NavApp: Explosives Worksheet

Learning Objectives

- review key concepts learned throughout the semester
- define an explosive and differentiate between low and high explosives
- define and calculate the oxygen balance of an explosive
- calculate the heat of explosion in on a per mol and per mass basis
- balance an explosives reaction to determine the moles of gas formed and the volume at STP

1. Introduction

A chemical explosion is basically a combustion reaction, but not all materials capable of combustion reactions can be used as military explosives. We will see that explosive reactions typically release large quantities of gas and heat very rapidly; the expansion of that gas as a result of the heat leads to the high pressures that cause the damage. In this module we will explore the basics of explosives, and utilize some fundamental chemical principles we have learned to model how they work.

2. Chemistry in the Operating Forces

The DoDM 6055.09M defines an explosive as a substance or a mixture of substances that is capable by chemical reaction of producing gas at such temperature, pressure, and speed as to cause damage to the surroundings. Combustions generally require oxygen and a fuel; explosive materials typically contain oxygen and fuel in a proportion that supports very rapid combustion in an enclosed, airless space. An explosion reaction is the ignition and rapid burning of the confined energetic materials, which builds up high local pressures, leading to breakup of the confining structure. Whether utilizing weapons with explosive materials or defending against the enemy's explosive weapons, it is important to understand the chemistry behind the material. The military determines which explosive to use based on a variety of factors. While availability, cost and sensitivity of material all play a role, we will examine the composition, density, and strength of the material.

3. Features of a Chemical Explosion Reaction

A chemical explosive is a compound or mixture which, upon the application of heat or shock, decomposes or rearranges with extreme rapidity, yielding much gas and heat. Many substances not ordinarily classed as explosives may do one, or even two, of these things but, for a chemical to be an explosive, it must exhibit all of the following: (1) formation of gases; (2) evolution of heat; (3) rapid propagation of reaction through the material; and (4) capability of controlled initiation of reaction.

- Formation of Gases

Gases may be evolved from substances in a variety of ways. When wood or coal is burned in the atmosphere, the carbon and hydrogen atoms in the fuel combine with the oxygen in the atmosphere to form carbon dioxide and steam, together with flame and smoke. When the wood or coal is pulverized, so that the total surface area in contact with the oxygen is increased, and burned in a furnace or forge where more air can be supplied, the burning can be made more rapid and the combustion more complete.

Some examples: 1. dust explosion demo or video https://www.youtube.com/watch?v=Jg7mLSG-Yws
2. speeding up a barbecue with liquid oxygen: https://www.youtube.com/watch?v=1bjvj5FjUPE

- Evolution of Heat.

The generation of heat in large quantities accompanies every explosive chemical reaction. It is this rapid liberation of heat that causes the gaseous products of reaction to expand and generate high pressures. This rapid generation of high pressures of the released gas constitutes the explosion. It should be noted that the liberation of heat with insufficient rapidity will not cause an explosion. For example, although a pound of coal yields five times as much heat as a pound of nitroglycerin, the coal cannot be used as an explosive because the rate at which it yields this heat is quite slow.

-Rapidity of Reaction.

The very high speed of the reaction moving through the explosive material is one characteristic that distinguishes the explosive reaction from an ordinary combustion reaction. Unless the reaction occurs rapidly, the thermally expanded gases will be dissipated in the medium, and there will be no explosion. Again, consider a wood or coal fire. As the fire burns, there is the evolution of heat and the formation of gases, but neither is liberated rapidly enough to cause the effects associated with an explosion.

CHARACTERISTICS OF BURNING AND DETONATION (typical values)

CHARACTERISTICS	BURNING FUEL	 PROPELLANT	EXPLOSIVE DETONATION
typical material	coal-air	propellants	explosives
linear reaction rate, m/s	10^{-6}	10^{-2}	$2 - 9 \times 10^{3}$
type of reaction	redox	redox	redox
time for reaction completion, s	10^{-1}	10^{-3}	10^{-6}
factor controlling reaction rate	heat transfer	heat transfer	shock transfer
energy output, J/g	10^{4}	10^{3}	10^{3}
power output, W/cm^2	10	10^{3}	10^{9}
most common initiation mode	heat	hot particles and gases	high temp/high press. shock wave
pressures developed, atm	0.7 - 7	$7 - 7 \times 10^{3}$	$7 \times 10^{4} - 7 \times 10^{5}$
uses	source of heat, electricit y	controlled gas press; guns, rockets	brisance, blast, munitions, civil engineering

