

DECOMPOSITION REACTIONS

Lecture 8



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COMBUSTION

- burning, oxidation reaction
- irreversible
- fuel reacts with oxygen to release energy – exothermic
- produces oxides
- burning a fuel in propulsion system generates thrust



Hydrogen is a fuel used in space rockets. What is produced when hydrogen burns?



Gasoline is a fuel used in cars, which contains only carbon and hydrogen atoms. What is produced when gasoline burns?

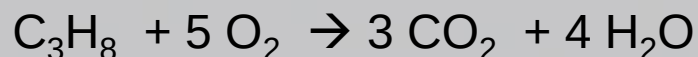


COMBUSTION, COMPLETE vs. INCOMPLETE

propane, C₃H₈: MM = 44.0 g/mol, O: MM = 16.0 g/mol,

complete combustion:

combined mass 44 + 10 x 16 = 204



$$\frac{\text{total mass of O}}{\text{combined mass}} \times 100\% = \frac{16 \times 10}{204} \times 100\% = 78.4\%$$

incomplete combustion:

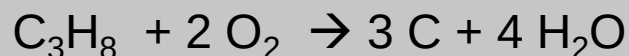
combined mass 44 + 7 x 16 = 156



$$\frac{\text{total mass of O}}{\text{combined mass}} \times 100\% = \frac{16 \times 7}{156} \times 100\% = 71.8\%$$

incomplete combustion:

combined mass 44 + 4 x 16 = 108



$$\frac{\text{total mass of O}}{\text{combined mass}} \times 100\% = \frac{16 \times 4}{108} \times 100\% = 59.3\%$$



BLACK POWDER

- blackpowder = gunpowder
- very first explosive composition produced accidentally in China (220 BC)
- first confirmed reference occurred in China almost 1000 years later as warning against:

“an assortment of dangerous formula of heated together sulfur, realgar (arsenic disulfide), and saltpeter with honey; smoke [and flames] result, so that (...) hands and faces have been burnt, and even the whole house burned down.”

- consists of a fuel and oxidiser.
 - fuel: powdered mixture of charcoal and sulfur
 - mixed with potassium nitrate, oxidiser
- potassium nitrate (salpeter)– naturally occurring mineral

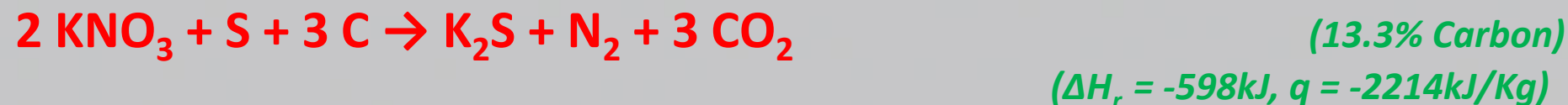
Besides selecting their raw materials carefully, the ancients learned to improve on nature by saturating the tinder with blood and urine ,mixed with potash-rich ashes. Later, this slow biological action was speeded up in 'nitre beds' - the waste and plant ashes were heaped up together, exposed to the air and watered at intervals. Eventually after the piles had been turned many times, this manure produced salpetre.

http://salt.org.il/frame_saltpet.html

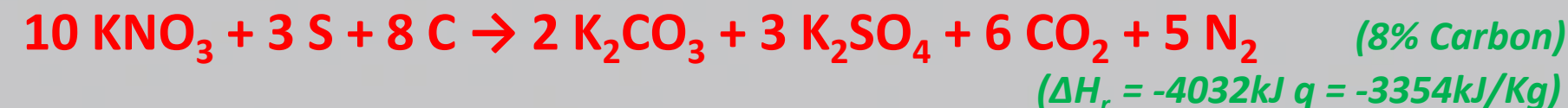


GUNPOWDER CHEMISTRY

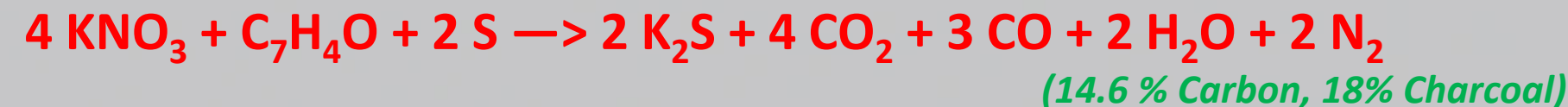
simple, commonly cited, chemical equation for combustion of black powder is:



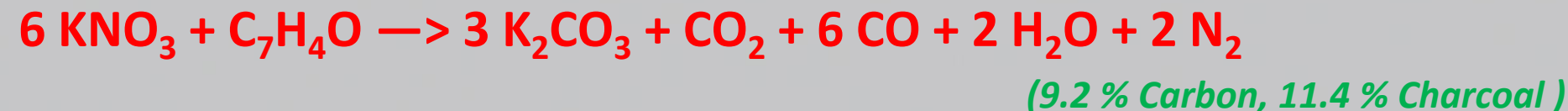
better balanced, more accurate but still simplified, equation is:



charcoal's chemical formula is $\text{C}_7\text{H}_4\text{O}$ with this even more accurate equation of the decomposition of black powder is:



black powder without the use of sulphur:



The burning of gunpowder – multistep reaction, the by-products are not easily predicted.

55.91% solid products: K_2CO_3 , K_2SO_4 , K_2S , S , KNO_3 , KSCN , C , $(\text{NH}_4)_2\text{CO}_3$,

42.98% gaseous products: CO_2 , N_2 , CO , H_2S , H_2 , CH_4

1.11% water

GUNPOWDER CHEMISTRY

The optimum proportions for black powder:

74.64% [Potassium nitrate](#),

13.51% [charcoal](#)

11.85% [sulfur](#) by weight. .

The current standard for black powder manufactured by pyrotechnicians today is:

75% potassium nitrate,

15% charcoal

10% sulfur by weight



11.6 % Carbon or 14.5% Charcoal

($\Delta H_r = -30596 \text{ kJ}$ $q = 3088 \text{ kJ/Kg}$)



<https://www.youtube.com/watch?v=nf1mCiAodl0>

<https://www.youtube.com/watch?v=rmtK2BgmGCw>

COMBUSTION vs. DETONATION

The release of energy (energy extremely useful for military purposes) is fundamental to both these phenomena. In both **combustion** and **detonation**, energy is released when a complex molecule is broken down into simpler constituent parts; however, **combustion** is a much slower process as it needs oxygen.

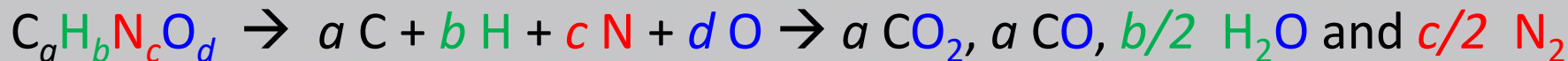
Low explosives (like black powder) rely on **combustion** to generate energy. It is limited both by the amount of fuel present and the amount of oxygen it comes in contact with.

Detonation is a process of intramolecular breakdown. It relies only on the presence of a single, suitable explosive material and enough energy to stimulate that breakdown. Because **high explosives** do not require oxygen (or any other co-reactant), they break down much more rapidly and are much more versatile than combustible materials.



DECOMPOSITION OF EXPLOSIVES

when an explosive reaction takes place, the explosive molecule



- breaks apart into its constituent atoms
- followed by a rearrangement of the atoms into a series of small, stable molecules of gases, such as H_2O , CO_2 , CO and N_2
- H_2 , C , Al_2O_3 , SO_2 , etc can be also formed
- the nature of the products depends upon the amount of oxygen available for the reaction
- this supply of oxygen depends on the quantity of oxidizing atoms in the explosive molecule.



