

3.3.9: Physics- Rocket Propellants



The space shuttle used 2 Solid Propellant Boosters (SRBs, white) and a tank of LOX/LH2 (large orange tank)

Introduction

Jet aircraft designed to fly in Earth's atmosphere carry just fuel, and rely on atmospheric O_2 , which is supplied in excess, to burn the fuel. Rockets designed for interplanetary flight need to supply both a fuel and an oxidant for their propulsion, and the ratio of the two has to be exactly right for maximum propulsion and minimum mass. If the wrong size tanks for fuel and oxidizer are designed, some portion of such a reactant will be left unchanged after the reaction. Conversely, at least one reagent is usually completely consumed. When it is gone, the other excess reactants have nothing to react with and they cannot be converted to products. The substance which is used up first is the **limiting reagent**.

Principle of Rocket Operation

Newton's Third Law of Motion is "every action is accompanied by an equal and opposite reaction." A rocket operates on this principle. The force exerted by the rocket on the ejected reaction products equals the force of the ejected particles on the rocket. So the "**impulses**" (the product of the force and time that it acts) are equal in magnitude and opposite in direction. Since the impulse ($F \times t$) equals the momentum ($m \times v$), the momentum of the spent fuel in one direction equals the momentum of the rocket in the other. The fuel and oxidant must be designed to rapidly heat and eject combustion products in one direction, causing motion of the rocket in the opposite direction.

The gauge of efficiency for rocket propellants is specific impulse, stated in seconds. The higher the number, the "hotter" the propellant.

Specific Impulse (I_{sp} is the period in seconds for which a 1-pound (0.45-kilogram) mass of propellant (total of fuel and oxidizer) will produce a thrust of 1 pound (0.45- kilogram) of force. The specific impulse for a fuel may vary somewhat due to conditions^[2]

NASA and commercial launch vehicles use four types of propellants: (1) petroleum; (2) cryogenics; (3) hypergolics; and (4) solids^[3]. Examples involving cryogenics (liquid hydrogen and liquid oxygen) and solids (aluminum and ammonium perchlorate, or Ammonium Perchlorate Composite Propellants, APCPs) are give below. Hypergolics are compounds that react upon mixing (without an ignition source), like nitrogen tetroxide and hydrazine^[4] which we'll discuss later. Petroleum derivatives include RP-1 (Rocket Propellant or Refined Petroleum-1), which is similar to kerosene and used with an oxidant like liquid oxygen.

Examples with cryogenics and solids

	LOX/RP-1 ^[5]	Hydrazine/ dinitrogen tetroxide ^[6]	ACPC ^[7]	LOX/LH2
Max Specific Impulse	~353	258	~250	444 ^[8]
Oxidizer to Fuel Ratio	2.56:1	0.77:1	calculate below	calculate below

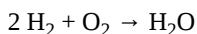
Example 1: LH2 + LOX

The Space Shuttle's large rust-orange booster fuel tank shown in the picture above holds liquid oxygen (LOX, 629,340 kg) and liquid hydrogen (LH2, 106 261 kg)^[9].

- Which is the limiting reagent?
- What mass of product will be formed?
- Did NASA make a mistake?

Solution

The balanced equation



tells us that according to the atomic theory, 2 mol H₂ is required for each mole of O₂. That is, the stoichiometric ratio $S(\text{H}_2/\text{O}_2) = 2 \text{ mol H}_2 / 1 \text{ mol O}_2$. Let us see how many moles of each we actually have $n_{\text{H}_2} = 1.06261 \times 10^8 \text{ g} \times \frac{1 \text{ mol H}_2}{2.016 \text{ g}} = 5.271 \times 10^7 \text{ mol H}_2$
 $n_{\text{O}_2} = 6.293 \times 10^8 \text{ g} \times \frac{1 \text{ mol O}_2}{31.999 \text{ g}} = 1.967 \times 10^7 \text{ mol O}_2$

If all the H₂ were to react, the stoichiometric ratio allows us to calculate the amount of O₂ that would be required:

$$n_{\text{O}_2} = n_{\text{H}_2} \times \frac{1 \text{ mol O}_2}{2 \text{ mol H}_2} = 2.63 \times 10^7 \text{ mol O}_2$$

This is more than the amount of oxygen present, so oxygen is the **limiting reactant** and H₂ is present in excess.

If all the O₂ reacts, the stoichiometric ratio allows us to calculate the amount of H₂ that would be required:

$$n_{\text{H}_2} = n_{\text{O}_2} \times \frac{2 \text{ mol H}_2}{1 \text{ mol O}_2} = 1.967 \times 10^7 \text{ mol O}_2 \times \frac{2 \text{ mol H}_2}{1 \text{ mol O}_2} = 3.934 \times 10^7 \text{ mol H}_2$$

We require less than the amount of H₂ present, so it is the **excess reactant**.

