible for a chemical reaction to proceed spontaneously, i.e., as written.

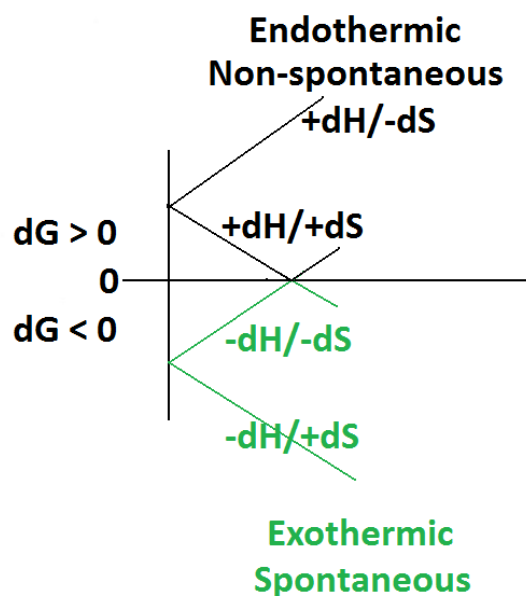
dG says NOTHING about reaction rate!

The arithmetic expression is:

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

where the "T" is the absolute temperature of the system.

When $\Delta G < 0$, the reaction goes as written. When $\Delta G > 0$, the reaction does NOT go as written, see graphic:



There is a relationship between 1st law, 2d law and Gibbs free energy:

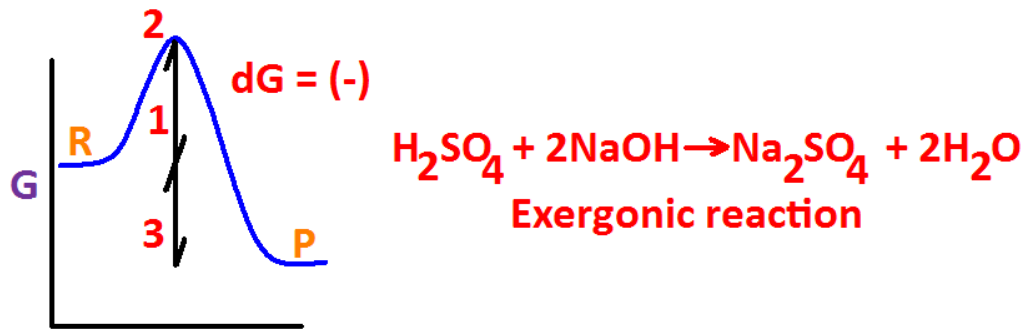
$$\Delta G = \Delta 1st\ law - T\Delta 2d\ law$$

or the change in free energy (ΔG) is equal to the change in the first law (enthalpy or ΔH) minus the absolute temperature (T) times the change in the 2d law (entropy or ΔS). This, then, may be re-written as

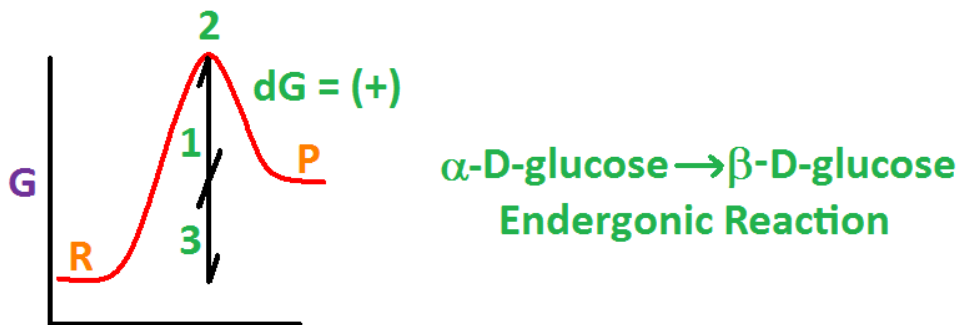
$$\Delta G = \Delta H - T \Delta S$$

In other words, the change in free energy is equal to the change in enthalpy less the change in entropy at some absolute temperature, T . The difference in this equation is sometimes called the Third Law of thermodynamics and may be stated as follows: as the energy of a reaction is changed from one form to another, entropy changes -- if the difference at a fixed absolute temperature is negative, the reaction goes spontaneously as written; if it is positive, it does NOT go spontaneously as written.

The following graphic illustrates this concept. Each graphic has ΔG on the vertical axis and the reaction course (reactant [R] to product [P]) on the horizontal axis. Note that in an exergonic reaction that the energy level for the reactants is higher than for the products. Note that for an endergonic reaction that the energy level for the reactants is lower than for the products. The region labeled #1 in each plot is the energy of activation, sometimes labeled ΔG^\ddagger or E_a ; #2 is the transition state -- where the energy is so high the bonds make-n-break -- if this energy is not reached, no bonds make-n-break; #3 is the free energy difference (ΔG).

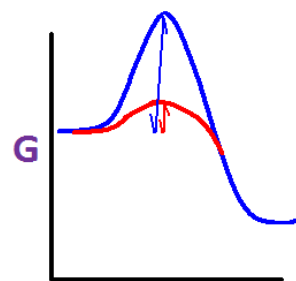


Reaction Course



Reaction Course

Is it possible to decrease the energy of activation? Yes! With a catalyst. A catalyst is something that speeds up the rate of the reaction without being consumed during the course of the reaction. Note in the graphic that the difference between the blue line ("regular" reaction) and the red line (catalyzed reaction) is the decrease in E_a . This decrease in E_a is caused by the catalyst.



Reaction Course
catalyzed
un-catalyzed

The Third Law of Thermodynamics says that the entropy of ANY pure, perfect crystalline element or compound at 0 K is ZERO: there is NO molecular movement. Impure substances also have NO molecular movement at 0 K, but since the impurity is not equally distributed, this causes an increasing entropy, i.e., entropy does not equal zero in impure substances at 0 K.

Elementary Reaction Rates

Definitions

A chemical reaction is defined as the result of collisions of adequate energy and appropriate orientation of reactants. Instantaneously rapid reactions are explosive and don't exist in large numbers. The reaction rate is defined as the rate at which the effective collisions happen; or as the number of effective collisions per unit time or per unit volume of reaction. It may also be defined as the amount of reactant converted to product per unit time (e.g., seconds, minutes, hours, days, years, ad nauseum).

The rate is the product of 3 parameters: the frequency of collision, the energy factor and the probability factor.

Frequency of Collisions

The frequency of collisions is the total number of collisions per unit volume or per unit time. The frequency of collisions, Z , depends upon 3 factors: 1) at what concentration or pressure the particles are [If you raise the concentration, it raises the rate of the reaction.], 2) how big the particles are and 3) the speed at which they are moving (this depends upon the weight and absolute temperature [If you raise the absolute temperature, it raises the rate and increases the energy factor.]).

The heavier weight causes particles to locomote slower at some absolute temperature and, therefore, lowers the frequency of collision. Heavier matter is generally larger and this causes an increased frequency of collision. These latter two characteristics tend to cancel each other out and, subsequently, yield no effect on the frequency of the collisions.

Probability Factor

The probability factor is the fraction of collisions with the appropriate orientation to drive the reaction forward. The probability factor, P , depends upon 2 factors: 1) particulate geometry and 2) reaction type (reactions closely related show little variation in probability factor).

Energy Factor

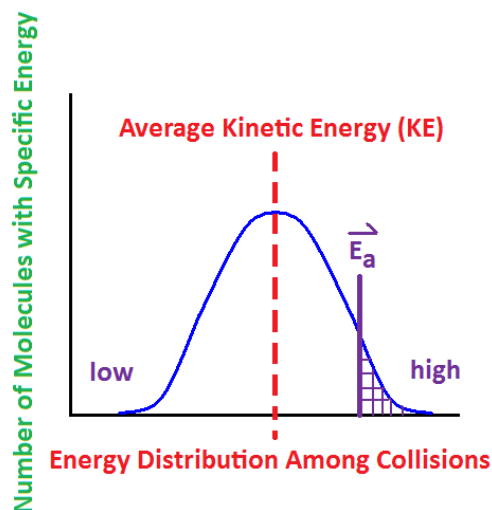
The energy factor is the fraction of collisions with adequate energy to drive the reaction forward. The energy factor, ϵ , is the most important factor in rate determinations and is defined as the fraction of collisions that are sufficiently energetic to drive the reaction forward. The energy factor is dependent upon 2 factors: 1) the absolute temperature (people can regulate this) and 2) the energy of activation, ϵ_a (specific to each reaction).

Kinetic Energy

In general, at some temperature, the particles have some average velocity (v). Each particle has a mass (m). Therefore, there is an average kinetic energy ($\frac{1}{2}mv^2$) typified in each reaction -- remember, too, that temperature is also a measure of kinetic energy.

ϵ_a by Distribution Curve

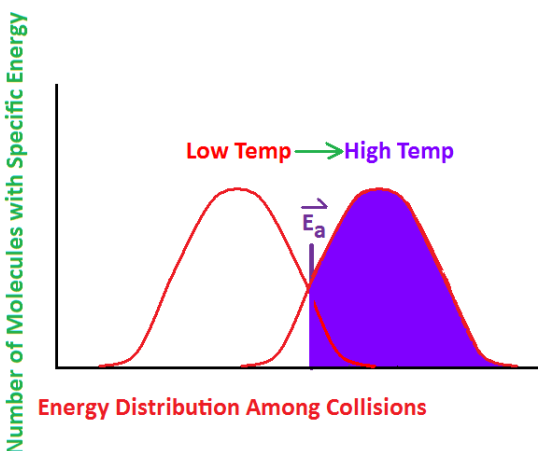
We can examine the energy in terms of ϵ_a by distribution curve, remembering that the bigger the ϵ_a , the smaller the fraction of collisions that have that energy and vice versa, i.e., the smaller the ϵ_a , the faster the reaction. The figure illustrates a distribution curve for the energy distributed among collisions on the x axis vs the number of molecules with a specific energy on the y axis at constant absolute temperature. Note that the average kinetic energy is represented at the peak of the bell curve and that at the far right of the curve is a very small area hashed to represent the fraction of particles at or above the E_a for this generic reaction.



The actual fraction of the particles at or above the ϵ_a may be calculated as follows:

$$\frac{\text{shaded area on curve}}{\text{whole bell curve area}} = \text{fraction of collisions} \geq \epsilon_a$$

What, though, happens with temperature variability? As one increases the temperature, the kinetic energy is increased. When the kinetic energy is increased, as you might expect, the curve undergoes a shift to the right. Therefore, increasing the absolute temperature of the reaction mixture increases, also, the area under the curve that is shaded (hashed) and increases the rate of the reaction. Note that the area that is hashed is considerably larger, now, meaning that there are more collisions at or above the ϵ_a . In other words, the reaction rate = $P \cdot Z \cdot \epsilon_a$.