OXYGEN BALANCE

the amount of oxygen expressed as wt% needed or produced to ensure the complete oxidation of all the carbon, hydrogen, or other elements to CO_2 , H_2O , (and SO_2 , Al_2O_3 , *etc.*)

used to indicate the degree to which an explosive can be oxidized

for an explosive with the general formula $\text{C}_a\text{H}_b\text{N}_c\text{O}_d$ and molecular weight **MW**:

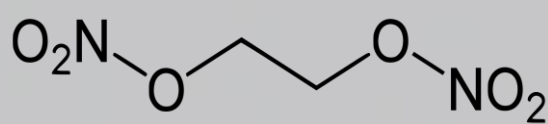
$$\Omega = \frac{16}{MW} \times \left[d - (2a) - \left(\frac{b}{2} \right) \right] \quad \text{oxygen balance}$$

The **sensitivity**, **strength** and **brisance** of an explosive depend upon oxygen balance and tend to approach their maxima as oxygen balance approaches zero.



OXYGEN BALANCE

EXAMPLE 1:



ethylene glycol dinitrate
(nitroglycol)

As a result of detonation, the explosive molecule EGDN ($C_2H_4N_2O_6$, MW = 152) is fully oxidized to form gaseous products, CO_2 , H_2O and N_2 . Calculate the oxygen balance for EGDN.



a = 2
b = 4
d = 6

just enough oxygen in EGDN to oxidize reactants fully to CO_2 and H_2O

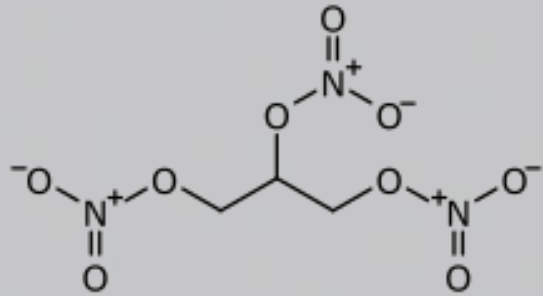
$$\Omega = \frac{16}{MW} \times \left[d - (2a) - \left(\frac{b}{2} \right) \right] = \frac{16}{152} \times \left[6 - (2 \times 2) - \left(\frac{4}{2} \right) \right] = 0$$

zero oxygen balance



OXYGEN BALANCE, cnt

EXAMPLE 2:



As a result of detonation, nitroglycerin ($\text{C}_3\text{H}_5\text{N}_3\text{O}_9$, MW = 227) is fully oxidized to form gaseous products, CO_2 , H_2O and N_2 . Calculate the oxygen balance for nitroglycerine.



$$a = 3$$

$$b = 5$$

$$d = 9$$

excess of oxygen in NG to oxidize reactants fully to CO_2 and H_2O

$$\Omega = \frac{16}{\text{MW}} \times \left[d - (2a) - \left(\frac{b}{2} \right) \right] =$$

$$= \frac{16}{227} \times \left[9 - (2 \times 3) - \left(\frac{5}{2} \right) \right] = +3.5\%$$

positive oxygen balance

amount of oxygen liberated

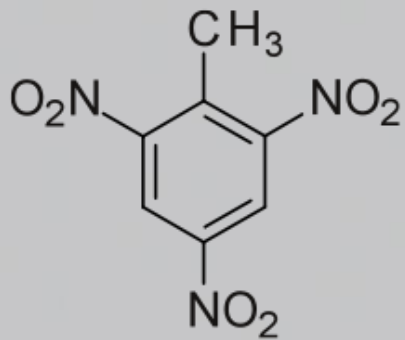
$$\text{wt}\% \text{ O} = \frac{\left(\frac{1}{2} \times 16 \right) \times 100}{227} = +3.5\%$$

wt% of O as the total MW of O atoms in the product ($\frac{1}{2} \times 16 = 8$) divided by the MW of nitroglycerin

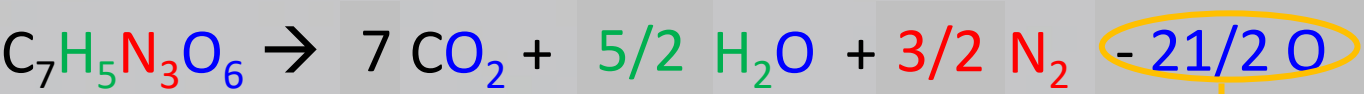


OXYGEN BALANCE, cnt

EXAMPLE 3:



As a result of detonation, the explosive molecule TNT ($C_7H_5N_3O_6$, MW = 227) is fully oxidized to form gaseous products, CO_2 , H_2O and N_2 . Calculate the oxygen balance for TNT.