When the reaction ends, $3.934 \times 10^7 \text{ mol}$ of H₂ will have reacted with $1.967 \times 10^7 \text{ mol}$ O₂ and there will be $(5.271 \times 10^7 \text{ mol} - 3.934 \times 10^7 \text{ mol}) = 1.337 \times 10^7 \text{ mol}$ H₂ left over. Oxygen is therefore the limiting reagent.

- Since the hydrogen doesn't all react, we need to calculate the amount of water produced from the amount of oxygen consumed, by using the stoichiometric ratio:

$$n_{\text{H}_2\text{O}} = n_{\text{O}_2} \times \frac{2 \text{ mol H}_2\text{O}}{1 \text{ mol O}_2} = 3.934 \times 10^7 \text{ mol H}_2\text{O}$$

The mass of water is then calculated by using the molar mass:

$$3.934 \times 10^7 \text{ mol H}_2\text{O} \times \frac{18.01 \text{ g}}{1 \text{ mol H}_2\text{O}} = 7.08 \times 10^8 \text{ g H}_2\text{O}$$

- The excess hydrogen is not a mistake. The reaction is so exothermic that it ejects some of the unreacted hydrogen. This doesn't matter, since any ejected mass contributes to the backward momentum of fuel, and the forward momentum of the rocket. Since the mass of hydrogen is small, its velocity is large, and it can contribute to a large forward velocity of the rocket.

These calculations can be organized as a table, with entries below the respective reactants and products in the chemical equation. We can calculate (hypothetically) how much of each reactant would be required if the other were completely consumed to demonstrate which is in excess, and which is limiting. We use the amount of limiting reagent to calculate the amount of product formed.

Calculations of Solutions to Example 1

	2 H ₂	+ O ₂	→ H ₂ O
m (g)	1.063 x 10 ⁸	6.293 x 10 ⁸	
M (g/mol)	2.016	31.999	18.015
n (mol)	5.271 x 10 ⁸	1.967 x 10 ⁸	--
if all H ₂ reacts	-5.271 x 10⁷	-2.636 x 10⁷	+5.271 x 10 ⁷
if all O ₂ reacts	-3.934 x 10 ⁷	-1.967 x 10 ⁷	+3.934 x 10 ⁷
Actual Reaction Amounts	-3.933 x 10 ⁷	-1.967 x 10 ⁷	+3.933 x 10 ⁷
Actual Reaction Masses	-7.930 x 10 ⁷	-6.293 x 10 ⁸	+7.086 x 10 ⁸

In the end, $1.063 \times 10^8 - 7.930 \times 10^7 = 2.70 \times 10^7$ g of H₂ will remain, along with 7.08×10^8 g of water, for a total of 7.35×10^8 g. The mass of the reactants was also $1.063 \times 10^8 + 6.29 \times 10^8 = 7.35 \times 10^8$ g.

General Strategy for Limiting Reactant Problems

From this example you can begin to see what needs to be done to determine which of two reagents, X or Y, is limiting. We must compare the stoichiometric ratio $S(X/Y)$ with the actual ratio of amounts of X and Y which were initially mixed together. In Example 1 this ratio of initial amounts

$$\frac{n_{\text{H}_2}(\text{initial})}{n_{\text{O}_2}(\text{initial})} = \frac{5.271 \times 10^7 \text{ mol H}_2}{1.967 \times 10^7 \text{ mol O}_2} = \frac{2.68 \text{ mol H}_2}{1 \text{ mol O}_2}$$

was less than the stoichiometric ratio $S\left(\frac{\text{H}_2}{\text{O}_2}\right) = \frac{2 \text{ mol H}_2}{1 \text{ mol O}_2}$. This indicated that there was not enough O₂ to react with all the hydrogen, and oxygen was the limiting reagent. The corresponding general rule, for any reagents X and Y, is

$$\text{If } \frac{n_X(\text{initial})}{n_Y(\text{initial})} \text{ is less than } S\left(\frac{X}{Y}\right), \text{ then X is limiting.} \quad (3.3.9.1)$$

$$(3.3.9.2)$$

$$\text{If } \frac{n_X(\text{initial})}{n_Y(\text{initial})} \text{ is greater than } S\left(\frac{X}{Y}\right), \text{ then Y is limiting.} \quad (3.3.9.3)$$

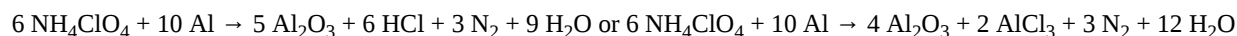
Of course, when the amounts of X and Y are in exactly the stoichiometric ratio, both reagents will be completely consumed at the same time, and neither is in excess.