Relative Reaction Rates

The first reactions that we will explore are the chlorination and bromination of methane, i.e., the addition of a Cl or Br atom to methane (CH₄) by extracting a hydrogen atom from the CH₄. We will explore these under identical conditions, i.e., absolute temperature and concentration are identical. These two hydrogen atom extraction reactions are summarized below.

			e _a (calories)
Cl + CH ₃ --H	→	H--Cl + CH ₃ ·	4,000
Br + CH ₃ --H	→	H--Br + CH ₃ ·	18,000

The frequency of collision is cancelled out as Br is heavier AND larger. The probability factor is UNLIKELY to cause a difference in reactivity. Therefore, the energy factor is the only variable that will effect the rate of the reaction. We can express this arithmetically as follows, remembering that P and Z eventually drop out, where T = absolute temperature, e = 2.718 (natural log base) and R = 1.986.

$$\text{Fraction of Particles with Energy } > \epsilon_a = e^{\frac{-\epsilon_a}{RT}}$$

Based upon this equation we can readily see that a small change in the energy of activation (ε_a) will cause a huge effect on the fraction of collisions and on the rate of the reaction. Before we examine our specific example with the bromine and chlorine, above, let's examine, arithmetically, what might happen if we had reactions with ε_a 's of 5000 calories, 10000 calories and 15000 calories, respectively, by calculating the fraction of collisions with energy greater than ε_a, first, at 25° C (298 K):

$$\text{fraction} = 2.718^{\frac{-5000}{(1.986 \times 298)}} = 0.00021 \Leftrightarrow 21 \text{ out of } 1,000,000 \text{ collisions}$$

$$\text{fraction} = 2.718^{\frac{-10000}{(1.986 \times 298)}} = 4.6 \times 10^{-8} \Leftrightarrow 0.046 \text{ out of } 1,000,000 \text{ collisions}$$

$$\text{fraction} = 2.718^{\frac{-15000}{(1.986 \times 298)}} = 9.85 \times 10^{-12} \Leftrightarrow 9.85 \times 10^{-6} \text{ out of } 1,000,000 \text{ collisions}$$

Then, let's recalculate the fractions at 275° C (548 K):

$$\text{fraction} = 2.718^{\frac{-5000}{(1.986 \times 548)}} = 0.01 \Leftrightarrow 10,000 \text{ out of } 1,000,000 \text{ collisions}$$

$$\text{fraction} = 2.718^{\frac{-10000}{(1.986 \times 548)}} = 0.0001 \Leftrightarrow 100 \text{ out of } 1,000,000 \text{ collisions}$$

$$\text{fraction} = 2.718^{\frac{-15000}{(1.986 \times 548)}} = 0.000001 \Leftrightarrow 1 \text{ out of } 1,000,000 \text{ collisions}$$

From this we may conclude the following: 1) at cooler absolute temperature, there is a reduced particulate fraction for collisions, 2) at warmer absolute temperatures, there is an increased particulate fraction for collisions (see Figure) and 3) at cooler absolute temperatures, the rate difference is much, much greater than for warmer absolute temperatures as summarized below:

Rxn ϵ_a (calories)	Rxn Number	# collisions per 10^6 at 298 K	# collisions per 10^6 at 548 K	Reaction 1 is faster than by (at 298 K)	Reaction 1 is faster than by (at 548 K)
5000	1	21	10000	-----	-----
10000	2	0.046	100	456 times	100 times
15000	3	$9.85 \cdot 10^{-6}$	1	$2.13 \cdot 10^6$ times	10000 times

So, now, to return to our original examples of chlorine and bromine reacting with methane, we can calculate their fractions, as well:

$$\text{Cl fraction} = 2.718^{\frac{-4000}{(1.986 \cdot 548)}} = .0253 \Leftrightarrow 23,500 \text{ out of } 1,000,000 \text{ collisions}$$

$$\text{Br fraction} = 2.718^{\frac{-18000}{(1.986 \cdot 548)}} = 6.6 \times 10^{-8} \Leftrightarrow 0.066 \text{ out of } 1,000,000 \text{ collisions}$$

For perspective, the chlorine is about 350,000 times as reactive as the bromine. This comparison is valid **ONLY** when reactions are so closely related that P and Z "drop out".

What about the reactivities of the halogens with ethane (C_2H_6)? The table, following slide, summarizes the energies of activation for the specific halogens during the generic halogenation of ethane. Note that "X" means any halogen in the generic sense.

Generic Halogenation Reaction		ϵ_a for X in kcal/mol			
		F	Cl	Br	I
A	$\text{X}_2 \rightarrow 2\text{X}\cdot$	+38	+58	+46	+36
B	$\text{X}\cdot + \text{C}_2\text{H}_6 \rightarrow \text{HX} + \text{C}_2\text{H}_5\cdot$	-38	-5	+10	+27
C	$\text{C}_2\text{H}_5\cdot + \text{X}_2 \rightarrow \text{C}_2\text{H}_5\text{X} + \text{X}\cdot$	-82	-23	-23	-19

Reaction "A"

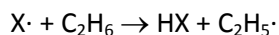
Reaction "A" requires the "demolecularization" of the halogen to atomic halogen. This step is endothermic and requires energy.



More specifically, reaction "A" is the chain initiation step. It requires heat or light. Energy is absorbed and the molecular halogen is cleaved into reactive atoms. This is endothermic and requires the heat or light as catalysts to move forward.

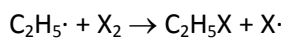
Reaction "B"

Reaction "B" extracts the hydrogen atom to form the hydrohalic acid.



Reaction "B" is called a chain-propagating step. In this reaction, the atomic halogen consumes the reactive hydrogen atom and generates reactive alkyl groups. This step is both endothermic and exothermic, i.e., it absorbs energy until it "gets going", then gives off energy once it's underway.

Reaction "C"



Reaction "C" "splits" the molecular halogen to form the halohydrocarbon and another reactive atom of halogen. This sort of reaction sequence is called a chain reaction. Reaction "C" is also a chain-propagating step. The reactive alkyl groups and the reactive atomic halogen (intermediates) continue to be generated and consumed. This step is exothermic.

Reactions "B" and "C" continue to progress until chain termination steps occur. There are 3 kinds of chain termination steps: 1) atomic halogen reacts with atomic halogen to form molecular halogen, 2) reactive alkyl groups react with each other forming unreactive organic molecules and 3) organic radicals and atomic halogen combine perfectly proportionately to form halohydrocarbon. The bottom line with chain termination steps is that reactive atoms and alkyl groups are consumed, BUT not generated, or are being captured by the walls of their reaction vessels.

Reaction "B" (the hydrogen atom extraction step) is more energetically difficult than reaction "C" (the step that reacts the alkyl group with the molecule of halogen). This step ("B"), since it determines the overall rate of the reaction, is called the rate limiting step -- a classroom example is that students don't get their grades back on exams until after the last person turns in his or her exam. That student is the rate-limiting step.

We can examine this graphically, in detail, as well. In the graphic at the top right of the following page, note that energy is plotted on the y axis vs the reaction coordinate on the x-axis. Note that we start with reactants on the left and end with products on the right. There are, however, two "speed bumps" in this curve. The difference between the reactant and top of the first speed bump is the energy of activation for the formation of the hydrohalic acid and reactive alkyl group. Note that this ϵ_a is more

than the ϵ_a for the reaction of the alkyl group with the molecular halogen. This step, the one with the greatest ϵ_a , is the one that determines the overall rate of the reaction. The top of the speed bump is called the intermediate or transition stage or state.

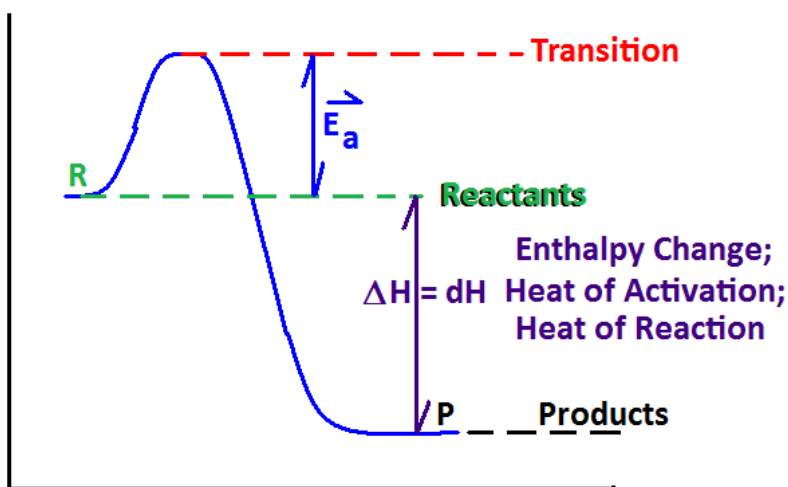
Halogens

A last note about halogens. Not all halogens are created equally. Iodine is a funny one. The problem with iodine is that in reaction "B", the energy of activation is +27 kcal. This reaction is endothermic, making it very slow and difficult. Reaction "A", the dissociation of molecular iodine to atomic iodine, is slow, which "triggers" chain terminating steps instead of chain propagating steps. Hence, this means that for iodine, effectively, there is NO chain.

Transition State

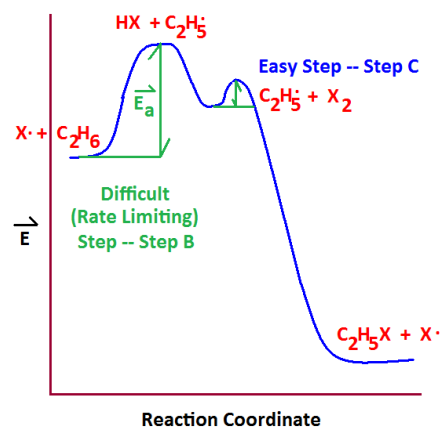
A chemical reaction is a process that does NOT go from "A" to "D" with nothing in between. It HAS to have intermediates, i.e., something in between "A" and "D", like "B" and "C". "B" and "C" are the intermediates -- neither products nor reactants, but in between them. Another way to consider it is as a gradual transition from reactant to product.