-Explosives categories

High explosives (HE), also known as detonating explosives, are materials that react very violently, producing almost instantaneous decomposition. Typically, high explosives contain, in effect, their own oxidizer and fuel within the structure of the molecule. This leads to very rapid reaction and the generation of the supersonic shock wave. High explosives are used for their destructive power as the main charge of a warhead and their detonation produces a supersonic shock wave. High explosives are further divided into two subcategories:

Subcategory	Characteristic	Use
Primary HE	Extremely sensitive to shock, friction, heat or spark	Detonator or primer
Secondary HE	Insensitive to shock, friction and heat	Booster and main charge

Low explosives, sometimes called deflagrating explosives, react slowly in their decomposition, creating a subsonic shock wave. Because of the slower decomposition, the large amount of energy produced is often used as a propellant charge. The gas produced is used to move projectiles.

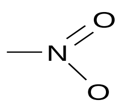
The different effects of low and high explosives depend on how fast heat and gas are produced by the reaction; this, in turn, depends on how fast the reaction moves through the material. Three thousand feet per second is the speed that has been chosen to mark the division between a low explosive and a high explosive.

Black powder, a mixture of potassium nitrate, charcoal, and sulfur, is a _______________ explosive, used in guns and in quarrying rock for building stone. TNT (trinitrotoluene), and RDX (cyclotrimethylene trinitramine) are examples of _________ explosives. RDX is a military explosive with a detonation velocity as high as 27,000 fps. Interestingly, stoichiometry and energy considerations do not really distinguish the two types of explosives; both release large volumes of gas, and significant amounts of heat during the combustion. The difference in reaction speed is more a matter of the kinetic mechanism (discussed in SC112).

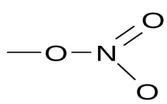
Scientific Practices

Because all explosives must contain both oxidizing and reducing agents (a topic covered in SC112), the use of electronegative elements like nitrogen, oxygen, fluorine, and chlorine is common to satisfy the oxidizing agent requirement. The lighter carbon and hydrogen elements often serve as the reducing agents. The 'internal' oxygen of an explosive compound is usually found in functional groups (structural fragments) that are rich with that element. Most explosive compounds contain nitrogen, usually in *nitro* (-NO_2), *nitrate* (-ONO_2), or *nitramine* (-N-NO_2) groups and less frequently in *azide* (-N_3) and other groups. A few explosive compounds contain no nitrogen but are characterized by strong oxidizing agents such as *peroxide (-OO-)*, *ozonide (C-(OO)(O)-C-)*, or *perchlorate (*ClO_4*)* groups.

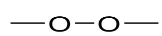
Common Functional Groups in Explosive Compounds



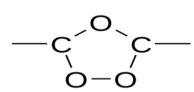
nitro-



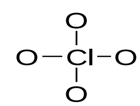
nitrate



peroxide



ozonide



perchlorate

For most organic nitro, nitrate and nitramine compounds, the power and brisance ('shattering power') is directly related to the oxygen balance (discussed below), and is a maximum when the oxygen balance is close to zero.

From a molecular point of view, most of these atomic arrangements are relatively unstable, so breaking them apart does not cost a lot of energy. However, when the atoms recombine as products, they form *very* stable compounds such as CO_2, N_2, and H_2O. *Making* such strong bonds *releases* a lot of energy.

Bond *breaking* always ____________________ energy

Bond *making* always _____________________ energy.

Some common military explosive reactants and products are listed below:

Explosive Reactants	Formula	ΔH°f (kJ/mol)
Nitroglycerin	$C_3H_5N_3O_9$	-333.7
RDX	$C_3H_6N_6O_6$	+83.8
HMX	$C_4H_8N_8O_8$	+104.8
PETN	$C_5H_8N_4O_{12}$	-514.6
TNT	$C_7H_5N_3O_6$	-54.4
Tetryl	$C_7H_5N_5O_8$	+38.9
TNAZ	$C_3H_4N_4O_6$	+73.5

Explosive Products	Formula	ΔH°f (kJ/mol)
Carbon Monoxide (g)	CO	-110.5
Carbon Dioxide (g)	CO_2	-393.5
Water (g)	H_2O	-241.8
Hyrdogen (g)	H_2	0.0
Nitrogen (g)	N_2	0.0
Oxygen (g)	O_2	0.0

Stoichiometry: Nearly all explosives contain some combination of carbon, oxygen, hydrogen, and nitrogen. Since the explosion is similar to a combustion, we should expect that typical combustion products will be formed. The actual products of any chemical reaction must be determined experimentally, but some generalizations can be used to predict the products of related reactions, such as those of explosives.