$a = 7$
 $b = 5$
 $d = 6$

insufficient oxygen in TNT to oxidize reactants fully to CO_2 and H_2O

$$\Omega = \frac{16}{MW} \times \left[d - (2a) - \left(\frac{b}{2} \right) \right] =$$
$$= \frac{16}{227} \times \left[6 - (2 \times 7) - \left(\frac{5}{2} \right) \right] = -74\%$$

amount of oxygen taken in

$$wt\% O = \frac{-168 \times 100}{227} = -74\%$$

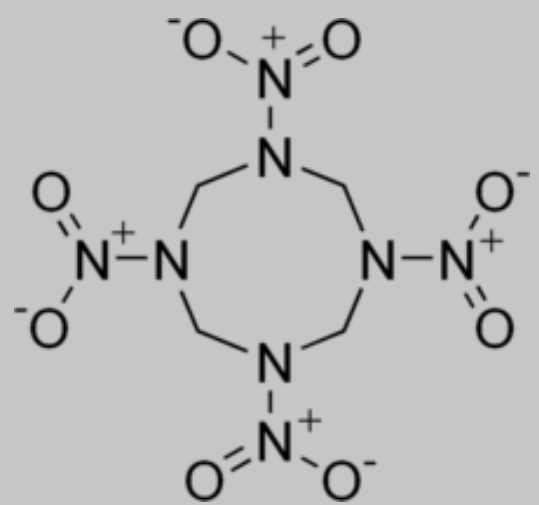
negative oxygen balance

wt% of O as the total MW of O atoms in the product ($10\frac{1}{2} \times 16 = 168$) divided by the MW of TNT



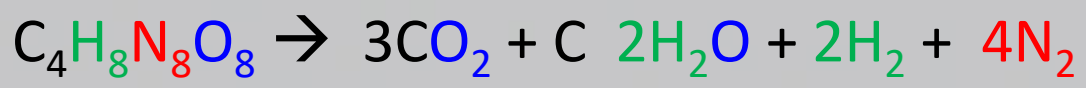
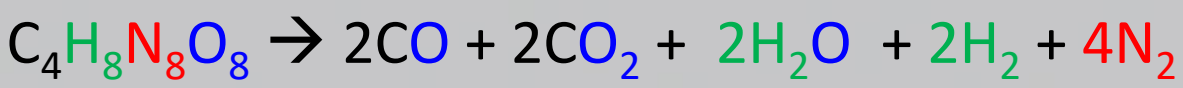
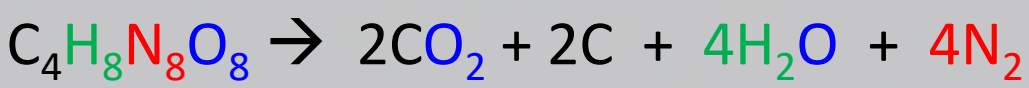
incomplete combustion; a large amount of toxic gases like CO produced

DECOMPOSITION REACTIONS



HMX (octogen)

a = 4, b = 8, d = 8



$$\Omega = \frac{16}{MW} \times \left[d - (2a) - \left(\frac{b}{2} \right) \right] = \frac{16}{296} \times \left[8 - (2 \times 4) - \left(\frac{8}{2} \right) \right] = -21.6\%$$



KISTIAKOWSKY-WILSON RULES

for moderately oxygen-deficient explosives with $\Omega > -40.0$ (HMX, $\text{C}_4\text{H}_8\text{N}_8\text{O}_8$)

Rule	Conditions	Products
1	C atoms converted to CO	$4 \text{ C} \rightarrow 4 \text{ CO}$
2	Remaining O oxidizes H to H_2O	$4 \text{ O} \rightarrow 4 \text{ H}_2\text{O}$
3	Still remaining O, oxidizes CO to CO_2	No more O left
4	All N converted to N_2	$8 \text{ N} \rightarrow 4 \text{ N}_2$

overall reaction for decomposition of HMX:



MODIFIED KISTIAKOWSKY-WILSON RULES

for explosives with $\Omega > -40.0$ (TNT, $\text{C}_7\text{H}_5\text{N}_3\text{O}_6$)

Rule	Conditions	Products
1	H atoms converted to H_2O	$5 \text{ H} \rightarrow 2\frac{1}{2} \text{ H}_2\text{O}$
2	Remaining O oxidizes C to CO	$3\frac{1}{2} \text{ O} \rightarrow 3\frac{1}{2} \text{ CO}$
3	Still remaining O, oxidizes CO to CO_2	No more O left
4	All N converted to N_2	$3 \text{ N} \rightarrow 1\frac{1}{2} \text{ N}_2$

overall reaction for decomposition of TNT:



SPRINGALL ROBERTS RULES

unmodified Kistiakowsky-Wilson rules PLUS two more conditions (TNT, C₇H₅N₃O₆)

Rule	Conditions	Products
1	C atoms converted to CO	6 C → 6 CO
2	Remaining O oxidizes H to H ₂ O	No more O left
3	Still remaining O, oxidizes CO to CO ₂	No more O left
4	All N converted to N ₂	3 N → 1½ N ₂
	This results in equation: C ₇ H ₅ N ₃ O ₆ → 6 CO + C + 2½ H ₂ + 1½ N ₂	
5	1/3 of CO converts to CO ₂	2CO → C + CO ₂
6	1/6 of original CO converts to C and H ₂ O	CO + H ₂ → C + H ₂ O

Overall reaction for decomposition of TNT:



PRACTICE PROBLEM

For explosive compound nitrocellulose ($C_6H_7O_{11}N_3$) calculate the oxygen balance. Use the K-W and S-R rules to determine the decomposition products of NC

K-W

Rule	Conditions
1	C atoms converted to CO
2	Remaining O oxidizes H to H_2O
3	Still remaining O, oxidizes CO to CO_2
4	All N converted to N_2

S-R

Rule	Conditions
1	C atoms converted to CO
2	Remaining O oxidizes H to H_2O
3	Still remaining O, oxidizes CO to CO_2
4	All N converted to N_2
5	1/3 of CO converts to CO_2
6	1/6 of original CO converts to C and H_2O



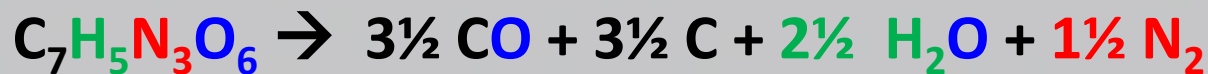
VOLUME OF GASEOUS PRODUCTS OF EXPLOSION

- **IMPORTANT** because the volume of gas produced during an explosion provides information on the amount of work done by the explosive.
- **STP** (**0 °C** or **273K**, **1 atm**)
 - volume of gas varies with temperature at which the measurement is taken.
 - enable comparisons between one explosive and another.
 - one mole of gas occupies **22.4 dm³** (molar gas volume)
- volume of gas **V** liberated from an explosive during detonation can be calculated from its equation of decomposition
- $\text{C}_3\text{H}_6\text{N}_6\text{O}_6 \rightarrow 3 \text{CO (g)} + 3 \text{H}_2\text{O (g)} + 3 \text{N}_2 \text{(g)}$
 - **9 moles** of gas are produced from **1 mole** of RDX (MM = 222.1 g/mol)
 - at **STP 9 moles** of gas will occupy (9 moles x 22.4 dm³/mol) **201.6 dm³**
 - **1 g** of RDX will produce 201.6 dm³ / 222.1 g) **0.908 dm³/g** (**908 cm³/g**)



PRACTICE PROBLEM

The chemical equation for an explosion of TNT ($\text{C}_7\text{H}_5\text{N}_3\text{O}_6$) was derived using the modified K-W rules and is shown below.



Calculate the **volume** of all gas products liberated upon detonation of **one mole** of TNT.

What **volume** of gases is produced from **1 g** of TNT?

