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

Water is an inherent need to sustain military operations in peace and war. Usable water is scarce on naval vessels. Usable forms are prioritized for maintaining systems (cooling electronics) vice crew comforts (air conditioning).

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. It is important to note that explosive material typically contains oxygen and fuel in a proportion that supports rapid combustion in an enclosed, airless space. An explosion reaction is the ignition and rapid burning of the confined energetic materials 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. 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.

Some common military explosive reactants and products are listed below:

Explosive Reactants	Formula	ΔH^o_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^o_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

Explosives categories include high explosive and low explosives.

High explosives (HE), also known as detonating explosives, are materials that react very violently, producing almost instantaneous decomposition. 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 slow decomposition, the large amount of energy produced is often used as a propellant charge. The gas produced is used to move projectiles.

To balance an explosive reaction, it is helpful to determine 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:

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

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:

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

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: $C_4H_8N_8O_8 \rightarrow 4H_2O + 4CO + 4N_2$

With a balanced equation, we can now determine many other important chemical properties of the explosive. We can also now calculate the Heat of Explosion (ΔH^o_{exp}) for the number of moles of explosive used:

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

Or the heat of explosion with respect to the mass of the explosive:

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

As explosives produce primary gaseous products, it is important for us to further apply the ideal gas law. We can now determine the volume of the gas produced at standard temperature and pressure (0^oC and 1 atm pressure). The formula for $Volume_{stp}$ is:

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

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:

$KEavg = \frac{1}{2}mu^2_{rms}$, where $u^2_{rms}$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 TNAZ, $C_3H_4N_4O_6$

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.

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 mole of TNAZ in (kJ/g)?
    c. How much heat would be released by 100.00 g 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