– All the nitrogen in the explosive is converted to nitrogen gas (N_2).
– All the hydrogen in the explosive is converted to water vapor (steam).
– Carbon is usually converted to carbon dioxide. If not enough oxygen is present to convert all of the carbon to carbon dioxide, then some carbon monoxide forms. If some carbon remains, then only carbon monoxide and soot (solid carbon), with no carbon dioxide, forms.

Oxygen Balance - High explosives typically are the ONLY reactant in the reaction, so clearly the amount of oxygen present in the molecule is critical. This is quantified in a measure called the **oxygen balance**. A zero oxygen balance occurs when the explosive contains enough oxygen to convert all the hydrogen and carbon to $H_2O(g)$ and $CO_2(g)$ respectively. A positive oxygen balance is when oxygen remains after the conversion of hydrogen and carbon to $H_2O(g)$ and $CO_2(g)$, while a negative oxygen balance is when there is not enough oxygen to convert all the hydrogen and carbon to $H_2O(g)$ and $CO_2(g)$. A simple formula can be used to determine oxygen balance:

$$OB_{\%}=[\left(\frac{-16}{MWexp}\right)\left(2C+\frac{H}{2}+M-O\right)]*100\%,$$

MWexp=molecular weight of the explosive (g/mol)
C= # carbon atoms
H= # hydrogen atoms
M= # metal atoms
O= # of oxygen atoms

Once you determine the explosive's oxygen balance, you can balance the equation using the following seven steps:

Priority	Reaction	
1	Metal + Chlorine → Metallic Chloride (solid)	
2	Hydrogen + Chlorine → Hydrogen Chloride	
3	Metal + O → Metallic Oxide (solid)	
	If OB% ≥-40%	If OB% < -40%
4	C + O → CO	2H + O → H_2O
5	2H + O → H_2O	C + O → CO
6	CO + O → CO_2 (using CO formed during step 4)	CO + O → CO_2 (using CO formed during step 5)
7	2O, 2H, and 2N → O_2, H_2, N_2 (all in the gaseous state)	2O, 2H, and 2N → O_2, H_2, N_2 (all in the gaseous state)
CO, CO_2 and H_2O are assumed to be in gaseous form.		

Using HMX, $C_4H_8N_8O_8$, as an example, I first determine the oxygen balance:

$[\left(\frac{-16}{296.16}\right)\left(24+\frac{8}{2}+0-8\right)]*100\%$ = -108.05%, Next I use the OB% < -40% steps:

Step	Reaction	Result
1	No metal or chlorine	None
2	No chlorine	None
3	No metal	None
4	8H+4O	$4H_2O$ (remaining O=4)
5	4C+4O	4CO (remaining O=0)
6	No oxygen remaining	None
7	8N	$4N_2$

Therefore, my balanced reaction is: $C_4H_8N_8O_8$ → $4H_2O$ + 4CO + $4N_2$

Energetics - With a balanced equation, we can now determine many other important chemical properties of the explosive. We can calculate the Heat of Explosion (ΔH^o_{exp}) for the number of moles of explosive used as we would for any other reaction, using standard molar heats (enthalpies) of formation:

$$\Delta H^0_{exp} = \Sigma[\Delta H^0_f(explosive\ products)] - \Sigma[\Delta H^0_f(explosive\ reactants)]$$

Values of ΔH^o_f for a number of high explosives and common reaction products are in the tables above. Similar to the "fuel value" measured in Exp. 30B, the heat of explosion with respect to the mass of the explosive is also a useful parameter
:

$$Q = \frac{\Delta H^0_{exp}}{MWexp}$$

You may be wondering whether the energy release or the release of expanding gases is more important for an effective explosive. These two factors can actually be combined into an "explosive strength" metric, calculated with the "Berthelot approximation". This equation gives a value of strength relative to TNT and results in a % of the strength of TNT. (TNT has a strength of 100% by definition. All strengths should be reported as a %.)

$$\text{Explosive Strength (\%)} = |(645\ \Delta n\ \Delta H^\circ_{exp})|/MM^2$$

where Δn is the number of moles of *gas* released per mole of explosive, ΔH°_{exp} is the heat of the explosion in kJ/mol explosive, and MM is the molar mass of the explosive in g/mol.