One mole of TNT produces $7\frac{1}{2}$ moles of gas which will occupy 168 dm^3 and 1 g of TNT will produce $0.740 \text{ dm}^3/\text{g}$ ($740 \text{ cm}^3/\text{g}$) of gas at 'STP' as shown in Equation

$7\frac{1}{2} \text{ mol of gas will occupy } 22.4 \times 7\frac{1}{2} = 168 \text{ dm}^3$

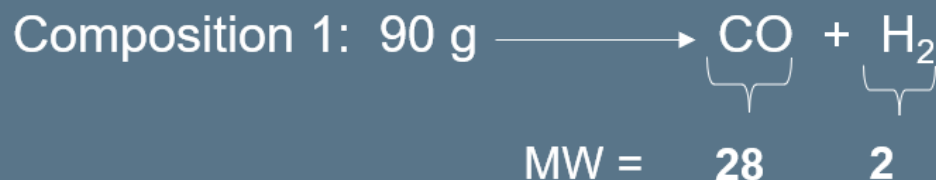
Therefore, 1 mol of TNT produces 168 dm^3 of gas

1 g TNT produces $168/227 = 0.740 \text{ dm}^3/\text{g}$ where the molecular mass of TNT is 227



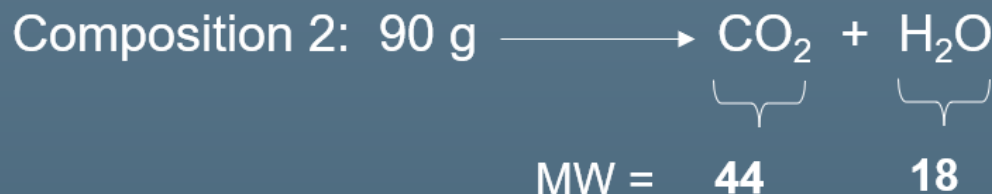
Gas Volume

1 mole of a gas occupies 22.4 L at STP (Ideal)



Volume of Gas (L)

$$90 / 30 = 3 \times 2 \text{ moles}$$
$$\therefore \text{volume of gas} = 22.4 \times 6 = 134.4 \text{ L}$$



$$90 / 62 = 1.45 \times 2 \text{ moles}$$
$$\therefore \text{volume of gas} = 22.4 \times 2.9 = 65.0 \text{ L}$$

$\therefore$ Gas volume increases as Ω decreases

Propellants and Explosives are thus formulated with a –ve oxygen balance

Some high explosives have the general formula $C_a H_b N_c O_d$. The oxidiser (O) and the fuel (C, H) are present in the same molecule. Nitrogen atoms are present so that there is a highly exothermic production of hot N_2 gas.

- a) For an unknown explosive of general formula $C_a H_b N_c O_d$ and a molar mass of 152 g/mol, determine the coefficients a , b , c and d if 152 g of this material decomposes to form 44.8 dm³ of CO_2 , 44.8 dm³ of H_2O , and 22.4 dm³ of N_2 .



If the molar mass of this explosive is 152 g, it corresponds to 1 mol decomposed.

22.4 L is a volume of 1 mol of a gas, so there are 2 moles of CO_2 , 2 moles of H_2O , and 1 mol of N_2 formed as the result of decomposition of 1 mol of unknown explosive.



So, $a = 2$, $b = 4$, $c = 2$ and $d = 6$. The formula of this explosive is $C_2H_4N_2O_6$

- b) For the explosive determined in a) calculate the per cent by mass of oxygen.

In one mol of $C_2H_4N_2O_6$ there are 6 moles of oxygen atoms with total mass (6 x 16) 96 g.

In 152 g of this explosive there are 96 g of oxygen which corresponds to ((96/152) x 100%) 63.2 % of oxygen

- c) The oxygen balance of an explosive is the mass of oxygen either in excess (the balance is positive) or in deficit (the balance is negative) of that required for complete oxidation of C and H. The oxygen balance is expressed as a percentage of the molar mass of the explosive. Calculate the oxygen balance for explosive with the formula determined in part a).

$$\Omega = \left(\frac{16}{MM} \right) \times \left[d - \left(2a \right) - \left(\frac{b}{2} \right) \right] \times 100\% = 0\%$$