As you can see from the example, in a case where there is a limiting reagent, *the initial amount of the limiting reagent must be used to calculate the amount of product formed*. Using the initial amount of a reagent present in excess would be incorrect, because such a reagent is not entirely consumed.

APCP Solid Propellants

Solid Rocket Boosters (SRBs) are the type implicated in the infamous Challenger Disaster^[10], where a poor seal allowed escape of hot gases. Each SRB motor contains a propellant mixture (weighting about 590,000kg) consisting of ammonium perchlorate (oxidizer, 69.6% by weight), and aluminum (fuel, 16%). A catalyst (iron oxide, 0.4%), a binder (which also acts as secondary fuel, 12.04%), and a curing agent (1.96%).^{[11][12]} This propellant is commonly referred to as Ammonium Perchlorate Composite Propellant (APCP).

a. An amateur rocketeer wants to make 100g of propellant. He mixes the propellant with 69.6 g of ammonium perchlorate (the required 69.6%), but he has no binder, so uses 16.0 g of Al plus another 12.0 g Al in place of the binder (which is also a fuel), or 28% aluminum in the mixture. Is this ratio correct? b. If not, which is the limiting reactant? c. Calculate the mass of Al₂O₃ produced by the first reaction below.



Solution

The stoichiometric ratio connecting Al and NH_4ClO_4 is $S\left(\frac{\text{Al}}{\text{NH}_4\text{ClO}_4}\right) = \frac{10 \text{ mol Al}}{6 \text{ mol NH}_4\text{ClO}_4} = \frac{1.67 \text{ mol Al}}{1 \text{ mol NH}_4\text{ClO}_4}$. The initial amounts of Al and NH_4ClO_4 are calculated using appropriate molar masses $n_{\text{Al}}(\text{initial}) = 28.0 \text{ g} \times \frac{1 \text{ mol Al}}{26.982 \text{ g}} = 1.04 \text{ mol Al}$

$n_{\text{NH}_4\text{ClO}_4}(\text{initial}) = 69.6 \text{ g} \times \frac{1 \text{ mol NH}_4\text{ClO}_4}{117.489 \text{ g}} = 0.592 \text{ mol NH}_4\text{ClO}_4$. Their ratio is $\frac{n_{\text{Al}}(\text{initial})}{n_{\text{NH}_4\text{ClO}_4}(\text{initial})} = \frac{1.04 \text{ mol Al}}{0.592 \text{ mol NH}_4\text{ClO}_4} = \frac{1.76 \text{ mol Al}}{1 \text{ mol NH}_4\text{ClO}_4}$. Since this ratio is larger than the stoichiometric ratio, you have more than enough Al to react with all the NH_4ClO_4 . NH_4ClO_4 is the limiting reagent, so the ratio isn't stoichiometric. b) The amount of product formed in a reaction may be calculated via an appropriate stoichiometric ratio from the amount of a reactant which was *consumed*. Some of the excess reactant Al will be left over, but all the initial amount of NH_4ClO_4 will be consumed. Therefore we use $n_{\text{NH}_4\text{ClO}_4}(\text{initial})$ to calculate how

much Al_2O_3 can be obtained $n_{\text{NH}_4\text{ClO}_4} \xrightarrow{S(\text{Al}_2\text{O}_3/\text{NH}_4\text{ClO}_4)} n_{\text{Al}_2\text{O}_3} \xrightarrow{M_{\text{Al}_2\text{O}_3}} m_{\text{Al}_2\text{O}_3}$ $m_{\text{Al}_2\text{O}_3} = 0.592 \text{ mol NH}_4\text{ClO}_4 \times \frac{5 \text{ mol Al}_2\text{O}_3}{6 \text{ mol NH}_4\text{ClO}_4} \times \frac{101.961 \text{ g}}{\text{mol Al}_2\text{O}_3} = 50.3 \text{ g Al}_2\text{O}_3$

You may want to verify the rest of the values in the table:

	6 NH_4ClO_4	+ 10 Al →	5 Al_2O_3	+ 6 HCl	+ 3 N_2	+ + 9 H_2O
m (g)	69.6	28.0				
M (g/mol)	117.49	26.982	101.961	36.461	28.013	18.015
n (mol)	0.592	1.04	--	--	--	--
if all NH_4ClO_4 reacts	-0.592	-0.987				
if all Al reacts	-1.04	-0.622				
Actual Reaction Amounts	-0.592	-0.987	+0.493	+0.592	+0.296	+0.887
Actual Reaction Masses	-69.6	-26.63	+50.30	+21.59	+8.29	+15.99

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