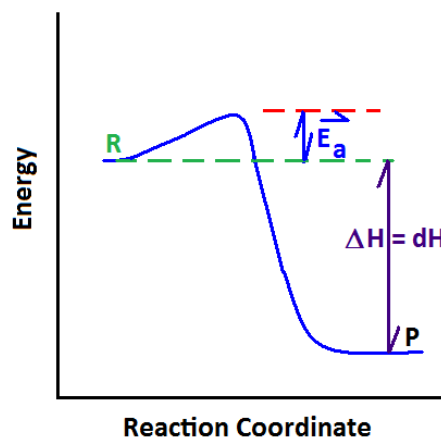
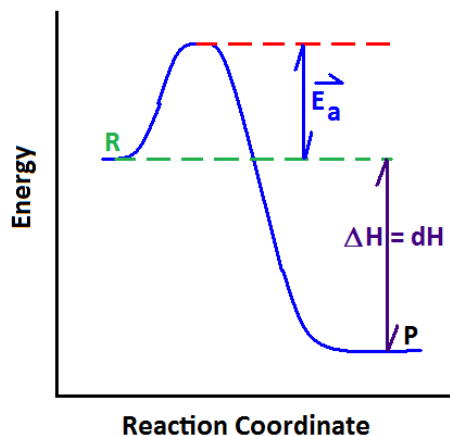
Intermediates, while difficult to isolate, are, nevertheless, treated as molecules to visualize the reaction process. Intermediate structure[s] is [are] called the transition state[s] and on an energy diagram corresponds to the top of the energy peak (the "speed bump"), Figure, right. Of note in this graphic is the actual demarcation of the energy of activation (the difference in energy states between the energy of the reactants and the energy of the transition state) and the enthalpy change (the energy difference between the reactants and products, not including the transition state, and is also called the heat of activation).



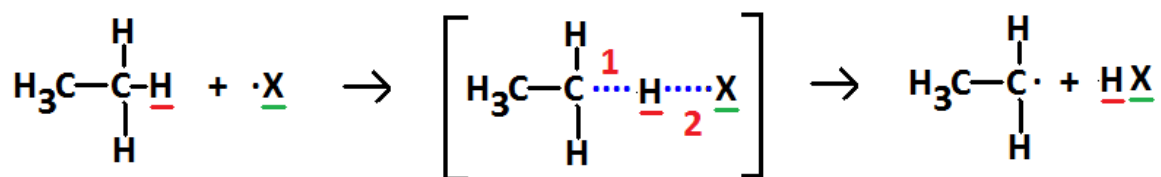
Transition State Stability

To understand this concept of transition states, let's study its stability. This is significant as **anything** that stabilizes the transition-state with respect to the reactants REDUCES the energy of activation. The large energy of activation in the top left graphic, next page, is what one would expect to find with an unstable intermediate. The small energy of activation in the top right graphic, next page, is what one would expect to find with a stable intermediate.

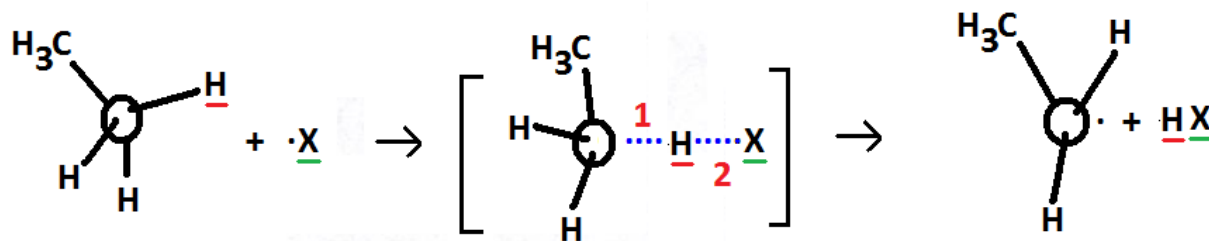




If, though, the transition-state is so rapid as to appear imaginary, how can we continue its progression to understand reactions? Let's use the halogenation of ethane with hydrogen atom abstraction/extraction as our example. note that we are starting with Reaction "B" -- the rate-limiting step. In order for the hydrogen atom to bond with the atomic halogen, the bond is stretched, but neither broken nor formed (**1 (bond stretched, not broken) and 2 (bond started, not formed)**), causing the one electron to be shared between the alkyl group and the halogen. Eventually, if there is enough energy to get over the speed bump (the energy of activation), the bonds "make or break". This means that the reaction "goes" as written and the alkyl group/radical and the hydrohalic acid are formed.



Note the orientation of the carbon atom as it goes through the reaction sequence. Note that the intermediate (transition-state) is somewhere "in between" an sp^2 and sp^3 hybridization as the electron is shared temporarily between the two moieties.



We can match the geometry with the energy. The carbon is in sp^3 hybridization on the left side of the energy diagram, goes through the sp^3/sp^2 hybridization at the top of the energy curve, then to the sp^2

hybridization at the bottom of the curve as it's in the reactive radical form and the hydrohalic acid is obtained.

When the energy of activation and the probability factor are replaced with the enthalpy change, ΔH , which is then combined with ΔS (entropy -- chaos -- of activation) arithmetically, we obtain the mathematical expression for determining Gibb's Free Energy, ΔG , which is equal to $\Delta H - T\Delta S$:

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

In general, if the ΔG is negative, the reaction goes as written; if the ΔG is positive, the reaction does not go as written. The smaller the ΔG (the more negative, that is), the faster the reaction.

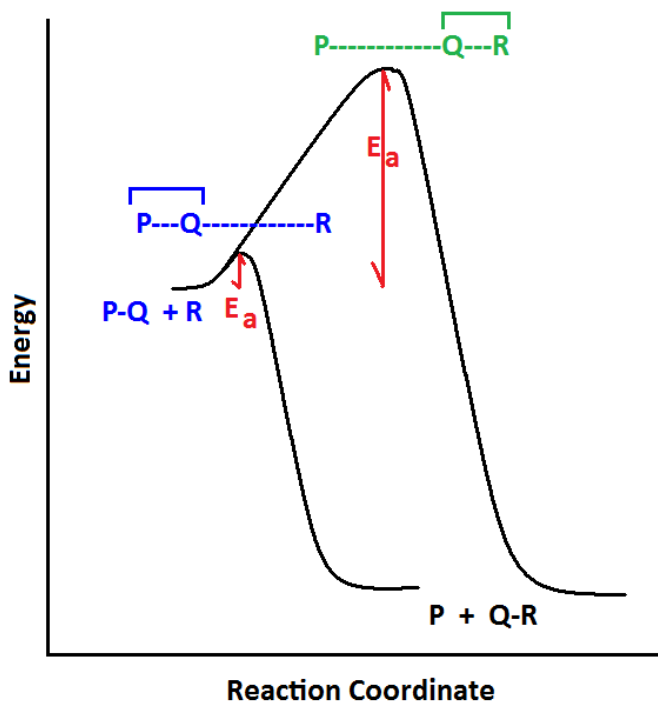
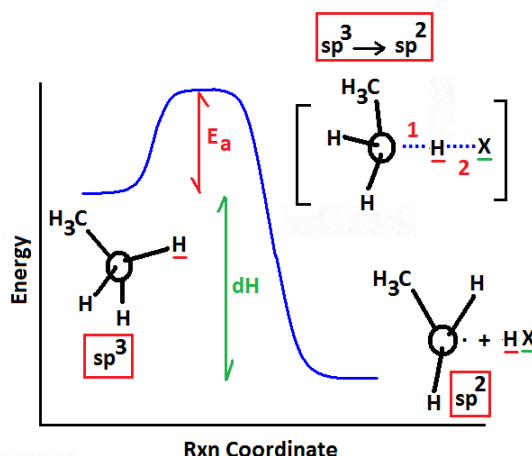
ASIDE: ΔS is chaos or entropy, i.e., equilibrium favors the side of the reaction where the atoms, molecules and/or ions are least restricted and the faster the reaction goes. A large (positive) ΔS means 1) few restrictions are placed on the transition state atomic positions and 2) the reaction goes rapidly. END OF ASIDE.

In addition, the greater the energy of activation, the later the transition state is reached in the reaction.

In this graphic, note that $PQ + R$ forms $PQ\cdots R$ at the top of the curve. This is a low energy of activation and the intermediates more closely resemble the reactants and the intermediate state is reached earlier. In the case where $PQ + R$ forms $P\cdots QR$, there is a higher energy of activation, the transition state is reached later and the intermediate more closely resembles the products. Therefore, attacks by reagents with high reactivity cause a transition state that resembles reactants -- with reagents with low reactivity, transition states resemble the products.

Hydrogen Abstraction/Extraction

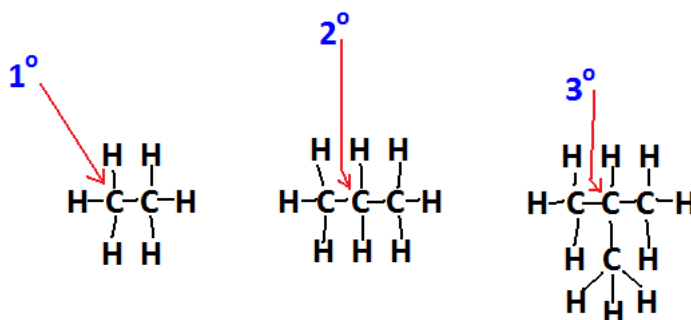
The energy of activation also explains the difference in removal of hydrogen from carbons in different positions in carbon chains. Carbons to which only one other carbon is directly attached (bonded) are first degree or primary carbons. Carbons to which only 2 other carbons are directly bonded are



secondary or second-degree carbons. Carbons that are directly bonded to 3 carbons are third degree or tertiary carbons.

The hydrogens bonded to the above-described carbons are called, primary, secondary or tertiary hydrogens based upon which carbon they are bonded to. The first example (ethane) in the graphic has only primary carbons. The middle example (propane) in the graphic has 2 primary carbons and 1 secondary carbon. The right example (isobutane) has 3 primary carbons and 1 tertiary carbon. The hydrogens on the carbons are labeled the same way, i.e., primary, secondary, tertiary.

In hydrogen abstraction, the controlling step is halogenation, i.e., hydrogen extraction with the atomic halogen. The figure illustrates, graphically, that the energies of activation for the removal of a **methyl hydrogen**, **primary hydrogen**, **secondary hydrogen** and **tertiary hydrogen** are highest for the methyl hydrogen and lowest for the tertiary hydrogen removal. That means that the tertiary hydrogen is easiest to remove and the methyl hydrogen is the most difficult hydrogen to remove.