Modeling an Explosion From Basic Chemistry Principles

Clearly, explosives represent an application of chemistry which is of significant interest in military operations, and which is important in the civilian sector as well. Explosive processes are quite complex, but we can approximate the problem as a series of simple steps, all of which involve concepts and calculations you have examined in the SC111 course:

a. **An explosion occurs in a closed container and releases some amount of heat and gases.**
b. **The heat from the reaction raises the temperature of the released gases.**
c. **The temperature increase affects the pressure of the gases in the closed container.**
d. **The container bursts and the hot gases expand to occupy a different volume at ambient pressure.**

We have already explored the stoichiometry and energetics of the explosive reaction. The heat released by the reaction is transferred to the gases produced in a way similar to your calorimetry measurements in Exp. 30B - the heat released by the reaction is absorbed by the gases, raising their temperature:

$$q_{rxn} = -q_{gases} \quad \text{and thus} \quad q_{rxn} = -\, n_{gas}C_{gas}\Delta T$$

The latter two points of the model, relating to product gas behavior, can be treated through the ideal gas law. We can now determine the volume of the gas produced at "standard temperature and pressure" (STP, 0^{o}C and 1 atm pressure). The formula for $Volume_{stp}$ is:

$$Vstp = moles\ of\ gas\ formed * (\frac{22.4\ liters}{mole})$$

Note that this equation ONLY apples at STP; it cannot be used under general conditions, where the full ideal gas law is required. Finally, the effect of increased temperature on volume and pressure of the resulting gases can be treated with the ideal gas law, PV = nRT.

Additional equations of interest are discussed in chapter 9, Properties of Gases: The Air We Breathe.

Please consider the following when answering the questions below:

$$KEavg = \frac{1}{2}mu_{rms}^2$$, where u_{rms}^2 is the root-mean-square speed

$$u_{rms} = \sqrt{\frac{3RT}{M}}$$, where R=8.314 $\frac{kg * m^2}{s^2 * mol * K}$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$, where V is volume and T is temperature at constant P and n

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$, where P is pressure and T is temperature at constant V and n

$$\frac{P}{n} = constant\ (at\ constant\ V\ and\ T) and\ \frac{V}{n} = constant\ (at\ constant\ P\ and\ T)$$

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$ at constant n

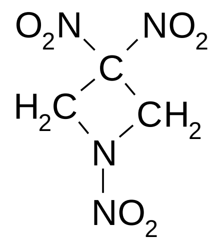
And finally, the ideal Gas law and Dalton's Law of Partial Pressure respectively:

$$PV = nRT$$

$$P_{total} = P_1 + P_2 + P_3 + \cdots$$

4. Questions

Consider the explosion of the high explosive TNAZ (1,3,3-trinitroazetidine), $C_3H_4N_4O_6$



1. Molecules, Ions, Atoms, Dimensional Analysis, and Mass Percent
   a. Determine the molecular weight of TNAZ using the periodic table in the front of your book to two decimal places.
   b. Determine the percent by mass of oxygen in a sample of TNAZ.
   c. Determine the oxygen balance of TNAZ.
   d. Balance the chemical equation for the reaction of TNAZ.
   e. Determine the grams of CO_2 produced in a 1.00cm^3 sample of TNAZ. The density of TNAZ is 1.832 g/cm^3
2. Thermochemistry
   a. What is the heat of explosion for 1 mole of TNAZ (kJ/mole)?
   b. What is the heat of explosion for 1 g of TNAZ in (kJ/g)?
   c. How much heat would be released by 100.00 mL of TNAZ? The density of TNAZ is 1.832 g/cm^3?
   d. If the molar heat capacity of all gases is approximated to be 29.1 J/(mol gas ^{o}C), determine the temperature change. Hint, you will need to use the answer from part c.

3. Gas Laws
   a. How many moles of gas are produced from 1 mole of TNAZ?
   b. What is the mole fraction of N_2 in the mixture of product gas?
   c. If the temperature rises to 6529^{o}C in a 1.00 cm^3 container, what is the pressure (in atm) within the container?
   d. The 1.00 cm^3 container has now burst at 6529^{o}C. What volume (in L) do the gases occupy when they reach 1.00atm?
   e. Which of the product gases would be moving fastest. Do not do any calculations.

References and Additional Readings

References are given in the figure captions, where available/applicable.

https://www.wbdg.org/FFC/DOD/DODMAN/605509-M-V8.pdf

https://www.nap.edu/read/10998/chapter/6#60