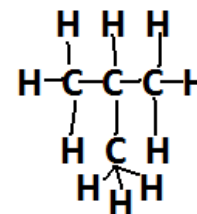
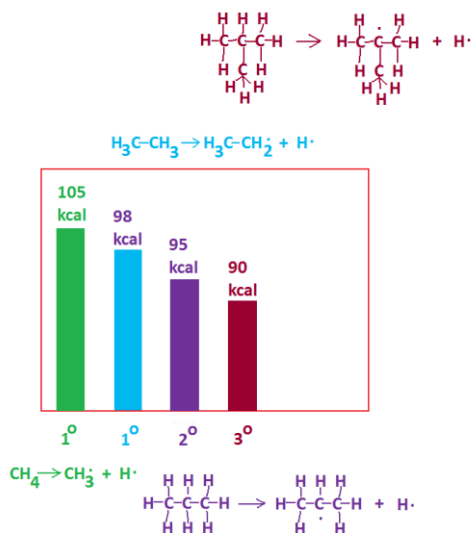


Based upon our discussion, thus far, we may draw the following conclusions: 1) the ease of reactivity of the hydrogen atoms go from tertiary to secondary to primary to methyl; 2) the intermediate with the lowest energy of activation will have the most stable intermediate; 3) the tertiary radical is the easiest to form and the methyl the most difficult.

Under normal hydrogen atom abstraction, the relative rates per hydrogen atom are (tertiary, secondary and primary, in order): 5.0 :: 3.8 :: 1.0. With this sort of information, we can predict the per cent of halogenated isomers from a specific hydrocarbon with single bonds between carbons (the definition of an alkane), e.g., isobutane, C₄H₁₀ -- this has only 2 possible mono-halogenated isomers (1-chloro-2-methylpropane and 2-chloro-2-methylpropane):

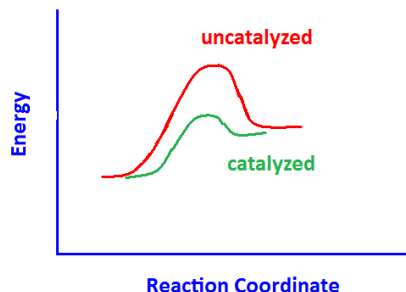
$$\frac{\% \text{ i - bu Cl}}{\% \text{ t - bu Cl}} = \frac{\# \text{ of } 1^\circ \text{ H} * \text{reactivity of } 1^\circ \text{ H}}{\# \text{ of } 3^\circ \text{ H} * \text{reactivity of } 3^\circ \text{ H}} = \frac{9}{1} * \frac{1.0}{5.0} = \frac{9}{5} \Leftrightarrow \frac{64\% \text{ i - bu Cl}}{36\% \text{ t - bu Cl}}$$

The relative rate of extraction per hydrogen atom is alterable by increasing the absolute temperature, which increases primary hydrogen extraction the greatest and increases tertiary hydrogen atom extraction the least AND equalizes the ratios of **5.0 :: 3.8 :: 1.0 to 1 :: 1 :: 1**, Figure, top next page. Thus, we may make a general statement: with increasing temperature, a specific reagent becomes LESS

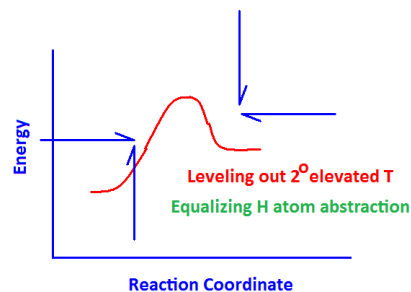


selective towards the site of reagent attack, e.g., levels out energy of activation differences and equalizes hydrogen atom abstraction.

Catalysts



Catalysts, likewise, reduce the energy of activation to speed up the reaction, Figure, left. This graphic compares the rate of the same reaction where one has a high energy of activation (**uncatalyzed**) and the other has a **catalyst** added and has a significantly lower energy of activation.



An Overview of Nuclear Chemistry

Many of you will have never seen anything about nuclear chemistry in your "pre" classes, yet will be expected to understand something about it in your "advanced" coursework or continuing education, e.g., WMD's, hence, an overview section is presented here.

The table, below, summarizes the salient features differentiating nuclear chemistry from "ordinary" chemistry.

Nuclear Chemistry	Ordinary Chemistry
Elements are converted from one to another.	No new elements are produced.
Particles within the nucleus are involved.	Usually only the outermost electrons are involved.
Tremendous amounts of energy are released or absorbed.	Relatively small amounts of energy are released or absorbed.
The rate of the reaction is NOT influenced by external factors.	The rate of the reaction is dependent upon factors like concentration, absolute temperature, catalyst, pressure, ad nauesum.

Definitions

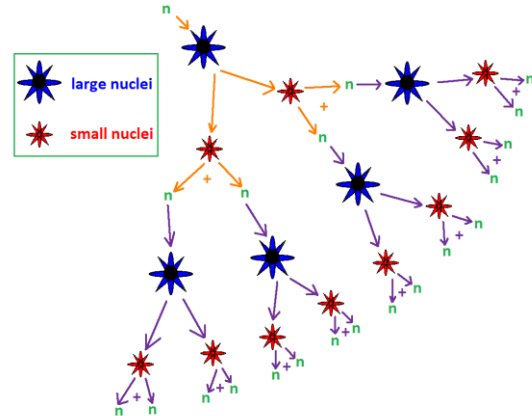
Nuclear fission is defined as splitting a heavy nucleus into lighter nuclei. Nuclear fusion is defined as the combination of light nuclei to make a heavy nucleus.

Nuclear Fission

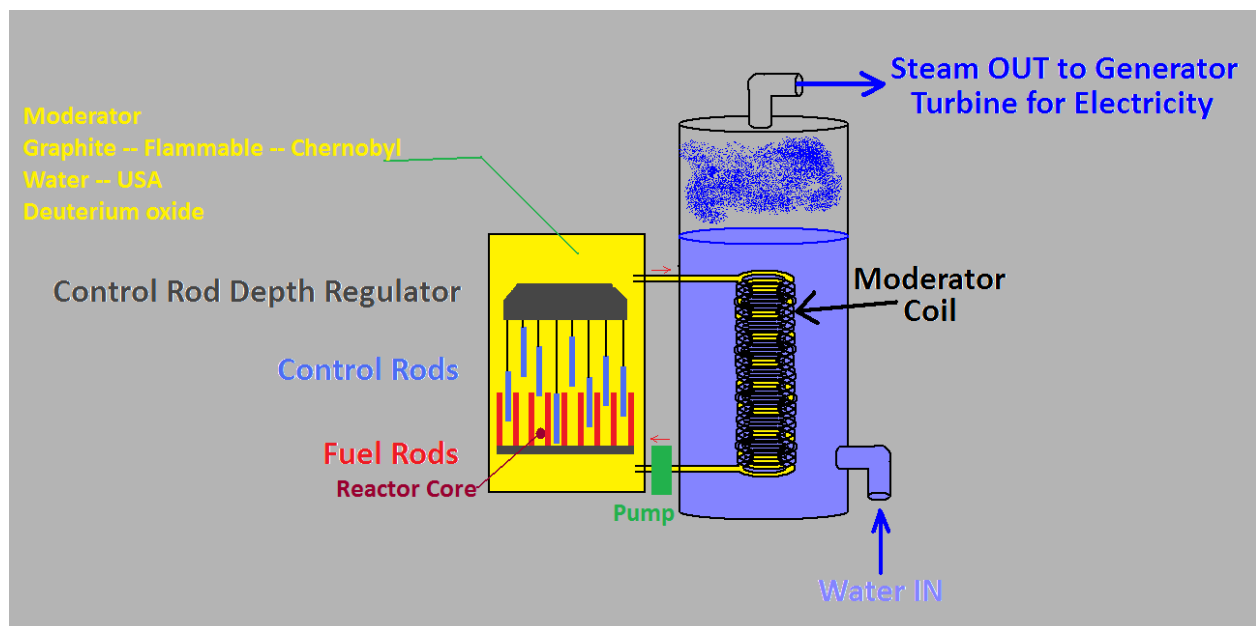
Splitting a heavy nucleus into 2 or more lighter nuclei with the release of energy (Image top next page). Fission PRODUCES more neutrons than it UTILIZES. HENCE: Nuclear Chain Reaction occurs. This liberates huge amounts of energy and can quickly get out of control without some kind of regulation. Minimum mass required to support this self-sustaining chain reaction = CRITICAL MASS.

Subcritical Mass

Less than critical mass; most neutrons escape into surroundings without hitting a nucleus. First A-bombs (Trinity and Fat Man): subcritical mass wedges surrounded by Implosives; Little Boy was a gun-type atomic bomb. Drove wedges together to each critical mass. Explosion: 0.01-0.02 megaton blast in 1945. In 1995, add a few grams of tritium to improve efficiency of explosion: 60 megaton. (REFERENCE: **ALL bombs exploded in WW II = 6 megatons**)



Fission Reactor



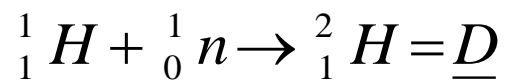
Control Rods: made from neutron absorbing metals: Cd and B. Too few neutrons and reaction dies out. Too many neutrons and get overheating, core melted down and maybe thermonuclear explosion (SAFETY SYSTEMS!) Moderator: slows neutrons to most appropriate Energy for ^{235}U fission initiation.

Fission Rate Regulation

Increase Fission Rate: Raise control rods in core; Decrease Fission Rate: Lower control rods in core. When rods are full "IN" core, shuts down reactor.

Fuel Rods

Are enriched from 0.7% to 3.0% used with water because increased numbers of neutrons combine with hydrogen instead of uranium, right. D_2O is more efficient because



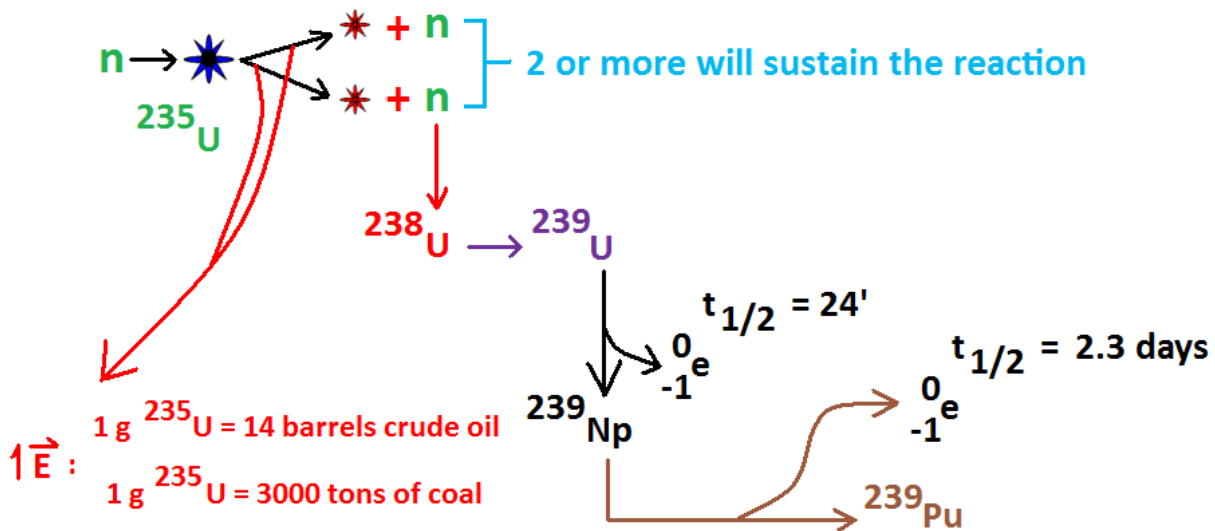
neutrons do NOT combine well with deuterium.

Therefore, D₂O reactor runs on the cheaper 0.7% fuel pellets (in the rods; UO₂), BUT, D costs money to make, hence 6 of one and a half dozen of the other.

Supercritical Mass

More than the critical mass; Most neutrons will hit nucleus; If this happens to be ²³⁵U or ²³⁹Pu, will cause explosion

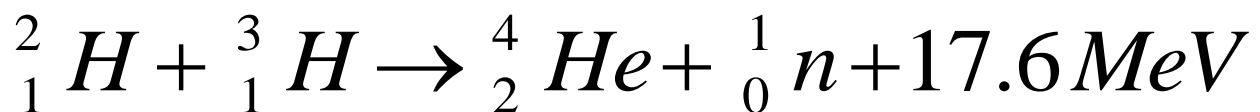
- Trinity, 16 July 1945, Los Alamos
- Little Boy, 6 August 1945, Hiroshima
- Fat Man, 9 August 1945, Nagasaki



- Ivy Mike, 1 November 1952, Enewetak Atoll

FUSION

Combination of light nuclides to form heavy nuclides – are THERMONUCLEAR REACTIONS because they only occur at high temperature. “Cold Fusion” – never reproduced. FUSION REACTORS: best so far seems to be:



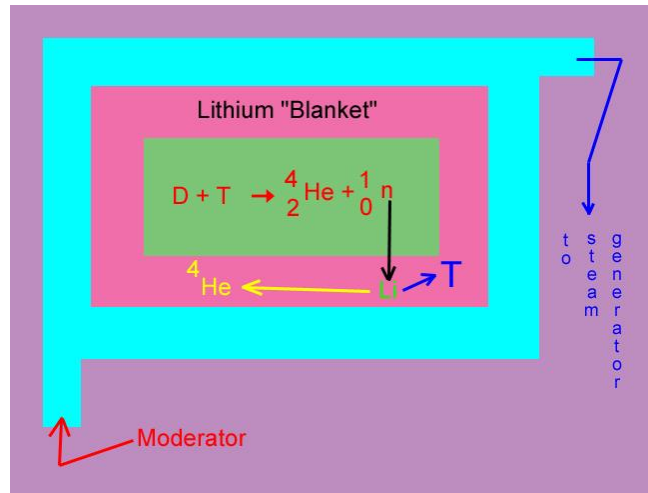
This reaction requires an energy of activation of 10 keV, but the energy obtained is 17.6 MeV! Fusion reaction products do NOT produce waste with long half lives.

PROBLEM

T is very rare – how make more? With Li! Wrap D and T in a Li “blanket”

Li Blanket Tritium Production

BIG Problem: the temperature required to run the D+T reaction in the Li blanket is 2×10^8 K! At this temperature, matter is present as PLASMA: gas made up of separated electrons and positively charged nuclei. Plasma is the fourth state of matter. Simply stated, a plasma is an ionized gas, a gas into which sufficient energy is provided to free electrons from atoms or molecules and to allow both species, ions and electrons, to coexist. How do you confine this "plasma"? It vaporizes everything solid known to man!

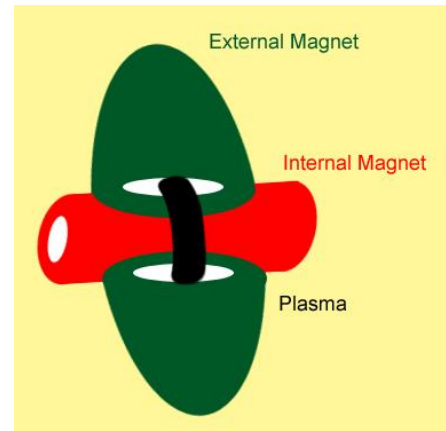


Magnets Confine the Plasma

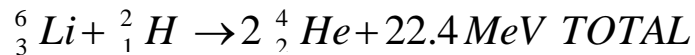
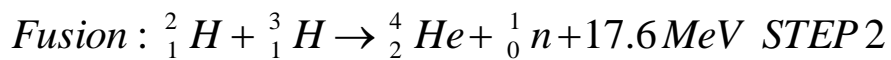
This answer was reached in response to learning that magnetic fields are known to restrict motion of charged particles in space.

Fusion

Greatest success, though, so far, is the hydrogen bomb (H-bomb) Lithium-6-deuteride: ${}^6\text{Li}^2\text{H}$ or ${}^6\text{LiD}$. The energy from the fission portion of the 2-step reaction is in the form of γ emissions. This energy is used to "drive" the second reaction to completion.

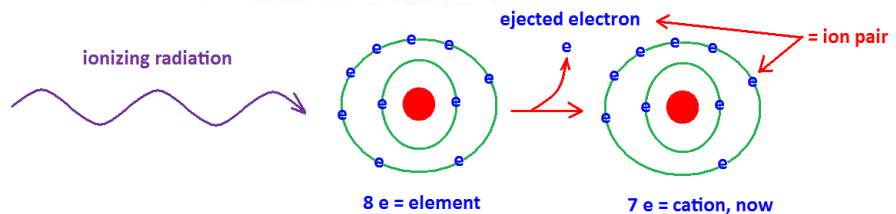


Two Staged Reaction



Ionizing Radiation

Ionizing radiation is defined as any type of radiation which has the energy to "bump" an orbital electron from the atom with which it is interacting.



The remaining product (the cation and the ejected electron) is called an ion pair.

Ionizing Radiation

Emissions with enough energy to ionize/fragment atomic particles along the path of the emissions. Hazardous to health because can cause damage to living cells and cause genetic defects, as well. Examples include Hiroshima and Nagasaki – 1945, Chernobyl – 1986, Fukushima – 2011.

RadioACTIVITY

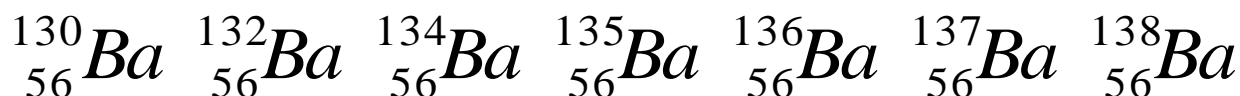
The number of atoms that disintegrate per unit time; SI = Becquerel (Bq) = 1 disintegration per second (dps) OR Curie (Ci) = disintegration rate of 1 gram of Radium (3.7×10^{10} dps); 1 Ci = 3.7×10^{10} Bq

Atomic Nomenclature of Nuclear Arrangements

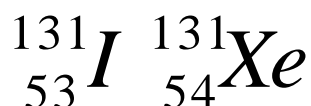
Definitions and Terms

Arrangement	Atomic number	Atomic mass	Neutron number	Examples
Isotope	Same	Different	Different	Barium Nuclides
Isobar	Different	Same	Different	Iodine and Xenon
Isotone	Different	Different	Same	Iodine, Xenon and Cesium
Isomer	Same	Same	Same	Glucose and Galactose

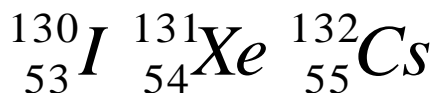
Barium Nuclides -- **Isotopes** – note atomic NUMBER



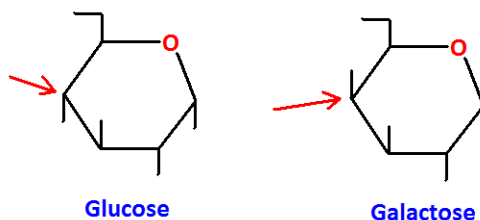
Iodine and Xenon – **Isobars** – Note atomic weight



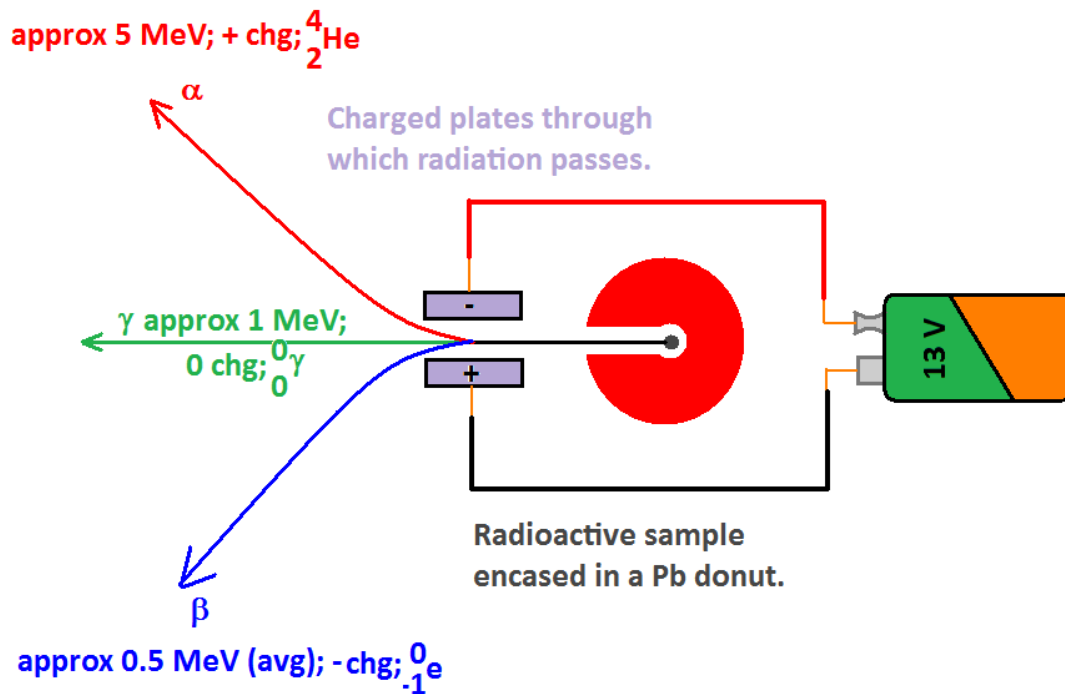
Iodine, Xenon and Cesium – **Isotones** – note difference between mass and number = 77 neutrons



Glucose and Galactose -- **Isomers**

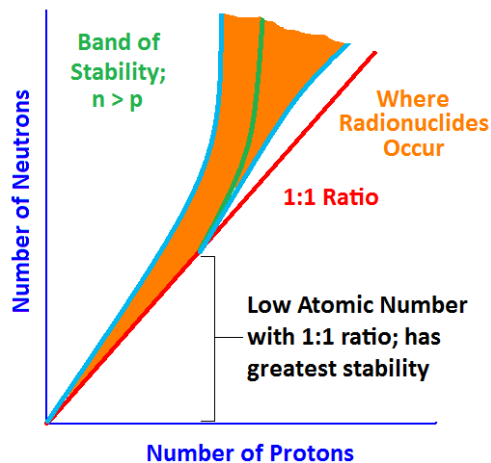
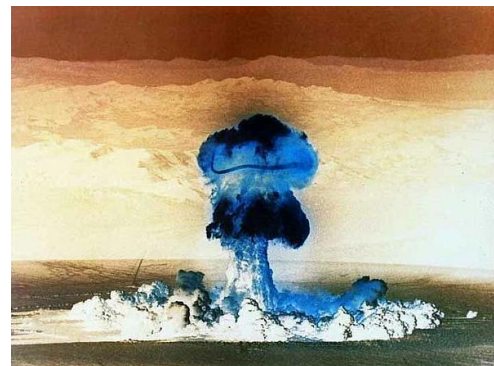


Radionuclides/Radioisotopes: Nuclei that Decay Spontaneously



1 MeV = 1.602×10^{-13} J = 3.829×10^{-14} cal; 1.64×10^{-7} Watts when measured for 1 hour or 2.20×10^{-4} HP;

The average energy released from fission of one Pu-239 atom = 210 MeV (0.046 HP; 1000 atoms of Pu-239 = 46 HP = 1.663×10^{-21} mol Pu-239 ~ 1970 VW 1600 cc engine horse power ~ horsepower in HD 883 at 6000 rpm). **1 mol Pu-239 fissioning (assuming 100% fission) = 7.65×10^{22} HP = 239 g ~ 0.5 lb; 6.2 kg (13.64 lbs) of Pu-239 used in Trinity → 2.09×10^{24} HP → 1.34×10^{21} kT of TNT – in reality, only about 18-20 kT of TNT equivalence.** Colors inverted in image of Trinity at right.

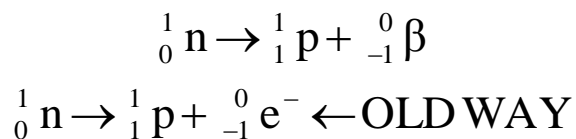


In order to "be" a radioisotope, an element must be above or below the band of stability. This band of stability is shown, left. It is determined by plotting the number of neutrons in an element vs the number of protons in that same element. Note that the band of stability does NOT follow a one to one ratio, rather it is curvilinear, following the one to one (1:1) ratio at low molecular weights (these elements have the greatest stability). Once this region is passed, the curve begins to take on 1.2:1, 1.4:1 and 1.5:1 ratios, i.e., a curvilinear relationship. The region marked by the orange color above and beneath the band of

stability (solid green line), but NOT including the band, itself, is the region where radioactive nuclides occur.

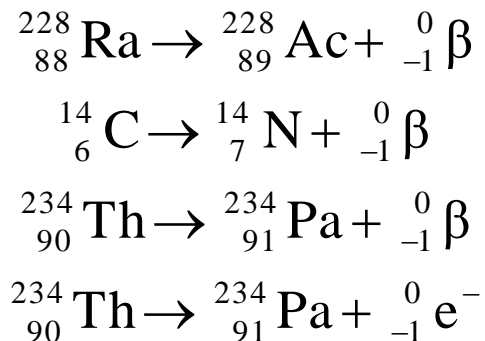
Decay Equations – Particulates

Above the Band of Stability



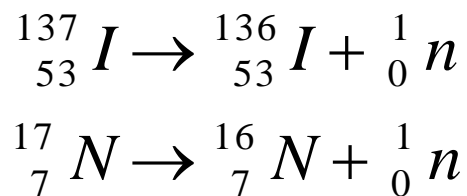
In this case, the number of neutrons is much greater than the number of protons so these nuclides want to lower their n/p ratio. There are two mechanisms by which they can do this: beta (β) decay or neutron emission. β -emission occurs when a neutron decomposes to a proton and an electron. Note the "old way" of showing this, as there are still those of us around who demonstrate it this way.

Examples of β -emission are illustrated below. Note that the top number is the atomic mass and the bottom number is the atomic number. Note also that the numbers all add up on both sides of the reaction (decay), hence, 228 radium 88 (Molecular Weight, Element, Atomic Number) decays to 228 actinium 89 and an electron. Likewise, 14 carbon 6 decays to 14 nitrogen 7 and an electron. 234 thorium 90 decays to 234 protactinium 91 and an electron.



Neutron Emission

Although neutron emission is uncommon, there are some examples below. Note that 137 iodine 53 decomposes to 136 iodine 53 and a neutron. 17 nitrogen 7 decays to 16 nitrogen 7 and a neutron.



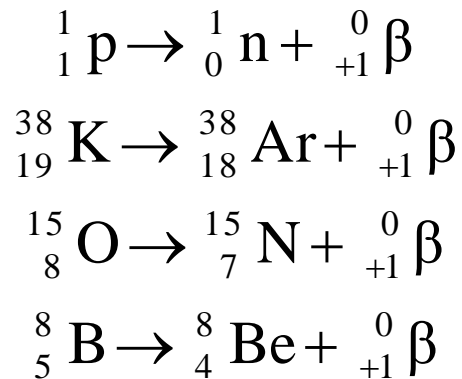
Decay Equations – Particulates

Below the Band of Stability

In this instance, the nuclides want to raise their n/p ratio. They may do this via positron emission or by K electron capture. It is of great importance to remember that the "K" referred to in the previous sentence is NOT a potassium ion, rather it is a K shell electron that will be captured.

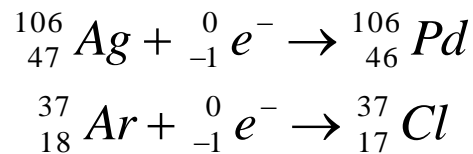
Positron Emission

In positron emission, a proton is decomposed to a neutron with a mass of 1 and a charge of zero and a positively charged electron (positron) of mass zero and a charge of +1. Examples of positron emission are shown right. Note that 39 potassium 19 decays to 38 Argon 18 and a positron. 15 oxygen 8 decays to 15 nitrogen 7 and a positron. 8 boron 5 decays to 8 beryllium 4 and a positron.



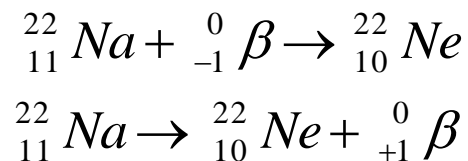
K Capture

Examples of K capture are illustrated below. Note that 106 silver 47 captures an electron (K type) to form 106 palladium 46. 37 argon 18 captures an electron to form 37 chlorine 17. 7 beryllium 4 captures a K electron to form 7 lithium 3.



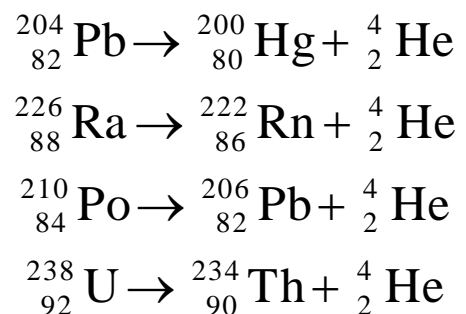
Some Radioisotopes Undergo Both Positron Emission and K Capture

3% of the time, 22 sodium 11 captures a K electron to form 22 neon 10. 97% of the time, 22 sodium 11 undergoes positron emission to form 22 neon 10.



Below the Band of Stability or with Atomic Number > 82

The particles emitted members of this group are helium atoms (${}^4\text{He}_2$; read 4 helium 2) and the decay is called alpha (α) decay or emission. The emission of an α particle raises the n/p ratio, right. 204 lead 82 undergoes alpha decay to form 200 mercury 80 and a helium atom. 226 radium 88 undergoes alpha decay to form 222 radon 86 and a helium atom. 210 polonium 84 decays to 206 lead 82 and a helium atom. Note that the



numbers add up, again, on both sides of the decay equation. 238 uranium 92 decays to 234 thorium 90 and a helium atom.

Thus far we have looked at particulate forms of ionizing radiation. Remember that electromagnetic radiation has dualistic properties, i.e., it has both particulate properties and wave-form properties. The wave-form properties are the next area of study.

Characteristics of Selected Radiations

We have examined the decay of some nuclides in terms of very superficial chemistry. We have not examined them in terms of the ranges they will travel in two media: air and soft tissue. The table, below, does exactly that:

Type of Radiation		Range	
		In Air	In Soft Tissue
α	Particulate	1-10 cm	0.1 mm
β		0-10m	0-2 cm
X	Wave-form	0-100 m	0-30 cm
γ		0-100 m	0-30 cm

The clinical correlation to this is that α particles can be stopped with newspaper, β particles can be stopped with appropriate "plastic" shielding; X and γ rays will penetrate the body –

Point: 1) detrimentally, e.g., Hiroshima and Nagasaki and/or 2) usefully as in x-rays of the body for diagnostic purposes.

Keep in mind that as the patient becomes more and more obese that it becomes more and more difficult to obtain meaningful radiographs "on" these patients.

Gamma radiation has been shown to be very safe in sterilizing foodstuffs for long term storage and to prevent infectious, fatal, bacteria from causing disease, e.g., E. coli strains (O157H7) that have caused JITB syndrome.

The general public, though, remains uninformed and fears this technology -- much like the fear felt when MRI was called NMR imaging. Didn't change the technology, just changed the name and blitzed the public with a spin on the technique.

Decay Equations -- Wave-Form

Gamma (γ) Radiation

When a positron (anti-matter) collides with an electron (matter), the process is called annihilation and gamma rays are emitted. Positrons are short-lived as there are so many electrons present in nature. Gamma radiation is high-energy radiation.

Remember back to earlier CHEM 121 lectures about Planck's and Einstein's equations, below. Remember, too, that when these two equations are equated, that they tell us that mass may be converted to energy -- Hiroshima and Nagasaki are devastating reminders of this concept.

$$E = h\nu$$

Planck's

$$E = mc^2$$

Einstein's

$$h\nu = mc^2$$

$$\frac{h\nu}{c^2} = m$$

Let's take a look at Planck's equation, first. Max Planck observed a relationship between energy, the speed of light in a vacuum, the wavelength of light and a proportionality constant. The latter was named in his honor

$$E = \frac{hc}{\lambda} = h\nu$$

Remember that $\nu = \frac{c}{\lambda}$

$$c = 3 * 10^8 \text{ m/s}$$

$$h = 6.626 * 10^{-34} \text{ Js}$$

$$\nu = \text{sec}^{-1}$$

and is called Planck's constant. As you can see in this figure, energy is related to the frequency of the "light" through the speed of light (c) and its wavelength (l). While the values for c and Planck's constant (h) are shown in the graphic, you are not going to be held accountable for memorizing them.

$$E = h\nu = \frac{hc}{\lambda}$$

$$\lambda = \frac{hc}{E} = \frac{(6.626 * 10^{-34} \text{ Js})(3 * 10^8 \text{ m/s})}{5 \text{ J}}$$

$$\lambda = 3.9756 * 10^{-26} \text{ m}$$

$$\lambda = 3.9756 * 10^{-26} \text{ m} \left(\frac{1 * 10^9 \text{ nm}}{1 \text{ m}} \right) = 3.975 * 10^{-17} \text{ nm}$$

Planck's equation works for visible light and "invisible" light (ionizing radiation), as well. In this graphic, we are asked to determine the wavelength of light that gives off 5 Joules of energy. Note that when the numbers are crunched that the answer comes out in meters. For the most part, we prefer to work in units of nm, hence the answer is converted to nm from m.

$$E = h\nu = \frac{hc}{\lambda}$$

$$\lambda = \frac{hc}{E}$$

$$\lambda = \frac{(6.626 * 10^{-34} \text{ Js})(3 * 10^8 \text{ m/s})}{9.035 * 10^{-19} \text{ J}}$$

$$\lambda = 2.20 * 10^{-7} \text{ nm}$$

$$\lambda = 2.20 * 10^{-7} \text{ nm} \left(\frac{1 * 10^9 \text{ nm}}{1 \text{ m}} \right) = 220 \text{ nm}$$

Another example follows left to determine the wavelength of light: the energy given off by a beam of light is $9.035 * 10^{-19}$ Joules (J). What is the wavelength of the light? As you can see in the solution, the wavelength of light is 220 nm -- in the ultraviolet region of the spectrum.

Let's combine Planck's and Einstein's equations so that we may ask: what is the mass equivalent of a 400 nm photon of light? Note that the correct answer is 5.522 milli-

$$\text{since } E = E$$

$$h\nu = mc^2$$

$$\therefore m = \frac{h\nu}{c^2} = \frac{hc}{c\lambda} = \frac{h}{c\lambda}$$

$$m = \left(\frac{6.626 * 10^{-34} \text{ Js (s)}}{(3 * 10^8 \text{ m}) (400 * 10^{-36} \text{ m})} \right)$$

$$m = 5.522 * 10^{-36} \text{ kg} \Leftrightarrow 5.522 \text{ mafg}$$

atto-femto-grams, i.e., an incredibly small mass.

Energy Loss Mechanisms for Gamma Rays

The table, below, summarizes the three energy loss mechanisms with graphics following to illustrate these concepts:

Energy Loss Mechanisms for Gamma Rays	
Name	Definition
Photoelectric Effect	Gamma energy is absorbed with an inner shell electron ejected.
Compton Scattering	Alters the flight and energy of the gamma radiation with ejection of an outer shell electron.
Pair Production	The loss of a whole nucleus with electron and positron pair produced.

Photoelectric Effect

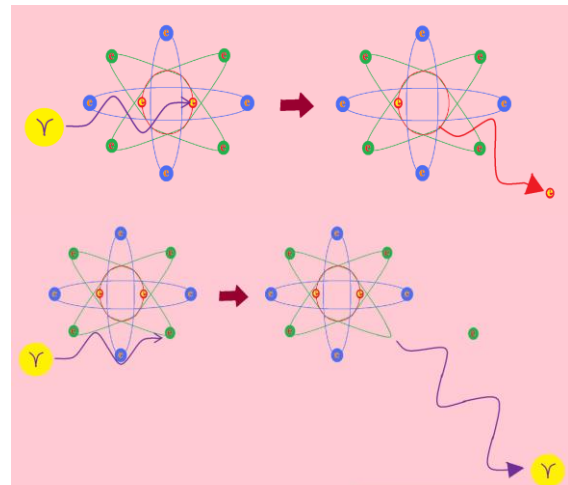
Gamma energy is absorbed with an inner shell electron ejected.

Compton Scattering

Alters the flight and energy of the gamma radiation with ejection of an outer shell electron.

Pair Production

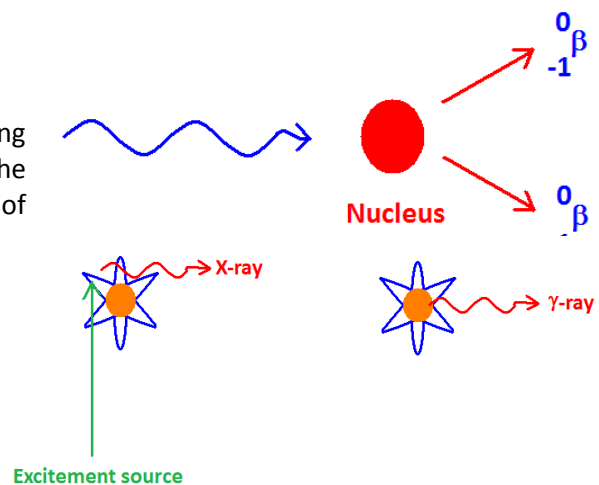
The loss of a whole nucleus with electron and positron pair produced.



Gamma Radiation vs X-Radiation

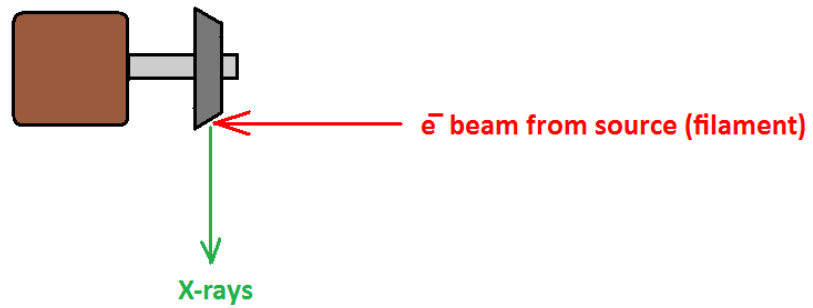
The putative sources of both of these sorts of ionizing radiation. It seems that the source of x-radiation is the electron cloud after excitation while the source of gamma radiation is from the nucleus of a radioactive atom. The former is commonly encountered via an electrical machine and the latter is spontaneously emitted.

At this level the "only" difference is the SOURCE -- BUT! If their energies are identical, you can't tell them apart.

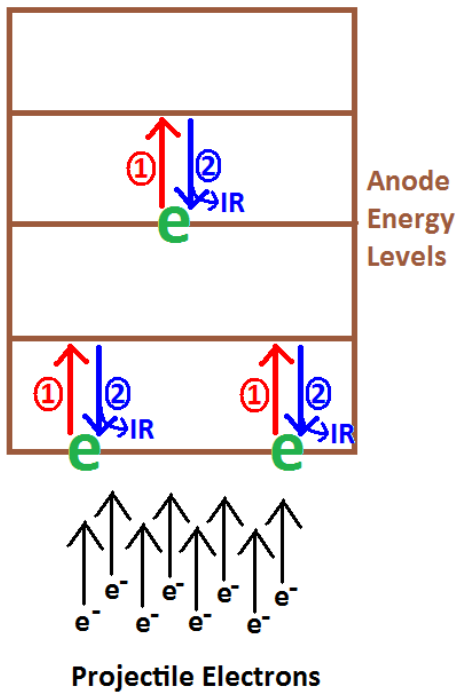


The Production of X-Radiation

The general idea behind the production of x-rays for clinical applications. In general, an electron beam is bombarded from a source (a filament) against a rotating anode (the "whirring" sound you've heard when you get an x-ray).



The electrons interact with the electron clouds (raising the electrons to a higher state, then relaxing them -- Figure at right -- blow up of electron clouds' energy levels) causing the x-rays to be "shot through" the patient onto x-ray film. Additionally, as the electrons relax, they give off infra-red energy -- heat! This is one reason why x-ray exam rooms are cold -- to preserve the rotating anode so it will last a long time (the oil in the head helps with this, too). The other reason has to do with the perceived fear of the "movement" of x-rays, i.e., in the early days, people were afraid that x-rays would travel throughout the building through the heating ducts and spread out over the building "twitching" everyone in it -- doesn't happen, yet still carries over as the lack of heating in many of these rooms even today.



You may have noticed in many emergency rooms (although this is changing), operating rooms and dentists' offices that when you get x-rays taken that there is no "whirr" -- only a "click". This is because many use fixed anodes for these machines. A fixed anode does not rotate. When bombarded with projectile electrons, the fixed anode develops a "pit" at that site and burns out faster than a rotating anode which is hit in many different spots by electrons.

It is important to also keep in mind that when working with β -emitters (electron emitters) that you do NOT want to protect yourself by placing lead shielding between you and it: x-rays will be formed! Use layers of multi-density "plastics" that are available.

Radiation "Dosage"

RAD = Radiation Absorbed Dose – the amount of radiation that results in the absorption of 0.01 J/kg of irradiated material. RBE = Relative Biological Effectiveness: α , p^+ , 1_0n RBE = 10; β , γ , x-rays RBE = 1 -- MEANING: 10 times the former are necessary to cause the same effect of the latter. REM: Radiation Equivalent for Man: Dose (REM) = RAD * RBE

USEPA Radiation Exposure Limits for Man

Radiation Workers: 5 REM/year; General Population: 0.5 REM/year; Average Natural Exposure: 0.15 REM/year; A SINGLE 500 REM dose will kill ½ of the exposed population within 30 days!

The Inverse Square Law

This law says that the intensity of radiation decreases by the square of the distance moving away from the source. Conversely, it says that the intensity of radiation increases by the square of the distance moving towards the source. Figure right illustrates this arithmetic relationship. Note that "I" is intensity and "d" is distance; "1" and "2" are self-explanatory.

$$\frac{I_1}{I_2} = \frac{d_2^2}{d_1^2} = \left(\frac{d_2}{d_1} \right)^2$$

An example: the intensity of x-rays at 4 feet is 10 intensity units (we're not gonna get hung up on the correct units -- I want you to get the idea of this). What is the intensity at 16 feet? By crunching the numbers, we find that the answer is 0.625 intensity units.

$$\frac{I_1}{I_2} = \frac{d_2^2}{d_1^2}$$
$$\frac{I_1 d_1^2}{d_2^2} = I_2$$

The reverse process, i.e., as we get closer to a source of radiation: the intensity of gamma rays at 8 feet is 8 intensity units. What is the intensity at 2 feet? The answer is 128 intensity units.

$$I_2 = \frac{(10)(4)^2}{(16)^2} = 0.625 \text{ intensity units}$$

$$\frac{I_1}{I_2} = \left(\frac{d_2}{d_1} \right)^2$$

$$I_1 \left(\frac{d_1^2}{d_2^2} \right) = I_2 = 8 \left(\frac{8}{2} \right)^2 = 128 \text{ intensity units}$$

The Rate of Decay

When working with radioactive compounds, it's always nice to know how long they'll "be around", e.g., ^{99m}Tc, thallium, radioactive iodine -- all used in clinical scenes for different scans. The decay of radioisotopes follows first-order kinetics:

$$\ln \left(\frac{A_o}{A} \right) = kt$$

- Note that
 - "ln" stands for natural log;
 - "A_o" is the concentration of "A" (the radioactive substance) at time zero;
 - "A" is the concentration of "A" at time = "t";
 - "t" = that time;
 - "k" is the decay constant (a fudge factor that is different for every nuclide).

Part of understanding the arithmetic behind the decay of nuclides is determining the half-life of the substance. The half-life ($t_{1/2}$) is the time it takes for 50% of your sample to decay (top left next page). Half life is NOT effected by chemical combination or by temperature or pressure changes.

The application of these two equations follows on the next slide (half-life determination [one may also obtain the rate (decay) constant from this equation, as well] and first-order kinetics, respectively) in example form:

$$A_o = 1 \quad \wedge \quad A = 0.5$$

$$\ln\left(\frac{A_o}{A}\right) = k t_{1/2}$$

$$t_{1/2} = \text{half life}$$

$$\ln\left(\frac{1}{0.5}\right) = k t_{1/2}$$

$$\ln 2 = k t_{1/2}$$

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

If the half life for 90 strontium 38 is 28 years and you have a 0.5 g sample, how much 90 strontium 38 was present 14 years ago? Note that the original sample (calculated) had an activity mass of 0.7072 g. For perspective, consider that a good portion of the radioactive waste that is being proposed to be stored in southern Nevada has a half life

on the order of several billion years. Not a problem in our life-time -- for future generations, though, consider the possibilities and draw your own conclusions.

$$1) \quad t_{1/2} = \frac{\ln 2}{k}$$

$$k = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{28 \text{ yrs}} = 0.02475 \text{ yr}^{-1}$$

$$2) \quad \ln \frac{A_o}{A} = kt$$

$$\ln A_o - \ln A = kt$$

$$\ln A_o = kt + \ln A$$

$$\ln A_o = (0.02475)(14) + \ln 0.5$$

$$\ln A_o = -0.3465$$

$$A_o = \text{anti ln} - 0.3465$$

$$A_o = 0.7072 \text{ g}$$

Problem Set 7

1. What kind of bond exists between Li and Br in LiBr?
2. What kind of bond exists between Ba and O in BaO?
3. What kind of bond exists between Al and N in AlN?
4. What kind of bond exists between Sr and S in SrS?
5. There are 2 parts to this question: 1) balance the following reactions and 2) identify which of these reactions is redox decomposition, non-redox decomposition, redox combination, non-redox combination, single replacement or double replacement reactions:

- A) $\text{Mg} + \text{Cl}_2 \rightarrow \text{MgCl}$
B) $\text{Na} + \text{N}_2 \rightarrow \text{NaN}_3$
C) $\text{Ba} + \text{S} \rightarrow \text{BaS}$
D) $\text{NaOH} + \text{H}_2\text{SO}_4 \rightarrow \text{NaSO}_4 + \text{H}_2\text{O}$
E) $\text{LiCO}_3 + \text{HCl} \rightarrow \text{LiCl}_2 + \text{H}_2\text{O} + \text{CO}_2 \uparrow$
F) $\text{Sr}(\text{NO}_3)_2 + \text{HCl} \rightarrow \text{SrCl} + \text{HNO}_3$
G) $\text{K} + \text{H}_2\text{O} \rightarrow \text{KOH} + \text{H}_2 \uparrow$
H) $\text{Al} + \text{O}_2 \rightarrow \text{Al}_2\text{O}_3$
I) $\text{MnSO}_4 + \text{HNO}_3 \rightarrow \text{Mn}(\text{NO}_3)_2 + \text{H}_2\text{SO}_4$
J) $\text{Fe} + \text{O}_2 \rightarrow \text{Fe}_3\text{O}_4$

Problem Set 3

1. How many mol of H_2SO_4 do you have if you have 24.5 g H_2SO_4 ?
2. How many mol of NaOH do you have if you have 10 g NaOH?
3. How many mol of $\text{C}_6\text{H}_{12}\text{O}_6$ do you have if you have 45 g $\text{C}_6\text{H}_{12}\text{O}_6$?
4. How many grams of CuSO_4 are present in 0.25 mol of CuSO_4 ?
5. How many grams of $\text{Al}(\text{OH})_3$ are present in 3.4 mol $\text{Al}(\text{OH})_3$?
6. How many grams of BaSO_4 are present in 0.78 mol BaSO_4 ?
7. $5 \cdot 10^{22}$ atoms of Li_2CO_3 are how many moles of Li_2CO_3 ?
8. $7 \cdot 10^{23}$ atoms of SrCl_2 are how many mols of SrCl_2 ?
9. $4 \cdot 10^{20}$ atoms of Li_2CO_3 are how many grams of Li_2CO_3 ?

Problem Set 5

1. Determine the % composition of Li in $\text{Li}_3\text{C}_6\text{H}_5\text{O}_7$.
2. Determine the % composition of Ca in $\text{CaSO}_4 \cdot 4\text{H}_2\text{O}$.
3. Determine the % composition of Mg in MgNH_4PO_4 .
4. Determine the % composition of H in MgNH_4PO_4 .
5. Determine the % composition of Cu in $\text{Cu}_3(\text{AsO}_4) \cdot \text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$.

Problem Set 9

1. 98 g H_2SO_4 are dissolved in 0.5 L H_2O . What is the resulting molarity of the solution?
2. 80 g NaOH are dissolved in 250 mL H_2O . What is the molarity of the solution?
3. 9.125 g HCl are dissolved in 300 mL H_2O . What is the molarity of the solution?
4. How many grams of $\text{Al}(\text{OH})_3$ are required to make a solution 0.25 M in 500 mL of solution?
5. 31.5 g HNO_3 are dissolved in 1 L H_2O . What is the molarity of the solution?

Problem Set 10

1. For the reaction $\text{SrCO}_3 + 2\text{HCl} \rightarrow \text{SrCl}_2 + \text{CO}_2\uparrow + \text{H}_2\text{O}$, how many grams of SrCl_2 are produced when 5 mL of 4 M SrCO_3 are reacted with HCl?
2. For the reaction $2\text{HCl} + \text{CaCO}_3 \rightarrow \text{CaCl}_2 + \text{CO}_2\uparrow + \text{H}_2\text{O}$, how many grams CaCl_2 are produced when 45 mL 0.34 M CaCO_3 react with the HCl?
3. For the reaction $\text{NaHCO}_3 + \text{HC}_2\text{H}_3\text{O}_2 \rightarrow \text{NaC}_2\text{H}_3\text{O}_2 + \text{CO}_2\uparrow + \text{H}_2\text{O}$, how many mL of 0.5 M $\text{HC}_2\text{H}_3\text{O}_2$ are required to react with 10 g NaHCO_3 ?
4. How many mL of 0.33 M HNO_3 are required to react with 15 g AgCl as follows: $\text{HNO}_3 + \text{AgCl} \rightarrow \text{AgNO}_3 + \text{HCl}$?
5. For the following reaction: $\text{N}_2 + 3\text{I}_2 \rightarrow 2\text{NI}_3$, if you start with 25 g I_2 and you obtain 15 g NI_3 , what is the per cent yield of NI_3 ?
6. For the following reaction: $2\text{Na} + 2\text{H}_2\text{O} \rightarrow 2\text{NaOH} + \text{H}_2\uparrow$, if you start with 10 g Na and you obtain 8 g NaOH, what is the per cent yield of NaOH?
7. For the following reaction: $\text{CO}_2 + \text{NH}_3 \rightarrow \text{CH}_4\text{N}_2\text{O}$ (urea) + H_2O , if you start with 6 g CO_2 and obtain 5 g urea, what is the per cent yield of urea?

Problem Set 8

1. If 2 mol HCl reacts with AgNO_3 as follows: $\text{HCl} + \text{AgNO}_3 \rightarrow \text{AgCl} + \text{HNO}_3$, how many mol AgCl are produced?
2. If 36.5 g HCl reacts with AgNO_3 as above, how many grams of AgCl will be produced?
3. If you also have 10 g AgNO_3 for the above two questions, which reagent is the limiting reagent?
4. Given the following reaction: $\text{N}_2 + 3\text{I}_2 \rightarrow 2\text{NI}_3$, if you have 28 g N_2 , how many grams of NI_3 will you be able to make?
5. If you also have 50 g I_2 for the above reaction in #4, what is the limiting reagent?

Problem Set 12

1. 454 g of paper are placed in a calorimeter at 25°C . The calorimeter has a mass of 3 kg and is made of iron. 500 kJ are added to the system. If the specific heat capacity of paper is 5 J/K/g, what is the final temperature of the system?
2. An aluminum pipe of 150 g is at 5°C . If the ends of this pipe are plugged after 400 g of Pb at 400°C are poured into it, what is the final temperature of the system?
3. A diamond container at 10°C has 150 g water at 75°C poured into it. The diamond container has a mass of 30 g. What is the final temperature of this system?